Impedance spectra of hot, dry gabbro at high temperature and pressure*

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Abstract Impedance spectra of hot, dry gabbro have been studied at 1.0~2.0 GPa and 593~1173 K. The experimental results indicate that complex impedance depends on frequency of altering current. Impedance arcs representing grain interiors and grain boundaries conduction mechanism are displayed in the complex impedance plane. The impedance arc corresponding to grain interiors occurs over the range of $10^2 \sim 10^5$ Hz, and the impedance arc corresponding to grain boundaries occurs over the range of $12 \sim 10^2$ Hz. Each element of equivalent circuit corresponding to grain interiors is fit for complex nonlinear least square program. When garnet occurs in gabbro, the electrical conductivity of gabbro abruptly changes.

Keywords: **high temperature and pressure, gabbro, impedance spectra, electrical conductivity, break.**

Some physical properties of the Earth's interior materials can be known by the electrical conductivity *in situ* measurement in the laboratory at high temperature and pressure, which will help electromagnetism workers explain the field magnetotelluric data[1]. The Moho discontinuity interface below the stable land region is usually not caused by phase transformation between gabbro and eclogite or between garnet granulite and eclogite[2], and whether phase transformation between gabbro and eclogite affects the result or not remains a puzzle. The data of electrical conductivity at high temperature and pressure is scarce, and there is no report about the impedance spectra measurement of gabbro. In this paper, we study the impedance spectra of gabbro in the frequency range of $12 \sim 10^5$ Hz and find that the electrical conductivity of gabbro abruptly changes when the garnet occurs in the gabbro.

1 Principle and character of impedance spectroscopy

Complex impedance is the total opposition of current flow in response to an AC signal, and is generally composed of a real component (resistance) and an imaginary component (capacitance), the complex impedance Z^* is given by

$$Z^* = Z_r - jZ_i, \qquad (1)$$

where Z^* denotes a complex quantity, Z_r a real quantity, Z_i an imaginary quantity, and j is $\sqrt{-1}$. The real and imaginary parts of the impedance are obtained from the measured quantities modulus $|Z|$ and phase angles ϕ, which are determined at a given frequency by

$$Z_r = |Z| \cos\phi, \qquad (2)$$

$$Z_i = |Z| \sin\phi. \qquad (3)$$

We can obtain various impedance arcs by projecting the data on the complex plane. Each arc has a different relaxation time, and corresponds to one or several conduction processes. The experimental impedance data can be analyzed with impedance spectroscopy and equivalent circuits. Thus parameters (R, C) corresponding to specific conductance and polarization mechanisms could be extracted. Fig. 1 (a) shows the ideal forms of the equivalent circuits, where R_1, R_2 and R_3 are resistors; C_{sys}, C_2 and C_3 are capacitors. Fig. 1(b) shows impedance spectra. Arc Ⅰ, which is equivalent to parallel R_1C_1 (generally, the value of C_1 is much smaller than that of C_{sys}, and therefore is masked by the latter one), stands for grain interiors conductance mechanism. Arc Ⅱ, which is equivalent to parallel R_2C_2, stands for grain boundary mechanism. Arc Ⅲ, which is equivalent to parallel R_3C_3, stands for sample/electrode mechanism. The center points of the three arcs are thought to be on the real axis.

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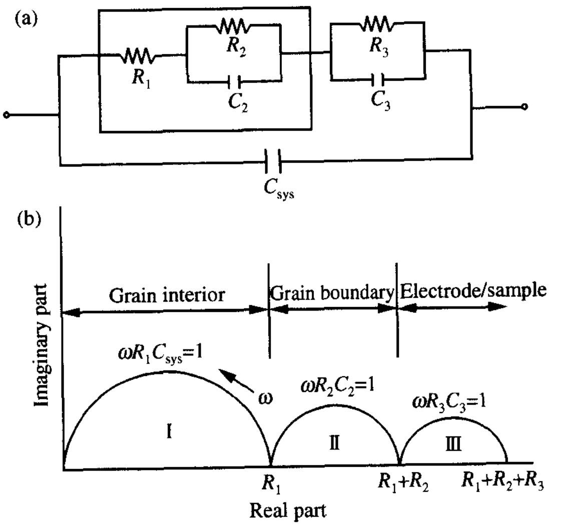

Fig. 1. The principle of modeling conduction mechanism of the polycrystalline sample system. (a) The form of the equivalent circuit; (b) impedance spectra.

