Electrical Conductivities of Mantle Minerals: In-situ High-Pressure High-Temperature Complex Impedance Spectroscopy

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Electrical conductivities for olivine at 10 GPa, wadsleyite at 15 GPa and ringwoodite at 20 GPa, all with San Carlos (Mg$_{0.9}$Fe$_{0.1}$)$_2$SiO$_4$ olivine starting composition were determined by complex impedance spectroscopy in a multianvil apparatus. Results for olivine are in good agreement with previous studies, both at elevated pressure and ambient pressure, suggesting that its conductivity is only weakly dependent on pressure. Conductivities for wadsleyite and ringwoodite are significantly higher than olivine (about 2 orders of magnitude), but with slightly lower activation energies. These differences can be attributed to the likely presence of ferric iron in the wadsleyite and ringwoodite.

1. Introduction

Observations of Earth's geomagnetic variations make it possible to determine its electrical conductivity profile as a function of depth. Without constraints placed by laboratory measurements, however, understanding mantle mineralogy is limited due to the many factors which influence the conductivity of minerals (temperature, pressure, Fe content, oxygen fugacity, and volatile (H, C) content). We have developed a technique to determine the electrical properties of materials in-situ at high pressures and temperatures using complex impedance spectroscopy in a multianvil apparatus. We present results of a study to determine the electrical conductivities of (Mg$_{0.9}$Fe$_{0.1}$)$_2$SiO$_4$ olivine, and its high pressure phases wadsleyite and ringwoodite.

2. Experimental Details

Complex impedance measured as a function of frequency was determined at pressures up to 20 GPa and temperatures up to 1300°C in a variety of high pressure assembly types using a 1000 tonne split-cylinder multianvil apparatus. All measurements used a parallel-plate sample geometry with shielding between sample and furnace (Fig. 1) except for two experiments: run H400 had a coaxial sample geometry to maximize sample volume, and run H633 had a parallel plate geometry without shielding to maximize the geometric cell constant. Experiments with shielding between sample and furnace allowed data with better signal-to-noise ratios to be obtained at frequencies below about 300 Hz. All samples were polycrystalline with a starting composition of San Carlos (Mg$_{0.9}$Fe$_{0.1}$)$_2$SiO$_4$ olivine with 5 wt% orthopyroxene added to buffer silica activity. Samples were hot-pressed at 1200°C in a separate experiment prior to the impedance measurement (olivine at 4 GPa, wadsleyite at 15 GPa, ringwoodite at 20 GPa). Complex impedance spectra were acquired over a frequency range of 1 MHz to 0.01 Hz (10 data points per decade frequency) with a Solartron 1260 impedance/gain-phase analyzer using an applied voltage of 1.0V. The spectra were characterized by single, semi-circular arcs which were fitted using a simple parallel RC equivalent circuit. Temperatures were measured by Pt/PtRh10 thermocouples with no EMF correction for pressure. Pressures were determined based on calibration runs involving phase transformations of various silicates at P and T conditions similar to the experiments of this study (e.g. coe-sti, α-β Mg$_2$SiO$_4$, β-γ Mg$_3$Si$_2$O$_6$).

3. Results and Discussion

Selected complex impedance spectra of olivine at 10 GPa and temperatures ranging from 900°C to 1200°C are shown in Fig. 2. The spectra are composed of single semi-circular arcs beginning at the origin (highest frequency) and looping toward the Z' axis (real impedance). Least-squares fitting the data to a circle gives its center very near to the real axis, confirming the data can be modelled by a simple parallel RC equivalent circuit. Best fit parameters provide the sample's capacitance and resistance, used to determine electrical conductivity. With increasing temperature, the width of the impedance arc decreases (Fig. 2), and the sample becomes more conductive, following Arrhenian behavior. No evidence of
additional impedance arcs are observed at lower frequencies, in contrast to 1 atmosphere measurements of polycrystalline olivine which have shown additional arcs in series, due to grain boundary impedance and polarization at the sample-electrode interface [1]. Although the data in Fig. 2 range only from 1 MHz to about 300 Hz because the sample was unshielded from the furnace, results from runs H578 and H668 (both ranging from 1 MHz to 0.01 Hz) also indicate only one impedance arc. The loss of a grain boundary conduction feature with increasing pressure is consistent with the complex impedance study of Huebner and Dillenburg [2] on a polycrystalline clinopyroxenite. With more intimate grain-to-grain contact at high pressure compared to a sintered sample at 1 atm, impedance becomes negligible across grain boundaries and is dominant in the grain interior. A sample-electrode polarization feature is only likely to be observed at frequencies lower than 0.01 Hz [1].

Fig. 2. Complex impedance spectra (imaginary vs real impedance) for olivine at 10 GPa from 900°C to 1200°C in 50° increments. This sample (H400) had a coaxial geometry without shielding. Frequencies range from 1 MHz (near origin) down to about 300 Hz. Lower frequency data are not shown due to interference from the furnace.

Complex impedance spectra for wadsleyite are shown in Fig. 3. Between 800°C and 1000°C, the impedance arcs are not ideally semi-circular, but tend to curve back toward the origin at low frequencies as they approach the Z' axis. This results in the center of the arc fitted slightly above the real axis and is likely to overestimate slightly the electrical conductivity at these lower temperatures. The cause for this behavior is unclear, and thus fitting the data to a more sophisticated equivalent circuit was not attempted. Above 1000°C, the centers of the arcs are very near the real axis, providing lower uncertainties in the determination of its conductivity. The entire frequency range of 1 MHz to 0.01 Hz is included in Fig. 3 and we find no indication of a grain boundary feature in the low frequency portion of the spectrum at any temperature.

