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Temperature and pressure dependence of electrical conductivity in synthetic anorthite

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ABSTRACT

Electrical conductivity measurements of synthetic anorthite were carried out as a function of pressure and temperature by a Solartron-1260 Impedance/Gain phase analyzer in a multi-anvil apparatus. The impedance spectroscopy was performed in a frequency range from 10–1 Hz to 106 Hz. The sample was synthesized at 1673 K in a high temperature furnace. Our experimental results show that (1) a dramatic increase in electrical conductivity with increasing temperature and a slightly decrease in conductivity with increasing pressure at constant temperature, however, the effect of pressure on the conductivity is less pronounced than that of temperature; (2) the activation enthalpy linearly increases with increasing pressure (1.86–1.91 eV) reflecting the mobility of $Ca2^{+}$ decreases as the anorthite framework becomes more compressed; (3) the activation energy at atmospheric pressure and activation volume are 1.83 eV and 2.39 cm^3/mol, respectively; (4) According to these Arrhenius parameters, it is proposed that the possible dominant mechanism of the charge transport in anorthite under experimental conditions is the hopping of $Ca2^{+}$ from one near aluminum oxygen site to another; (4) the diffusion coefficient of calcium was calculated from the present conductivity data using Nernst–Einstein equation, and compared with previous experimental results.

1. Introduction

Feldspars are the most abundant rock-forming minerals and constitute 60% of the Earth's crust, and are widely present in variety of igneous and metamorphic rocks [1]. Anorthite, as one of end-numbers in feldspars, has a large stability field, which extend to 3 GPa in pressure and to below 1000 °C in temperature [2–4]. Consequently, anorthite would play an important role in the composition of the uppermost upper mantle when it effectively plunge the continental slab into the mantle.

Electrical conductivity is one of the significant parameters to place constraints on the thermal structure and composition of the Earth's interior since it is highly sensitive to thermodynamic parameter such as temperature, pressure and chemistry of the constituent materials [5–7]. Laboratory-based electrical conductivity of geomaterials can provide independent data to help the interpretation of the field magnetotelluric results and borehole data. The electrical conductivity of anorthite would therefore make a significant contribution to the electrical structure of the Earth's crust and the uppermost upper mantle. In addition, the study on conduction behavior of anorthite at high temperature and pressure can aid in understanding the charge transport mechanism, and is an efficient probe of mass transfer processes for the diffusion. The electrical properties of feldspars have been the subject of numerous studies for decades [8–22], however, most previous studies are extensively concerning in the electrical conductivities of alkali feldspar and plagioclase with intermediate composition. Extremely limited publications reported the electrical conductivity of end-number anorthite. Maury [11] studied the electrical conductivity of the whole feldspar family, both natural and synthetic, at 672–1173 K and ambient pressure using impedance spectroscopy method, and the results indicated that the activation energies for all feldspars vary in the range of 0.72–0.87 eV. Recently, Bagdassarov et al. [15] investigated the variation of activation energy of electrical conductivity with pressure in order to determine the pressure dependence of anorthite glass transition, however, their aim was to discriminate glassy and liquid states by measuring the electrical conductivity of anorthite glass at high temperature, not focus on anorthite crystal over its stability field. Notably, no study has yet reported the electrical conductivity of anorthite crystal simultaneously under high temperature and high pressure condition.

As one of our systematic study on electrical property of feldspar family which have been partly reported in Hu et al. [19–21], the electrical conductivity of synthetic anorthite is measured at 1.0–3.0 GPa and 873–1173 K by means of complex impedance spectroscopy in a multi-anvil high-pressure apparatus. We discuss the conduction mechanism of anorthite at high temperature in details using the experimental results, and the diffusion coefficient of calcium was calculated from

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the conductivity data by using Nernst–Einstein equation, and compared it with previous Ca tracer diffusion coefficient.

2. Experimental procedures

2.1. Sample preparation

High-pure silicon dioxide (SiO2), aluminum oxide (Al2O3) and calcium carbonate (CaCO3) was used to prepare the starting material. The preparation of the experimental sample is carried out by the following two steps. (1) The oxide powders firstly were weighed, then mixed and ground under acetone in an agate mortar for 2 h. In order to remove the possible water, the mixtures were dried at 723 K for 4 h. The anorthite subsequently was synthesized in a stepwise fashion, and then kept at 1673 K under ambient pressure for 3 h in high temperature furnace and finally slowly cooled down to room temperature. The experimental products were confirmed to be anorthite crystals by the micro-focused X-ray diffractometer. (2) In order to obtain the cylindrical sample, the synthetic anorthite powder were ground again under ethanol in an agate mortar and dried at 723 K in a muffle furnace, then loaded into a copper capsule. The sample eventually was sintered at 573 K and 2.0 GPa for 1 h in multi-anvil apparatus in order to reduce porosity in the sample. The sintered sample was then cut and polished into the cylinder with a diameter of 6.0 mm and a height of 6.0 mm for subsequent electrical conductivity measurement. Finally, the sample was cleaned successively in acetone and ethanol using an ultrasonic cleaner, and later keeping dry in an oven before the sample assembly. The texture of the sample was examined using scanning microscope (SEM), which showed the foam texture and the grain size was nearly uniform (Fig. 1). The chemical composition was determined by EPMA-1600 electron probe (EMPA) operated at 25 kV and 10 nA and the results were showed in Table 1.