Due to different relaxation times, the above three mechanisms may occur at different relaxation frequencies, and arcs I, II and III may occur at high, medium and low frequencies, respectively. The complex impedance of single parallel RC is given by

$$Z^* = R/(1 + j\omega RC), \quad (4)$$

where, ω is the angular frequency, $\omega = 2\pi f$, f is frequency. In reality, the center points of arcs may not be on the real axis. In this case, the ideal equivalent circuit needs to be modified by introducing a constant phase element (CPE) to substitute for capacitor. Complex impedance of single parallel R-CPE is given by

$$Z^* = R/[1 + RC(j\omega)^n]. \quad (5)$$

When $n = 0$, the CPE behaves as an ideal resistor. When $n = 1$, the CPE behaves as an ideal capacitor; when $0 < n < 1$, the arc is depressed. The width of each arc on the real axis is equal to the resistance value of the corresponding resistor of the parallel RC circuit element. R and C can be obtained by fitting the experimental data with a complex nonlinear least square (CNLS) method. Impedance spectroscopy principle and data processing are described in detail in Refs. [3,4].

2 Sample preparation and experimental method

2.1 Sample preparation

The samples used in the experiment are fresh gabbro, whose chemical compositions (mass fraction wt%) are SiO_2 45.48, Al_2O_3 14.64, $TiO_2$0.8, FeO and Fe_2O_3 12.10, MnO0.21, MgO11.7, CaO 10.0, Na_2O 1.95, K_2O 0.5, H_2O^+ 1.62, $P_2O_5$0.08, and CO_2 0.70. The gabbro was cut and ground into cylinders, 5.8 mm and 5.6 mm in diameter, 6.60 mm and 5.60 mm in length, then the samples were soaked in acetone to eliminate grease and baked at 100～120 ℃ for 12 h to eliminate absorbed water.

2.2 Experimental methods

Our experiments were carried out in a cubic anvil apparatus on an YJ-3000T pressure machine. The apparatus was described in detail in Ref. [5]. The pressure, with an error of ±0.1 GPa, was increased to a desired value slowly and remained constant, then the temperature went up gradually. Various temperatures selected at a pressure remained long enough to ensure equilibrium state before measurement. The modulus $|Z|$ and phase angles ϕ were recorded simultaneously at a given frequency with a ZL-5 LCR meter (measurement accuracy: 0.05%) at each temperature point. Measurement voltage is 1 V, frequency is in the range of $12 \sim 10^5$ Hz.

3 Results and discussion

The impedance spectra of gabbro were measured respectively at 1.0 GPa, 593～893 K and 2.0 GPa, 623～1173 K. The experimental results showed a good reproducibility under the same conditions, and the results obtained under two pressure conditions were quite similar. Previous studies[6] showed that electrical properties of rock and mineral depend on frequency when they are measured with AC method, which can be seen from the effect of frequency on each part of complex impedance. The real parts follow the same law, and they decrease as frequency increases, especially at low temperature (Fig. 2 (a)). Imaginary parts reach to the biggest value as frequency increases, then decrease as frequency further increases (Fig. 2 (b)). Phase angles also depend on frequency, and the dependency becomes weak at elevated temperature, and phase angles decrease as frequency increases (Fig. 2 (c)). From these results, we know that frequency influences the real part, imaginary part and the phase angle, that is, frequency influences the complex impedance, which indicates that the electrical properties of rock and mineral depend on frequency.

It can be seen from Fig. 3 (a) that arc I occurs in the complex plane at each temperature. It becomes

