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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 based on an AC complex impedance method. With this system, we have successfully measured the electrical conductivity of San Carlos olivine under pressure up to 5 GPa. We explain the physical meaning of the activation enthalpies and activation volumes and give values for these data, which will be a great help for understanding the conduction mechanism for olivine.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The combination of the electric conductivity measurement of mantle materials with the electric conductivity profile derived from geomagnetic field measurements gives geothermal information. Recently there have been several attempts to measure the electric conductivity of mantle materials under mantle conditions [1]. In order to measure correctly the very low conductivity of mantle materials, an AC impedance technique is preferable. We have set up a high-pressure electric conductivity measurement system based on an AC complex impedance method, installed in a cubic-type multi-anvil apparatus [2]. Using this system, low conductivities of degree given by $\log \sigma = -7$ can be successfully measured up to 1500 °C and 5 GPa. We report results on the electric conductivity of San Carlos olivine under high-pressure and high-temperature conditions. Activation volumes were estimated from the pressure variation of the activation enthalpies. The physical meanings of the activation enthalpies and activation volumes were clarified in this study; this will be helpful for understanding the conduction mechanism of olivine.
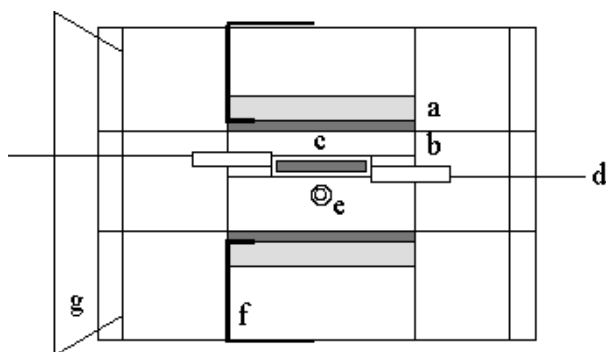
Figure 1. A cross-section of the cell assembly used for the measurement; a: stabilized zirconia; b: alumina tube; c: sample; d: W wire; e: TC; f: Mo electrode; g: gasket.

2. Experimental details

San Carlos olivine including 5 wt% pyroxene showing activity similar to that of a silica buffer was pressed and heated in a furnace with a controlled oxygen partial pressure of $f(O_2) = 10^{-9}$ atm at 1300 °C for three days. The sintered samples were cut into discs (4 mm in diameter and 0.6 mm in thickness) and used in the experiments.

The high-pressure environment is generated by using a DIA10-type multi-anvil press at Osaka University. The impedances were measured by a HP4284A LCR meter whose frequency range is 20 Hz–1 MHz. The cubic cell assembly used to measure electrical conductivity is shown in figure 1.

Two graphite heaters in the cell were connected to the upper and lower guide blocks by Mo ribbons and they can generate high temperatures up to 1500 °C. The W wires go through the opening between the guide blocks and connect to coaxial cables which lead to the LCR meter. The sample area can be widened if one uses a disc heater, which minimizes the influence of floating capacitance, resulting in and leading to more accurate recognition of the equivalent circuits. In this study, the electric conductivity measurements in the higher-resistivity region ($\log \sigma (S/m) < -7$) were carried out successfully under high-P (up to 5 GPa) and high-T (1500 °C) conditions. W–Re-type thermocouples (W97Re3–W75Re25) were employed to measure the temperatures.

3. Results and discussion

Representative complex impedance spectra of olivine are shown in figure 2.

Single semicircular arcs beginning at the origin of the plot were obtained. The bulk components of the electric conductivities were determined from the intercepts of the individual semicircles depicted in figure 2. An Arrhenius diagram of the conductivities is shown in figure 3.

