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Pressure and compositional dependence of electric conductivity in the $(Mg_{1-x}Fe_x)_{1-\delta}O$ ($x=0.01$–0.40) solid-solution

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ABSTRACT

$(Mg_{1-x}Fe_x)_{1-\delta}O$ ($x=0.01$–0.43) single crystals (~8 mm in diameter) were made by a melt-growth method. Electrical conductivity measurements were carried out as functions of temperature and frequency by a complex impedance method under pressure (~43 GPa and ~673 K and at 0.1 MPa and ~1400 K). Our experimental results show a change in charge transport mechanism in the $(Mg_{1-x}Fe_x)_{1-\delta}O$ solid solution at high temperature. The temperature of inflection point of the slope in Arrhenius plots depend greatly on both composition and extrinsic factors of crystals. The low-temperature conduction mechanism in $(Mg_{1-x}Fe_x)_{1-\delta}O$ solid solution is small polaron. Pressure effect of the electric conductivity was observed and the conductivity increased to 0.5 at log scale of S/m with increasing pressure up to 43.4 GPa. The activation energy was decreased linearly with increasing pressure. Chemical composition and homogeneity of specimen rather than pressure greatly influence the electric conductivity. The activation energy of 2.37(4) eV for the $(Mg_{0.99}Fe_{0.01})_{1-\delta}O$ solid solution might correspond to a migration enthalpy of O ions through thermally formed defects. It is proposed that a possible dominant electrical conduction mechanism in ferropericlase under the lower mantle conditions, at least in the higher temperature region, is super ionic conduction.
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1. Introduction

The $(Mg_{1-x}Fe_x)_{1-\delta}O$ rock salt-type solid solution (mineral name: ferropericlase) is believed to be one of the major constituents in the Earth's lower mantle that extends to a depth from 660 km to 2900 km [1,2]. The electrical conductivity of the mantle can be determined from geomagnetic studies. Geomagnetic models of the electrical conductivity of the Earth's mantle based on the observed variations of electric and magnetic fields yielded estimates of about 10^0 S/m for the conductivity of the uppermost lower mantle [3,4]. Temperature profiles in the mantle have been estimated by electric conductivity of mantle forming minerals. Information about the physical mechanism of electric conductivity in the $(Mg_{1-x}Fe_x)_{1-\delta}O$ solid-solution and its dependence on temperature and pressure would help to constrain the detailed temperature profile and composition in the Earth.

MgO (periclase) is well known as a good insulator ($<10^{-10}$ (ohm cm)$^{-1}$ at 1000 K) and a solid state ionic near melting temperature. $Fe_{1-\delta}O$ is a typical p-type defect semiconductor at lower temperature ($<10^{-2}$ (ohm cm)$^{-1}$ at 1000 K). The $(Mg,Fe)_{1-\delta}O$ solid solution with a moderate amount of iron is a good conductor at both ambient and high pressures and the conduction activation energy varies from 0.1 eV to 0.6 eV for the solid solutions containing more than 7% FeO [5–8]. The conduction activation energy also varies for samples with the same composition depending on the different preparation methods. Activation energy of electric conductivity of $(Mg_{1-x}Fe_x)_{1-\delta}O$ solid-solution was also reported as a function of FeO content by Hansen and Cutler [9]. They showed a discontinuous jump from 0.4 eV to 0.2 eV above 17.7 mol% FeO. On the other hand, Li and Jeanloz [7] showed that the activation energies were decreased smoothly with FeO content. Possible reasons to explain these differences are that these sintered powder samples were not homogeneous and that a Fe concentration was fluctuated in $(Mg_{1-x}Fe_x)_{1-\delta}O$ crystals because the samples were synthesized by sintering in range 1173 K to 1623 K.