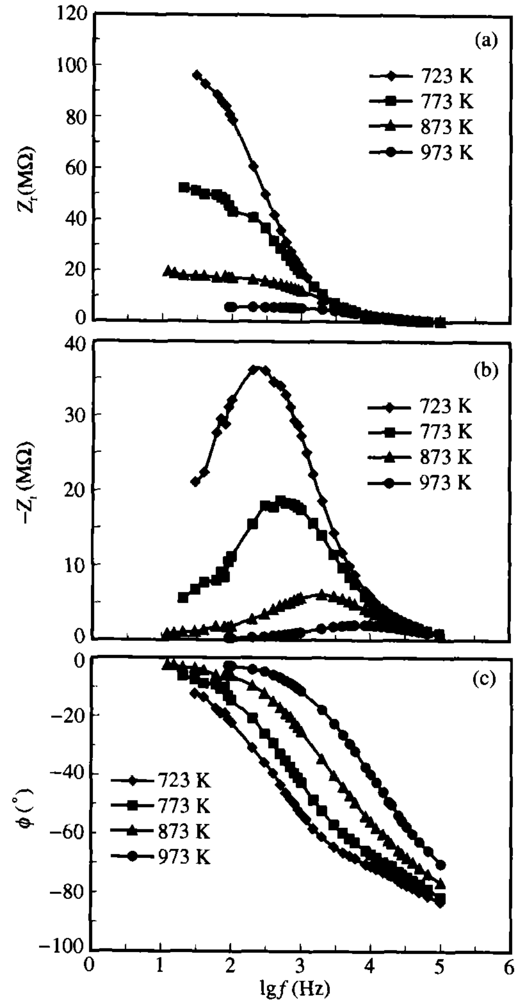

Fig. 2. The relationship between real part (a), imaginary part (b), angle phase (c) and frequency at 2.0 GPa, 623～973 K.

more and more complete as temperature increases, and its occurring is over the frequency range of 10^2～10^5 Hz in the experiment. According to the impedance spectra principle, this semicircle represents the conduction mechanism of the interior gabbro, which only occurs at high frequency. The center point of the arcs lies below the real axis, and the arc appears depressed, that is, $0 < n < 1$. The values of real and imaginary part markedly decrease with temperature increasing at a pressure, which indicates that the resistance of gabbro greatly depends on temperature. It can be seen from Fig. 3 (b) that arc Ⅰ and arc Ⅱ occur in the complex plane at each temperature. Arc Ⅰ, which stands for grain interiors mechanism, occurs over the frequency range of 10^2 ～ 10^5 Hz; arc Ⅱ, which stands for grain boundaries mechanism, occurs over the frequency range of 12 ～ 10^2 Hz. It suggests that arc Ⅰ and arc Ⅱ will shift toward higher frequencies as the temperature increases, similar results were reported by Duba et al.[7].

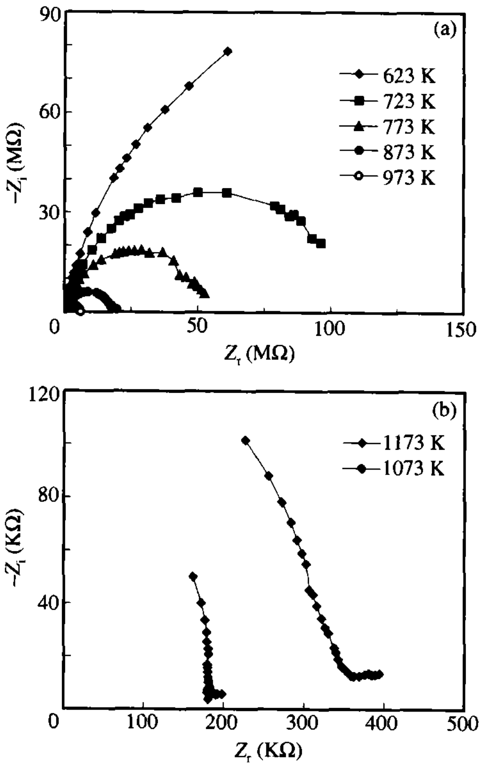

Fig. 3. The impedance spectra of gabbro at various temperatures at 2.0 GPa. (a) 623～923 K; (b) 1073～1173 K.

The resistance of the dry sample was very big and the frequency used in our experiments was limited. So, arc Ⅲ was out of our frequency range. Otherwise, arc Ⅲ would have occurred if the frequency used in our experiment was low enough, but it did not represent the intrinsic electrical properties of the samples, and did present the polarization effect between the sample and electrode. Therefore, arc Ⅲ has little to do with the electrical conductivity. DC resistance and capacitance for the arc Ⅰ are fitted with CNLS at 1.0 GPa and 2.0 GPa. Fitting parameters are shown in Table 1 with impedance spectra.

