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Electrical conductivity of $Alm_{82}Py_{15}Grs_3$ almandine-rich garnet determined by impedance spectroscopy at high temperatures and high pressures

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article info abstract

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Under conditions of 1.0 ~ 3.0 GPa, 973 ~ 1273 K and frequency range from 10^{-2} to 10^6 Hz, the electrical conductivity of Fe-rich garnet single crystal is measured by virtue of YJ-3000 t multi-anvil high-pressure apparatus and Solartron-1260 Impedance/Gain-phase Analyzer. A series of solid oxygen buffers including Fe₃O₄ + Fe₂O₃, $Ni + NiO$, Fe + Fe $3O_4$, Fe + FeO and Mo + Mo O_2 are chosen to control oxygen fugacity. Two branches of impedance spectra are obtained in the complex impedance plane, one $(10^2\t{-}10^6 \text{ Hz})$ showing a semicircular arc originated from the origin in the Nyquist and Bode diagram, another small tail in the low frequency of 10^{-2} -10² Hz. Experimental results show that with the rise of temperature (T), electrical conductivity (σ) tends to increase, and Log σ and $1/T$ satisfies the Arrhenius relation. Under control of a Ni + NiO oxygen buffer, with the rise of pressure, electrical conductivity decreases, and the pre-exponential factor also reduces, while the activation enthalpy rises, activation energy and activation volume of charge carriers are determined as 1.29 \pm 0.12 eV and 2.01 \pm 0.57 cm³/mol, respectively. The dominant electrical conduction mechanism of anhydrous almandine-rich garnet is the Fe²⁺ \rightarrow Fe³⁺ hopping of small polaron. At 3.0 GPa, electrical conductivity of almandine-rich garnet increases with increasing oxygen fugacity. The electrical conductivity of this sample can be represented by the relation $Log_{10}\sigma = (2.67 \pm 0.05) + (0.054 \pm 0.003)\tilde{n} log_{10}f_{02} + \frac{(-5446 \pm 68)}{T}$, where f_{02} is the oxygen fugacity (bar) and T is the absolute temperature (K) . At a typical temperature and pressure in the upper mantle, the influence of oxygen fugacity is substantial.

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1. Introduction

The in-situ laboratory-based electrical conductivity measurements of minerals and rocks at relevant temperatures and pressures can be applied to the interpretation of geophysical observation results on magnetotelluric (MT) and geomagnetic deep sounding (GDS) (e.g., [Evans, 2012; Ferri et al., 2013; Fuji-ta et al., 2004, 2007a, b,](#page-6-0) [2011; Hu et al., 2011, 2013; Jones et al., 2009, 2012; Kelbert et al.,](#page-6-0) [2009; Poe et al., 2010, 2012; Pommier, in press; Pommier and Le-Trong,](#page-6-0) [2011; Pommier et al., 2010a, b; Selway, 2013; Wang and Karato,](#page-6-0) [2013; Wang et al., 2006, 2008, 2010](#page-6-0)). On the other hand, results of experimental studies of the electrical conductivity of minerals and rocks at high T and P can be used to infer the physical and chemical properties of the Earth's interior, such as temperature distribution, thermodynamic structure, partial melting, point defect chemistry, mineralogical composition, element chemical migration, electronic

spin transition and water content of the Earth and other planets' interior (e.g., [Gaillard et al., 2008; Karato, 2011a, b; Karato and](#page-6-0) Wang, 2013; Laštovič[ková, 1991; Ni et al., 2011a, b; Nover, 2005; Xu](#page-6-0) [and McCammon, 2002; Xu and Shankland, 1999; Xu et al., 1998a,](#page-6-0) [b; Xu et al., 2000a, 2000b; Yang, 2011; Yang, 2012; Yang and](#page-6-0) [Heidelbach, 2012; Yang and McCammon, 2012; Yang et al., 2011;](#page-6-0) [Yang et al., 2012; Yoshino, 2010; Zhang et al., 2006, 2012; Zhou et al., 2011](#page-6-0)).

Garnet is the general term used for garnet-group minerals represented by the chemical formula of A_3B_2 [SiO₄] ₃, in which A stands for divalent cations such as Mg^{2+} , Fe²⁺, Mn²⁺ or Ca²⁺ and B stands for Al^{3+} , Fe³⁺, Cr³⁺, V³⁺, Ti⁴⁺ or Zr⁴⁺. Due to their similar characteristics in ionic radius, the B cations are prone to isomorphic substitution; thus, garnet minerals are divided into two subgroups of pyralspite garnets $[(Mg, Fe, Mn)_{3}Al_{2} [SiO₄]_{3}]$ and ugrandite garnets $[Ca₃ (Al, Fe, Cr, Ti, V, Zr) ₂ (SiO₄)₃].$ Garnet samples of various compositions are indicative of the typomorphic property (their formation conditions and genetic features), which facilitates the identification of their various genetic types (e.g., ultrabasic rock, granite, pegmatite, skarn and regional metamorphic rock) based on intrinsic characteristic elements [\(Mookherjee and Karato, 2010](#page-7-0)). Garnet has the widest depth distribution in the mantle. In view of its own complex chemical

