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Ionic conductivity measurements of zirconia under pressure using impedance spectroscopy

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Abstract

We have set up an electrical conductivity measurement system under high-pressure and high-temperature conditions with a multi-anvil high-pressure apparatus using an AC complex impedance method. With this system, we have successfully measured the electrical conductivity of stabilized ZrO_2 (Y_2O_3–ZrO_2 solid solution) under pressures up to 5 GPa in the temperature range from 300 to 1200 K. The electrical conductivities obtained under pressure are compatible with those of previous results measured at ambient pressure.

1. Introduction

Since the early stages of high-pressure science, electrical conductivity measurements under pressure have been extensively attempted in order to detect phase transitions. Most studies, however, have been done by means of DC conductivity measurements. Consequently, specimens that can be treated have been limited to metals and semiconductors that have relatively high electrical conductivities. The AC impedance technique is preferable for correct measurements for ionic or low electrical conductivity. By this technique, we can separate two conduction mechanisms: bulk and grain boundary conduction. If this technique is applicable at high pressure and high temperature, there are several applications. Combined with the conductivity profile of the Earth's interior derived from geomagnetic field data, the electrical conductivity of mantle materials gives geothermal information that is very important in geophysics. Pressure-induced phase transitions can be detected by the change in the ionic conductivity, which is sensitive to crystal structure. In the present study, we have attempted to set up a high-pressure AC impedance spectroscopy system using a multi-anvil apparatus, and measured the ionic conductivity of zirconia.

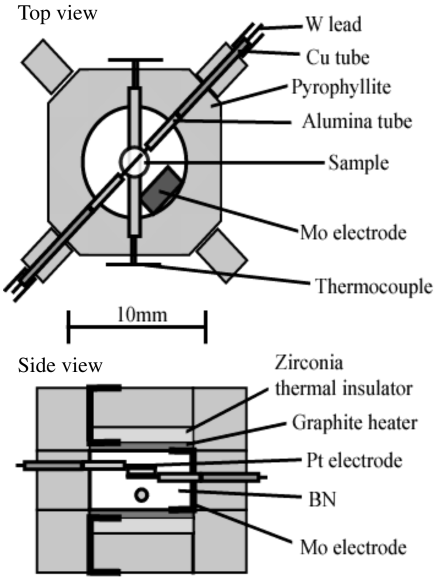

Figure 1. The cell assembly for the electrical conductivity measurement.

2. High-pressure AC impedance system

Figure 1 shows the high-pressure cell assembly for the conductivity measurements under high temperature and high pressures using a cubic-type multi-anvil apparatus. The anvil top is 10 mm and the pressure-transmitting medium is pyrophyllite in a 12.5 mm cube. The two graphite heaters in the cell are connected to upper and lower guide blocks by the Mo electrode and can generate high temperatures up to 1600 °C. W–Re-type thermocouples (W97Re3–W75Re25) are employed to measure temperatures. They are connected to side guide blocks. The temperature gradient for the sample geometry was confirmed to be within 20 K over the range up to 700 °C. To measure electrical conductivity, two W wires and Pt electrodes are used.

The pressure generated is estimated from the calibration curve which was determined using phase transitions in Bi (I–II, 2.55 GPa; III–V, 7.7 GPa) and Ba (I–II, 5.5 GPa) at room temperature. The pressure leak caused by heating is estimated to be 0.3 GPa at 700 °C [1].

AC impedances are measured by an HP4285A LCR meter with a frequency range of 20 Hz–1 MHz. W wires go through gaps in guide blocks and connect to coaxial cable which leads to the LCR meter. It is important for more accurate measurements to have coaxial cables approaching the multi-anvil press.

3. Ionic conductivity of zirconia

Using the system, we have measured the ionic conductivity of stabilized polycrystalline and single-crystal ZrO_2 (YSZ). YSZ is a well-known oxygen conductor and its conduction behaviour under pressure is interesting. Furthermore, there are many studies of the conduction properties made at ambient pressure that can be used to evaluate our high-pressure data.

The polycrystalline sample ($0.96ZrO_2$–$0.04Y_2O_3$) was prepared in our laboratory. Discs shaped from powder were sintered at 1400 °C for 48 h. These discs were 2 mm in diameter and 0.6 mm in thickness. A single-crystal sample ($0.9ZrO_2$–$0.1Y_2O_3$) was cut into a plate, $2 \times 2 \times 1$ mm. Since the variation of the sample geometry on compression is difficult to

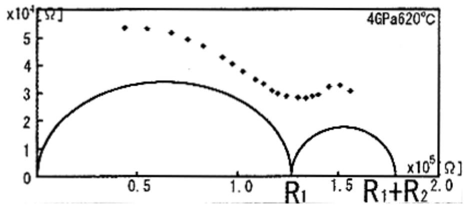

Figure 2. Representative complex impedance spectra of polycrystalline YSZ.