Table 1. The fitting parameters for gabbro at 1.0 GPa and 2.0 GPa and various temperatures with impedance spectra

P/GPa	T/K	R_1/Ω	C_1/F	n_1
	563	$(1.274 \pm 0.084) \times 10^8$	$(5.402 \pm 0.761) \times 10^{-12}$	0.888 ± 0.012
	643	$(5.860 \pm 0.185) \times 10^7$	$(4.499 \pm 0.422) \times 10^{-12}$	0.903 ± 0.008
1.0	743	$(1.288 \pm 0.022) \times 10^7$	$(3.575 \pm 0.498) \times 10^{-12}$	0.928 ± 0.012
	793	$(5.915 \pm 0.014) \times 10^6$	$(3.241 \pm 0.805) \times 10^{-12}$	0.932 ± 0.125
	893	$(1.312 \pm 0.063) \times 10^6$	$(4.992 \pm 0.624) \times 10^{-13}$	0.907 ± 0.006
	723	$(1.086 \pm 0.024) \times 10^8$	$(3.243 \pm 0.218) \times 10^{-11}$	0.761 ± 0.007
	873	$(1.835 \pm 0.123) \times 10^7$	$(3.351 \pm 1.065) \times 10^{-11}$	0.929 ± 0.012
2.0	973	$(5.918 \pm 0.096) \times 10^6$	$(3.324 \pm 0.454) \times 10^{-11}$	0.782 ± 0.027
	1073	$(1.179 \pm 0.039) \times 10^6$	$(8.409 \pm 3.360) \times 10^{-12}$	0.811 ± 0.009
	1123	$(3.597 \pm 0.036) \times 10^5$	$(5.379 \pm 1.737) \times 10^{-12}$	0.602 ± 0.021
	1173	$(1.808 \pm 0.016) \times 10^5$	$(1.967 \pm 0.012) \times 10^{-12}$	1.041 ± 0.057

Introducing the fitting parameters (R_1) to Eq. (6), we get

$$\sigma = (L/S)/R_1, \qquad (6)$$

where σ is electrical conductivity; L/S, geometry factor; L, the length; S, cross section areas of the electrodes; R_1, resistor.

So, the electrical conductivity at various temperatures is obtained by this equation, the logarithm electrical conductivity plotted against $1/T$ is shown in Fig. 4.

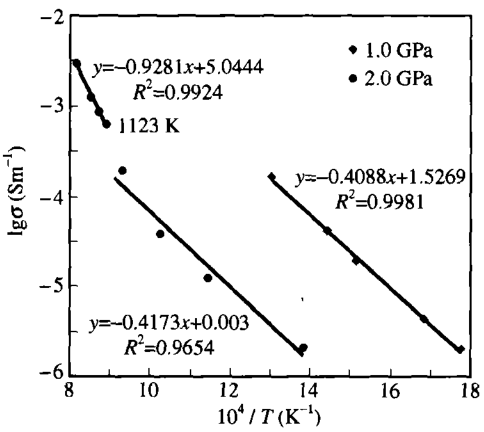

Fig. 4. The relationship between $\lg\sigma$ and $1/T$ at 1.0 GPa and 2.0 GPa for gabbro.

The values of R_2 and C_2 cannot be resolved reliably with CNLS because of few data available for arc Ⅱ. Huebner et al.[3] experimentally found that the resistance of grain boundary decreased markedly with pressure's increasing. When measuring the electrical conductivity of olivine at high pressure, Xu et al.[8] found that grain interiors dominated bulk electrical conductivity, and the contribution of grain boundaries to electrical conductivity could be omitted. It is evident that $\lg\sigma$ and $1/T$ have a linear relationship at 1.0 GPa (shown in Fig. 4), implying that the conductivity is likely to be dominated by a single mechanism over the range of 593~893 K. There is no new mineral phase observed in gabbro under a microscope. Under the condition of 2.0 GPa, the slope changes from −0.4324 to −0.6962 when the temperature is increased to 1123 K (shown in Fig. 4), that is, the electrical conduction changes, which implies that the conduction mechanism changes. The microscopic observation and electrical probe further confirmed the mineral phase transfer in the gabbro, and the mineral assembleage is composed of pyroxene, garnet and plagioclase. We found that the condition for garnet appearance is different from that reported by Ringwood et al.[2]. Ringwood thought that the assembly of pyroxene, plagioclase and garnet occupied a stable area of 0.20~1.25 GPa. However, we think the difference is not caused by the composition of the samples, because the ratio of FeO/MgO that we detected is lower than that of Ringwood. So it should be caused by the pressure and oxygen fugacity. In our opinion, garnet occurs at low temperature because of the elevated pressure, and the appearance of the garnet leads to the discontinuity of electrical conductivity. From this viewpoint, the factors causing the measurement variation are not only the composition of rock and mineral, but also the transformation of the mineral phase. So, when the other factors affecting the electrical conduction cannot interpret the discontinuity of the electrical conductivity, the transformation of the mineral phase might be an explanation.

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