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composition and structure stability, compared with electrical conductivity measurements on other representative rock-forming minerals such as olivine, orthopyroxene, clinopyroxene, wadsleyite and ringwoodite that only exist in the limited depth range in the upper mantle and the transition zone, in-situ experimental measurement of electrical conductivity for garnet at high pressure becomes more important [\(Dai and Karato,](#page-6-0) [2009a, b, c; Dai et al., 2008a, b, 2009, 2010, 2012; Du Frane and](#page-6-0) [Tyburczy, 2012; Du Frane et al., 2005; Huang et al., 2005, 2006; Karato](#page-6-0) [and Dai, 2009; Romano et al., 2006, 2009](#page-6-0)). As such, the knowledge of its electrical property is crucial to interpret the conductivity-depth profile of the earth's interior.

Electrical conductivity measurements on the natural majorite, almandine-rich and pyrope-rich garnets have been extensively performed (e.g., [Dai et al., 2009, 2012; Kavner et al., 1995; Romano et al.,](#page-6-0) [2006; Xu and Shankland, 1999](#page-6-0)). [Kavner et al. \(1995\)](#page-7-0) measured electrical conductivity of majorite garnet under conditions of atmospheric pressure and 20–100 °C to apply mantle conditions. However, it is difficult to extrapolate these results to high pressure and temperature conditions in the Earth's mantle.[Xu and Shankland \(1999\)](#page-7-0) measured electrical conductivities within orthopyroxene, clinopyroxene, and garnet $+$ ilmenite stability filed with the same starting material San Carlos orthopyroxene (the corresponding chemical composition is $(Mg_{0.92}Fe_{0.08})$ SiO₃ + 2.89 wt% Al₂O₃) at conditions of 1000–1400 °C and 5–21 GPa. However, the recovered sample after electrical conductivity was a mixture of ilmenite and garnet. [Romano et al. \(2006\)](#page-7-0) measured electrical conductivities of synthetic polycrystalline garnets with different chemical compositions from almandine (Fe₃Al₂Si₃O₁₂) to pyrope (Mg₃Al₂Si₃O₁₂) at 10–19 GPa and 300–1700 °C and confirmed the important influence of Mg/Fe ratio on garnet conductivity. In addition, recently, [Dai et al. \(2009a, 2012\)](#page-6-0) showed that electrical conductivities of hydrous and anhydrous pyrope-rich garnet were dependent on water content (from less than 10 to 7000 $H/10^6$ Si) and oxygen partial pressure at conditions of 1.0-16 GPa and 873–1473 K. However, as another crucial endmember of garnet group, the effect of oxygen fugacity on the electrical conductivity of almandine has never been reported till now at high temperature and high pressure.

In this study, we determined the electrical conductivity of almandinerich garnet at the frequency range from 0.01 Hz to 1 MHz using the impedance spectroscopy. A series of characteristic parameters including the pre-exponential factor, activation energy and activation volume have been obtained. At the pressure of 3.0 GPa, a functional relation model describing the electrical conductivity of almandine-rich garnet as a function of oxygen fugacity was constructed. The conduction mechanism of almandine-rich garnet has also been discussed in details.

2. Experimental procedures

2.1. Sample preparation

Dry gem-grade almandine-rich garnet single crystals were collected from the basaltic xenoliths in the Altai region of Xinjiang Uyghur Autonomous Region in China. The surfaces of samples were fresh, nonfractured, nonoxidized, rhombic trioctahedron crystallographic structure without any evidences of major alternation. The chemical compositions of the samples were determined by virtue of the EPMA-1600 electron microprobe at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences and listed in Table 1. In order to check the phase state during electrical conductivity measurements, a typical quenched sample image observation after EC measurement was investigated by an optical microscope of a plane-polarized reflected light and a back-scattered electron image derived from the analysis of scanning electronic microscope as shown in Fig. 1>. Firstly, almandine-rich garnets single crystals were cut and polished into a cylinder of φ 4.5 mm \times 5.0 mm with the ultrasonic drill and diamond slice; then, the samples were cleaned with the deionized distilled water, alcohol and acetone in turn. The samples were baked for 48 hrs in a 473 K

Table 1			

Chemical compositions of the starting material.

vacuum drying oven in order to remove the adsorbed water on the surfaces of the samples.