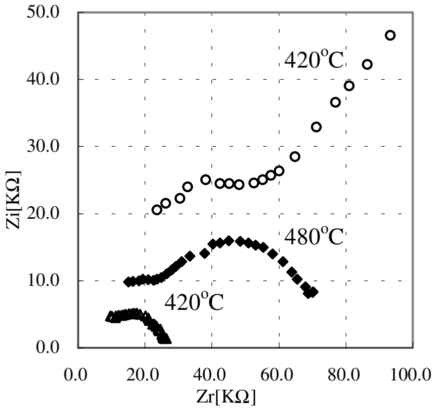

Figure 3. Complex impedance spectra of polycrystalline YSZ ($0.96ZrO_2$–$0.04Y_2O_3$) at 5 GPa.

estimate, the geometry with the original values (2 mm in diameter and 0.8 mm in thickness for polycrystalline samples and 2 mm square, 1 mm in thickness for single crystals) was used to calculate the conductivity.

Figure 2 shows representative complex impedance plots for a polycrystalline sample that shows two characteristic semicircles of bulk (R_1) and grain boundary (R_2) conduction [2]. The bulk conductivity is estimated from the real-axis intercept of the higher-frequency semicircle (R_1). Figure 3 shows complex impedance plots for polycrystalline YSZ at various temperatures. Each plot shows two semicircles, and the electrical conductivity decreases when temperature decreases. In order to compare with these results, we measured the electrical conductivity of single-crystal YSZ. Figure 4 is a complex impedance plot for single-crystal YSZ at various temperatures. There is a straight line at the right-hand end of the semicircle. This line is caused by the reaction between the sample and the electrodes. These plots each show only one semicircle of bulk conduction, because there are no grain boundaries in single crystal.

The electrical conductivity $\log \sigma T$ can be calculated from the equation

$$\log \sigma T = \log(DT/SR).$$

R is the measured value, T is the absolute temperature, D is the thickness of the sample, S is the size of the electrode for the electrical conductivity. Figure 5 shows Arrhenius plots of the conductivities obtained. The solid curve represents a previous study of YSZ at ambient pressure. Plots from this study show a similar behaviour to those from previous studies made at ambient pressure [3]. The change of slope corresponds to the conduction mechanism. The electrical conductivity of a single crystal containing 10% Y_2O_3 is higher than that of YSZ containing 4% Y_2O_3, because it has more oxygen vacancies which dominate the ionic conductivity.

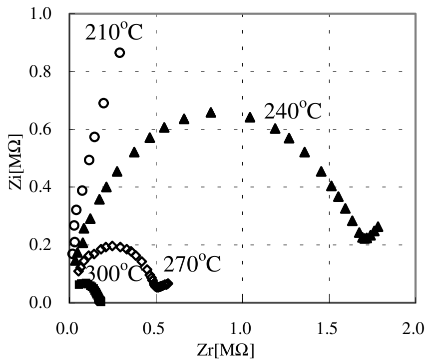

Figure 4. Complex impedance spectra of single-crystal YSZ ($0.9ZrO_2$–$0.1Y_2O_3$) at 5 GPa.

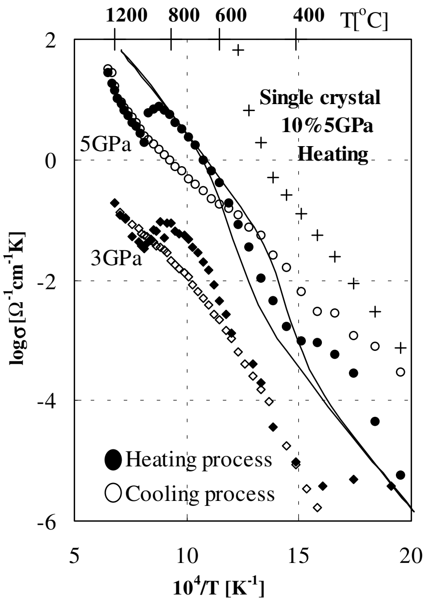

Figure 5. Arrhenius plots for YSZ at various pressures. Solid curve: YSZ ($0.96ZrO_2$–$0.04Y_2O_3$) at ambient pressure.

Acknowledgments

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