Three regimes—the high-temperature region (1428–1666 K), the low-temperature region (666–909 K) and the intermediate region—can be observed in this study. The activation enthalpies are 1.91–2.12 and 0.74–0.98 eV in the high-temperature and low-temperature regions, respectively. These two regimes were also apparent in previous data [3, 4]. Recent data obtained by Xu *et al* [5] had activation enthalpies of 1.23–1.62 eV in the temperature range of 1273–1673 K, which can be interpreted as indicating mixed-ion conduction. Summarizing
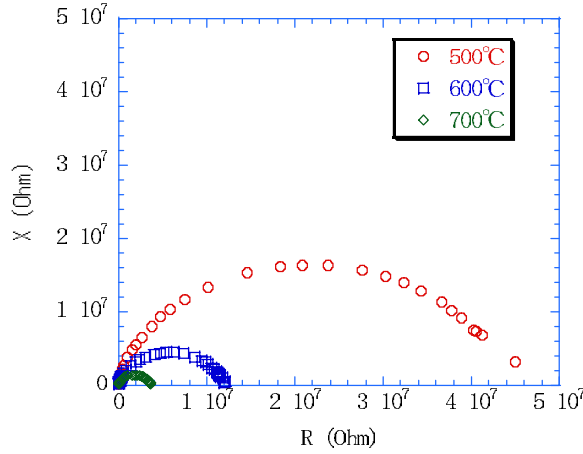
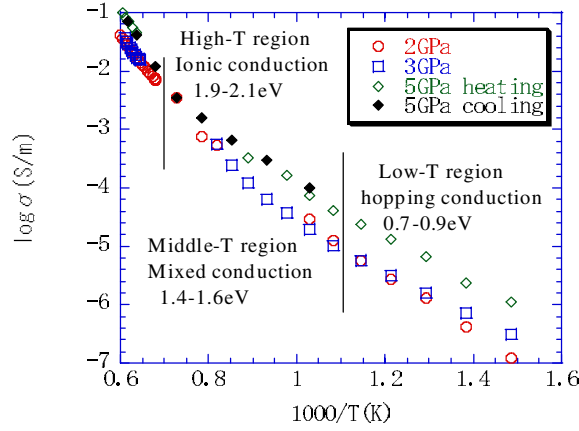**Figure 2.** Complex impedance spectra at 3 GPa.

Figure 3. An Arrhenius diagram ($\log \sigma - 1000/T$ plot).

these results, we can make the roughly classification that olivine has ionic conduction in the high-T region (1.91–2.33 eV), electronic conduction in the low-T region (0.74–0.98 eV) and a mixed ionic and extrinsic electronic conduction in the intermediate region (1.23–1.62 eV). Now, the physical meanings of the activation volume in ionic and hopping conduction will be described.

The increase in entropy for 1 mol of crystal upon mixing in activated complexes is expressed as follows (where N_m is the molar fraction of the activated complex):

$$\Delta S_{mix} = -R[(1 - N_m) \ln(1 - N_m) + N_m \ln N_m].$$

The variation of the mixing entropy in 1 mol of crystal is

$$\delta \Delta S_{mix} = \frac{d \Delta S_{mix}}{d N_m} \delta N_m = -R \ln \frac{N_m}{1 - N_m} \delta N_m.$$

The variation of the Gibbs free energy (δG) upon adding δn_m of the activated complex to the crystal containing N_m of the activated complex is

$$\delta G = \frac{\delta n_m}{N_a}(\Delta H - T(\Delta S_{mix} + \Delta S_m)) = \frac{\delta n_m}{N_a}\left(\Delta H_m - T \Delta S_m + RT \ln\left(\frac{N_m}{1 - N_m}\right)\right)$$

$$= \frac{\delta n_m}{N_a}(\Delta H_m - T \Delta S_m + RT \ln N_m) \qquad \text{(therefore } N_m \ll 1)$$

where N_a is the Avogadro number, ΔS_m is the migration entropy.