2.2. FT-IR measurement

In order to determine the water content of the samples, the infrared spectra of samples were obtained at wavenumbers from 1000 to 7000 cm^{-1} both before and after each conductivity experiment in the Department of Geology and Geophysics, Kline Geological Lab, Yale University, New Haven, Connecticut, USA. Detailed procedures for the FT-IR analysis are described as follows. Firstly, the sample was cut and polished in double sides up to less than 120 μm thickness

Fig. 1. Representative microscopic images of quenched almandine-rich garnet after electrical conductivity measurement derived from the plane-polarized reflected light (a) and the back-scattered electron images derived from the analysis of scanning electronic microscope (b).

using a Vibromet-2 Diamond Polisher and Ecomet-4 Diamond Polisher. The measurements were performed by a Fourier transform infrared spectrum analyzer (FT-IR, BIORAD, Varian 600 UMA). The IR absorption spectra of samples were measured by the unpolarized radiation with a KI beam splitter, a MCT detector and a Mid-IR light source. Two hundred fifty-six scans were collected for each spectrum. Apertures of 80 \times 80 μ m² square were applied for the measurements of selected sample areas. At least six spectra were conducted on the different areas of transparent sample surfaces and made an average value in order to avoid the heterogeneity effect of water distribution. Typical infrared spectra of the acquired samples before and after electrical measurements are shown in Fig. 2.

The water (hydrogen) content of a sample was calculated by the absorption spectrum at a wavenumber range from 3000 to 3750 cm⁻¹ using the equation proposed by [Paterson \(1982\)](#page-7-0),

$$
C_{OH} = \frac{B_i}{150\xi} \int \frac{K(v)}{(3780 - v)} dv
$$
 (1)

where C_{OH} is the molar concentration of hydroxyl (ppm wt H₂O or H/10⁶ Si), B_i is the density factor (cm H/10⁶ Si), ξ is the orientation factor (1/2), and $K(v)$ is the absorption coefficient in cm⁻¹ at a wavenumber v in cm⁻¹. The integration was conducted at a wavenumber range from 3000 to 3750 cm⁻¹. The water contents before and after conductivity measurements are less than \sim 3 H/10⁶ Si and \sim 6 H/10⁶ Si respectively, and thus, we call them as really "dry" almandine-rich garnet. The variation of water content during the electrical conductivity measurements of dry sample is not more than 20 %.

2.3. Oxygen buffer control

The solid oxygen fugacity buffers were obtained by homogenously mixing the 99 % high-purity powders of metals (e.g. Ni, Fe and Mo) and its corresponding metallic oxides (e.g. NiO, FeO, Fe₂O₃, Fe₃O₄, and $MoO₂$). The following reactions are employed to buffer the oxygen fugacity:

$$
MH: 4Fe3O4 + O2 \rightleftharpoons 6Fe2O3
$$
 (2)

$$
NNO: 2Ni + O2 \rightleftharpoons 2NiO
$$
 (3)

$$
IM: 3Fe + 2O2 \rightleftharpoons Fe3O4
$$
 (4)

$$
IW : 2Fe + O_2 \rightleftharpoons 2FeO
$$
 (5)

$$
MMO: Mo + O_2 \rightleftharpoons MoO_2
$$
\n⁽⁶⁾

For each given solid buffer, oxygen fugacity values are a function of pressure and temperature which can be expressed as [\(Chou,](#page-6-0) [1978; Chou and Eugster, 1976\)](#page-6-0):

$$
\text{Log } f_{\text{O}_2} = -\frac{\alpha}{T} + \beta + \gamma \frac{(P-1)}{T} \tag{7}
$$

Here, α , β and γ are constants directly related to the standard enthalpy, the standard entropy, and the molar volume variation of the solid combination before and after the balancing buffer reaction; T is the absolute temperature (K), and P is the pressure (atm). The theoretical calculation results of oxygen fugacities for five different solid buffers $[Fe₃O₄ + Fe₂O₃$ (MH), Ni + NiO (NNO), Fe + Fe₃O₄ (IM), Fe + FeO (IW) and $Mo + MoO₂$ (MMO)] under conditions of 3.0 GPa and 950–1350 K were shown in Fig. 3. In the typical upper mantle, the oxygen fugacity is inferred to be close to FQM (fayalite-quartz-magnetite) or NNO (nickel-nickel oxide) buffer [\(Frost and McCammon, 2008; McCammon et](#page-6-0) [al., 2004](#page-6-0)). Just as the technique described by [Dai et al. \(2009\),](#page-6-0) the oxygen

Fig. 2. FT-IR spectra of almandine-rich garnet for the wavenumber range from 3000–4000 cm-1 before and after electrical conductivity measurement.

fugacity is controlled and adjusted by changing the metal-bearing types in the shielding cases, electrodes and their corresponding buffer loops at a predetermined temperature and pressure. In addition, in order to verify the efficiency and accuracy of the solid oxygen buffer, it is crucial to perform the X-ray diffraction analysis on the recovery buffers after electrical conductivity measurements. If two phases for each metal and its corresponding metal oxide coexisted, it indicates that the oxygen fugacity is effectively controlled during the electrical conductivity measurements.