We have reported the precise structures and properties for the mantle minerals and related compounds using the high pressure apparatus and synchrotron radiation [10,11]. In this study, we have carried out the syntheses of homogeneous single crystals and electrical conductivity measurements as functions of temperature and frequency by the complex impedance method under pressure (~43 GPa and ~673 K and at 0.1 MPa and ~1400 K). We discuss the electrical conduction phenomena in the Earth's lower mantle using the experimental results.

2. Experimental

The $(Mg_{1-x}Fe_x)_{1-\delta}O$ ($x=0.01$–0.43) single crystals (2–8 mm in diameter) were prepared by a melt-growth method using a graphite

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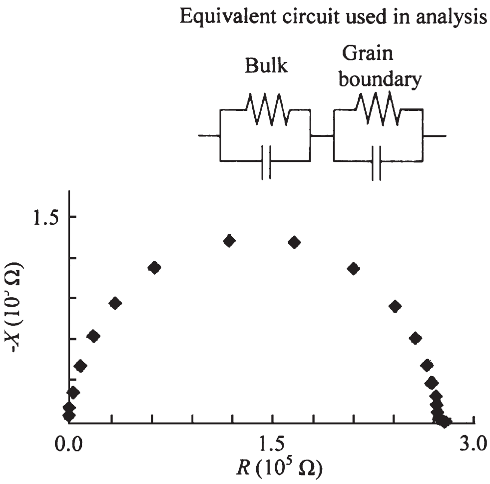

Fig. 1. Complex impedance plot of $(Mg_{0.68}Fe_{0.32})_{1-\delta}O$ single crystal.

heater (up to 3200 K) in the Ar atmosphere for colorless samples and by a FZ method in the CO_2–H_2 atmosphere ($pH_2/pCO_2=0.1$) for colored samples. Temperatures in the furnaces were monitored using a radiation thermometer and calibrated using the MgO and FeO melting points. MgO–$Fe_{1-\delta}O$ forms a continuous series of solid solution and melting temperatures decrease from 3120 K to 1640 K with FeO content. Electron Probe Micro Analysis (JEOL JCMA-733II) was executed to determine the composition and to confirm homogeneity. X-ray diffraction studies were performed and compositional dependence of the unit cell parameter was confirmed. Several percents or a few percent of the iron ions in the specimens are trivalent and the non-stoichiometric parameter δ varies from 0.011 of the $(Mg_{1-x}Fe_x)_{1-\delta}O$ solid solution containing 40% FeO to 0.003 of that containing 20% FeO. Details of the syntheses and characterizations such as X-ray topography and SEM images will be published elsewhere [12].

The form of single crystal samples was fixed to be 1 mm thick and 3 mm in diameter for the conductivity measurements. Both faces of the samples were coated with Pt paste and were held between platinum electrodes. Platinum electrodes were connected with heat resist shield wires near the sample. The assembly was placed in an alumina vessel and then in a horizontal furnace [13]. True bulk conductivities were measured between 5 Hz and 13 MHz by the complex impedance method with an impedance analyzer (LF impedance analyzer 4192A). The conductivity as a real part of the impedance Z was determined by a Cole–Cole plot [13]. Fig. 1 shows representative complex impedance plots for the $(Mg_{0.68}Fe_{0.32})_{1-\delta}O$ single crystal. The bulk conductivity is estimated from the real-axis intercept of the semicircle.

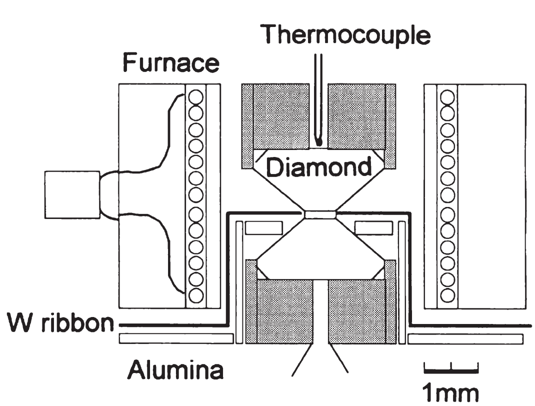

Fig. 2. Schematic drawing of diamond anvil cell apparatus for electric conductivity measurement under high pressure and moderate temperature.