The fraction of activated complex (N_m) under equilibrium conditions is

$$N_m = \exp\frac{\Delta S_m}{R}\exp\left(-\frac{\Delta H_m}{RT}\right) \qquad \left(\text{therefore } \frac{\delta G}{\delta n_m} = 0\right).$$

Therefore the expression of extrinsic ionic conductivity is

$$\sigma = \frac{AN\nu q^2 r^2}{kT}\exp\frac{\Delta S_m}{R}\exp\left(-\frac{\Delta H_m}{RT}\right)$$

where A is constant, N is the number of ions per unit volume, q is the ionic charge, ν is the vibrational frequency and r is the jump distance;

$$\sigma = \sigma_0 \exp\left(-\frac{\Delta H_m}{RT}\right) = \sigma_0 \exp\left(-\frac{\Delta U_0 + P \Delta V_m}{RT}\right).$$

The volume term ΔV_m can be interpreted as the molar fraction of the activation complex, if ΔH_m is expressed as the sum of ΔU_0 and $P \Delta V_m$ and if $P \Delta V_m$ corresponds to the work done in an isobaric process in which a diffusive ion moves from a regular lattice site to the saddle point.

Goddat [6] considered a physical meaning for the activation enthalpy in hopping conduction as follows:

$$H_a = \frac{E_b}{2} - J_0 \exp[-\eta(R - R_0)]$$

where E_b is the binding energy; J_0 is the exchange integral under ambient pressure and η is a parameter characterizing the spatial decrease of the wavefunction. R is the distance between two sites; R_0 is the distance between two sites at atmospheric pressure. This expression is expanded as follows:

$$H_a = \frac{E_b}{2} - J_0 \exp[-\eta(R - R_0)] = \frac{E_b}{2} - J_0\left(1 + \eta\frac{R_0}{3}\frac{P}{K}\right)$$

$$= \left(\frac{E_b}{2} - J_0\right) + P\left(-\eta\frac{R_0}{3K}\right) = \Delta U_0 + P \Delta V.$$

ΔV is considered as a parameter related to the spatial decrease of the d orbital in Fe-bearing minerals. For an Fe content such as 9 mol%, it is unknown whether the neighbouring Fe atoms are perfectly connected each other. However, it is certain that the hopping between partially connected Fe atoms is a dominant factor in determining the electric conductivity.

In the case of extrinsic ionic conduction, an activation volume ($=\Delta V$) is considered as a molar fraction of the activation complex. A diffusive ion in the saddle-point position expands the interstitial space and makes the surrounding ions displace; therefore it is assumed that ΔV is a positive value in the region of several $cm^3\, mol^{-1}$ [7]. On the other hand, ΔV shows negative values for Fe-bearing minerals in hopping conduction [6]. ΔV for olivine is shown in figure 4 as a function of ΔU_0. ΔV shows a positive value (5.91 $cm^3\, mol^{-1}$) in the high-T region, in contrast to its negative value (-5.02 $cm^3\, mol^{-1}$) in the low-T region. This supports the suggestion that olivine exhibits ionic conduction in the high-T region and hopping conduction in the low-T region.

A tendency for ΔV to increase with increasing ΔU_0 was identified from the present data in addition to previous data obtained by Xu *et al* [5], as shown in figure 4.
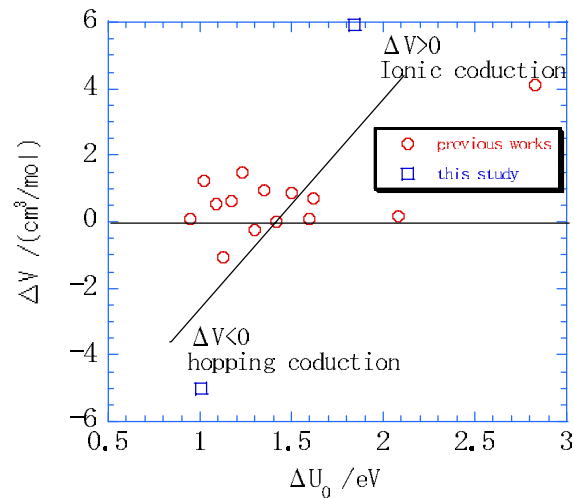
Figure 4. The relation between ΔU_0 and ΔV.

It can be concluded from this study that the variety of activation enthalpies which have been reported for olivine can be explained by the difference between the mixing rates for ionic and hopping conduction. The plots of ΔV as a function of ΔU_0 are somewhat scattered and the data do not lie perfectly on a line. This is caused firstly by experimental error and secondly by the variation of the mixing rate caused by the pressure.

References

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