2.2. Electrical conductivity measurements

Electrical conductivity measurements were carried out in an YJ-3000t multi-anvil apparatus. The sample assembly for the conductivity measurement resembles that in our previous studies [19–21]. The aluminum oxide (Al2O3) insulator, hexagonal boron nitride (HBN) sleeve, cubic pyrophyllite pressure media and other parts were heated at 1023 K for 5 h in a muffle furnace prior to sample assembly. The cylindrical sample was placed in a HBN sleeve with an inner diameter of 6.0 mm, and sandwiched by two Pt electrodes with the same diameter as HBN. After completing the assembly, it was further dried at 473 K in an oven overnight before the electrical conductivity measurement. In order to check the distortion of sample geometry during conductivity measurement, the sample cell after measurement was polished to section and the cross-section was shown in Fig. 2 in which the original sample geometry was largely preserved. Therefore, the distortion of sample dimension can be neglected during data processing.

Table 1
The chemical composition of synthetic anorthite by electron microprobe analysis (wt.%).

Oxide	Synthetic anorthite
SiO2	43.41
Al2O3	35.33
CaO	20.83
Cr2O3	0.04
Na2O	0.15
total	99.76

Impedance spectroscopy measurements were carried out in a multi-anvil apparatus by a Solartron 1260 impedance gain-phase analyzer at 873–1173 K and 1.0–3.0 GPa, with the applied alternating current voltage of 1 V in the frequency range of 10^{-1}–10^{6} Hz. Since water has a significant effect on the conductivity measurement, two or three heating and cooling cycles were undertaken to drive off any moisture in cell assembly and sample. For each run, the sample was firstly compressed to the desired pressure with a rate of 1.5 GPa/h. Then the temperature was changed in 50 K steps and simultaneously the impedance spectra were collected in subsequent heating or cooling cycles. The experimental results showed that the conductivity data from the first heating cycle obviously deviated from other cycles, therefore, only the reproducible data were chosen for the analysis process.

Impedance spectra showed that one semicircular arc and one small tail in the high and low frequency range, respectively. As the tail following the arc corresponds to grain boundary transport or sample-electrode interface process (discuss below), the semicircular arc representing the bulk conduction property is fitted by using an equivalent circuit of resistor and capacitor in parallel to obtain sample resistance. The conductivity was then calculated from the sample resistance and dimensions using the equation, $\sigma = L/SR$, where σ is the electrical conductivity, L and S are the sample length and cross-section area of electrode, respectively, and R is the sample resistance. Experimental errors are mainly from (1) the fitting error of impedance arcs that are no more than 5%, and (2) the uncertainty of temperature which is less than 10 K due to the thermal gradient along the length of sample cell. The error arising from the distortion of sample dimension can be neglected since the sample after conductivity measurement reserved its original geometry as shown in Fig. 2. Therefore, the total uncertainty of electrical conductivity is not more than 5%.

3. Results

Fig. 3 shows the typical impedance spectra of sample at 1.0 GPa. Each impedance spectrum shows one semicircular arc at high frequencies

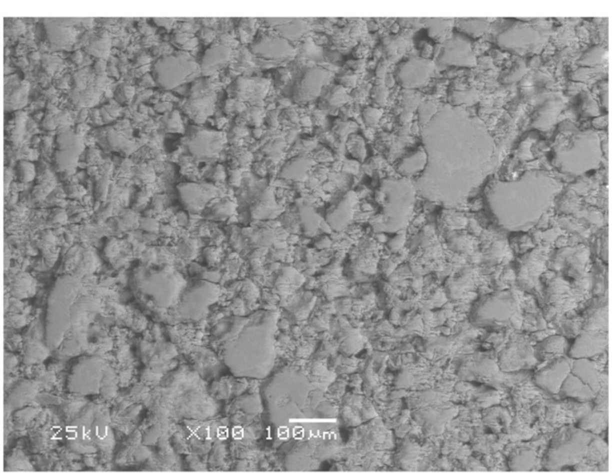

Fig. 1. Cross-section of the recovered sample cell from an electrical conductivity measurement. The original sample geometry was largely preserved.

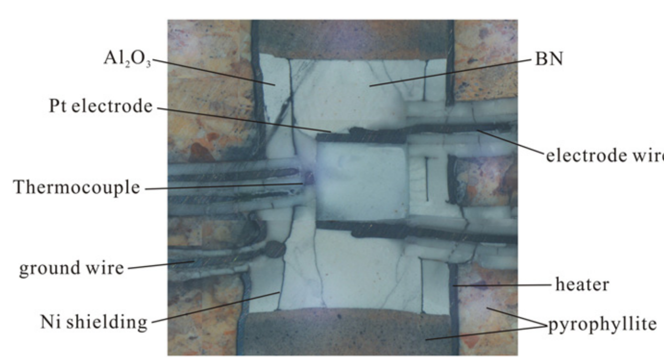

Fig. 2. Backscattered electron image of the microstructure of the sample after the conductivity measurements.