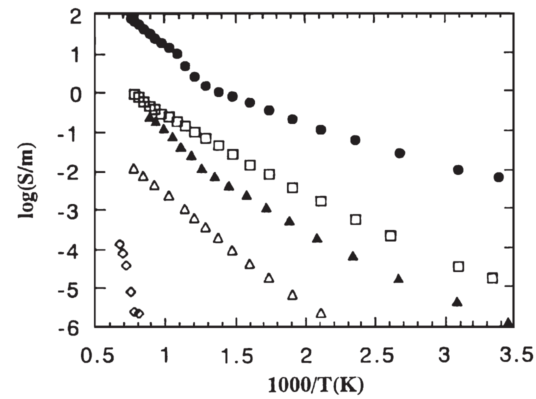

Fig. 3. Arrhenius plots for the conductivity σ in log(S/m) versus 1000 T^{-1} for the $(Mg_{1-x}Fe_x)_{1-\delta}O$ solid solution (ferropericlase) single crystals. The solid solutions with $x=0.01$ (◊), 0.056 (○), 0.20 (▲), 0.32 (□) and 0.40 (●), respectively.

Electric conductivity of $(Mg_{0.68}Fe_{0.32})_{1-\delta}O$ was measured under high pressure (~43 GPa) and temperature (~673 K) using an externally heated diamond anvil cell (Fig. 2). The single crystal was formed in the shape of a rectangle of 40×60 μm with a thickness of 40 μm and embedded on the curette of diamond with pyroxene powder as an insulator. Two tungsten ribbons were extended to the rectangle and touched the sample to each other. The difference of temperature in the cell is estimated beforehand and the difference between the thermocouple and sample was 12 degrees at 673 K.

3. Results and discussion

3.1. Electric conductivity at lower temperature and 0.1 MPa

Arrhenius plots for the conductivity σ in ln(S/m) versus 1000 T^{-1} at 0.1 MPa are shown in Fig. 3. The $(Mg_{1-x}Fe_x)_{1-\delta}O$ solid solution containing 40% FeO is 3 orders of magnitude more conductive than that containing 32% FeO at low temperature. At each temperature of 780 K for the $(Mg_{1-x}Fe_x)_{1-\delta}O$ solid solution with $x=0.20$, 1030 K for $x=0.32$ and 820 K for $x=0.40$, respectively, the slope of conductivity can be divided into two regions by a inflection point. The conductivity in the high temperature field has a steep slope in an Arrhenius plot, showing a change in charge transport mechanism with temperature.

The calculated activation energies at the low temperature region are presented in Table 1. The activation energy decreases with increasing iron concentration from 0.56 eV at 5.6% FeO to 0.23 eV at 42% FeO (Fig. 4). In Fig. 4, the activation energies are compared with previous results obtained using sintered powder samples. The activation energy of a single crystal indicates a large value by the same composition and its conductivity is smaller than a sintered sample's. It is presumable that the sintered powder samples were not homogeneous and that Fe concentration was fluctuated in crystals because the melting temperature of MgO (3120 K) is greatly different from that of $Fe_{1-\delta}O$ (1640 K).

3.2. Conductivity under high pressure

We have measured the electrical conductivity at high pressure and temperature simultaneously using a diamond anvil cell heated with

Table 1
Compositional dependence of conduction activation energy (E_a) and mean path length between two iron atoms (d_{Fe-Fe}) in the $(Mg_{1-x}Fe_x)_{1-\delta}O$ solid solutions in the lower temperature region.

FeO content x	0.056	0.20	0.32	0.40
E_a (eV)	0.56(3)	0.43(3)	0.36(3)	0.23(2)
d_{Fe-Fe} (Å)	8.61	5.66	4.85	4.43

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