Selected data for ringwoodite at 20 GPa are presented in Fig. 4. Ideal semi-circular impedance arcs were observed over the entire temperature range investigated. Unlike the results for wadsleyite, anomalously low Z' values at low frequencies are not encountered for ringwoodite, enabling us to rule out the possibility that our method is plagued by an artifact at high pressures. Similar to olivine and wadsleyite, only one impedance arc is observed over the entire frequency range.

Electrical conductivities determined from all of our measurements are listed in Table 1, expressed via the equation

$$\sigma = \sigma_0 e^{-E_a/kT}$$

where $\sigma_0$ and $E_a$ are constants, $k$ is Boltzmann’s constant, and $T$ is absolute temperature. Data for each measurement are plotted in Fig. 5, with their corresponding linear regressions also shown. Overall, results for olivine at 10 GPa are in fairly good agreement with other high pressure studies of natural olivine samples at similar composition [3,4], with only slightly higher values for the activation energy near 1.3 eV and log $\sigma_0$ near 1.8 determined in this study. These values are also in close agreement with room pressure studies conducted in controlled atmosphere furnaces. Activation energies from 1 atm measurements are near 1.4 eV with log $\sigma_0$ values also around 2 [1,5]. Considering the pressure range covered by this and previous high pressure and room pressure studies of (Mg$_{0.9}$Fe$_{0.1}$)$_2$SiO$_4$ olivine, conductivity appears to be insensitive to pressure in the temperature range 800 to 1200°C.
Table 1. Conductivities for olivine, wadsleyite and ringwoodite. Experimental data fit to Equation 1.

<table>
<thead>
<tr>
<th>Run# Sample</th>
<th>T range (°C)</th>
<th>P (GPa)</th>
<th>cell const. (mm)</th>
<th>log $\sigma$</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H400 Ol*</td>
<td>900-1200</td>
<td>10.2</td>
<td>0.21</td>
<td>1.87</td>
<td>1.32</td>
</tr>
<tr>
<td>H578 Ol</td>
<td>850-1200</td>
<td>10.3</td>
<td>0.39</td>
<td>2.13</td>
<td>1.36</td>
</tr>
<tr>
<td>H668 Ol</td>
<td>800-1200</td>
<td>10.4</td>
<td>0.43</td>
<td>1.42</td>
<td>1.24</td>
</tr>
<tr>
<td>H013 Wd</td>
<td>800-1200</td>
<td>15.5</td>
<td>0.39</td>
<td>2.36</td>
<td>1.03</td>
</tr>
<tr>
<td>H6353 Wd†</td>
<td>500-1200</td>
<td>15.6</td>
<td>1.45</td>
<td>2.01</td>
<td>0.92</td>
</tr>
<tr>
<td>H557 Rw</td>
<td>500-1300</td>
<td>20.7</td>
<td>0.36</td>
<td>2.10</td>
<td>0.99</td>
</tr>
<tr>
<td>H564 Rw</td>
<td>500-1200</td>
<td>20.8</td>
<td>0.38</td>
<td>2.92</td>
<td>1.16</td>
</tr>
</tbody>
</table>

Ol=olivine; Wd=wadsleyite; Rw=ringwoodite
*coaxial cell geometry, unshielded
†parallel plate geometry, unshielded

Both wadsleyite and ringwoodite conductivities are very similar to one another, and approximately two orders of magnitude greater than that of olivine at this composition (Fig. 5). The difference we observe between the conductivity of olivine and its high pressure polymorphs is greater than that reported by Omura [6] at similar composition. However, the lower conductivity jump from olivine to wadsleyite and ringwoodite determined by Omura possibly could be explained by the presence of small amounts of iron-rich oxide phases which were found in his wadsleyite and ringwoodite samples. This was suggested by Duba and von der Gonna [7] to rationalize its high rather than low conductivity, but this would depend on the distribution of the two (or more) phases in the sample. A highly conductive iron-rich layer formed between sample and electrode could mean an iron-poor thin insulating layer also had formed. In early attempts to transform and measure wadsleyite conductivity in single experiments as Omura had done, we encountered Fe diffusion near the electrode creating iron-poor and iron-rich zones. These experiments, which reached temperatures up to 1600°C in order to facilitate the olivine to wadsleyite transformation, resulted in lower overall conductance of the sample. Neither the wadsleyite nor ringwoodite samples in the present study, however, exhibit any irregular Fe distribution or the presence of other phases based on x-ray diffraction and electron microprobe analyses of the recovered samples.

The higher conductivities for the two high pressure polymorphs are probably due to small amounts of Fe$^3+$ in both wadsleyite and ringwoodite [8], compared to olivine which does not accommodate ferric iron at this composition. While activation energies are only slightly lower than for olivine, the conduction mechanism in both wadsleyite and ringwoodite is still likely to be electronic rather than ionic, with the lower activation energies due to more favorable charge transfer in the denser modified spinel and spinel structures.

4. Conclusions

Electrical conductivities for olivine, wadsleyite and ringwoodite have been determined by in-situ complex impedance spectroscopy in a multianvil apparatus. Spanning eight decades of frequency, the spectra exhibited no in-series grain boundary impedance feature, and thus they could be fitted to single parallel RC equivalent circuits. Olivine conductivity at 10 GPa compares well with previous studies both at high pressures and at atmospheric pressure. Wadsleyite and ringwoodite conductivities are very similar and about two orders of magnitude greater than for olivine, probably due to the presence of some ferric iron in the high pressure polymorphs. Our results are in good agreement with current geophysical models of upper mantle and transition zone conductivities [9]. Discerning variations in conductivity with changing structure type will begin to allow tighter constraints to be put on the chemical and mineralogical differentiation of the Earth's mantle. The need for good sample characterization both before and after measurement is stressed, particularly because high pressure techniques inherently require small sample volumes.

References