2.4. Impedance measurements

In-situ high-pressure electrical conductivity measurements of samples were performed in the YJ-3000 t multi-anvil press and Solartron-1260 impedance/gain-phase analyzer in the Laboratory for High Temperature and High Pressure Study of the Earth's Interior, Institute of Geochemistry, Chinese Academy of Sciences. A detailed description of the equipment was given previously by [Xu et al. \(1994\)](#page-7-0) and [Liu et al. \(2002\).](#page-7-0)

High pressures were generated by six cubic tungsten carbide anvils with a total surface area of 23.4 $mm²$. A diagram of the cross-section of

Fig. 3. Temperature dependence of oxygen fugacity for the $Fe₃O₄ + Fe₂O₃$, Ni + NiO, $Fe + Fe₃O₄$, Fe + FeO and Mo + MoO₂ buffers at the pressure of 3.0 GPa. Shown together is the oxygen fugacity value of Fayalite $+$ Quartz $+$ Magnetite (FQM).

high-pressure cell assembly for electrical conductivity measurements is shown in Fig. 4. A metal Faraday shielding case that is made of the 0.05 mm metal foil and connected to Earth's ground is installed between the pressure medium and the boron nitride insulation tube, and therefore it can efficiently reduce the temperature gradient inside the sample cell, minimize the current leakage across the pressure medium of pyrophyllite, and as well as prevent the chemical migration between the sample and pressure medium. A cylindrical sample (φ 4.5 mm \times 5.0 mm) was placed in the BN insulation tube between two symmetric electrodes of metal buffers. Boron nitride can provide a better insulation material than alumina (AI_2O_3) [\(Fuji-ta et al., 2007a\)](#page-6-0). Experimental temperature was monitored by a $Pt-Pt_{90}Rh_{10}$ thermocouple. The measurement errors from the temperature and pressure gradients were less than 10 K and 0.1 GPa, respectively. The electrical conductivity measurement errors were estimated at not more than 5 %, and the major error source was determined to be dimensional variations of sample, which are less than 8 %.

The complex impedance spectra measurements were conducted by virtue of the Solartron-1260 impedance/gain-phase analyzer. The sinusoidal alternating current signal voltage was applied within the frequency range from 0.01 Hz to 10^6 Hz during the high temperature and high pressure experiments. Two impedance semicircles were recognized within the high-frequency and low-frequency range, respectively. The sample resistance can be obtained only through fitting high-frequency semicircles when one appropriate equivalent circuit is selected. One typical equivalent circuit that is made up of a series of a parallel constant phase element (CPE) and a resistor was adopted.

3. Results

In the present studies, we have obtained the results of electrical conductivities of natural almandine-rich garnet single crystals $(Alm_{82}Py_{15}Gr_{3})$ under the conditions of pressures of 1.0-3.0 GPa and temperatures of 973–1273 K, and as well as 3.0 GPa, 973–1273 K, and five different oxygen buffers including WH, NNO, IM, IW and MMO. The frequency range of impedance spectra is 10^{-2} - 10^{6} Hz.

The representative Nyquist and Bode diagram of complex plane are shown in Figs. 5 and 6 under conditions of 3.0 GPa, 973–1273 K and a NNO oxygen buffer. The results obtained at other conditions are similar to those illustrated. Fig. 5 displays the relationship between the real part (Z') and imaginary part (Z'') of complex impedance spectra and satisfy the relation,

$$
Z^{'} = |Z| \cos \theta \tag{8}
$$

$$
Z^{''} = |Z| \sin \theta \tag{9}
$$

Fig. 4. Experimental assembly for electrical conductivity measurements at high temperature and pressure. 1: Pressure medium (baked to 973 K); 2: Metal shielding cases; 3: Pyrophyllite plug (baked to 1073 K); 4: BN insulation tube; 5: Buffer electrode and ring; 6: Al_2O_3 ; 7: Electrode lead and Al_2O_3 sleeve; 8: Tri-layers stainless steel heater; 9: $Pt-Pt_{90}Rh_{10}$ thermocouple; 10: Earth line.

Just as discussed by [Tyburczy and Roberts \(1990\)](#page-7-0), [Roberts and](#page-7-0) [Tyburczy \(1991\),](#page-7-0) [Roberts and Tyburczy \(1993a, 1993b, 1994\)](#page-7-0), [Roberts](#page-7-0) [and Duba \(1995\),](#page-7-0) [Roberts et al. \(2007\),](#page-7-0) [Bagdassarov et al. \(2007,](#page-6-0) [2011a\)](#page-6-0) and [Bagdassarov \(2011\)](#page-6-0), the high-frequency (102-106 Hz) mechanism of impedance spectra is interpreted as bulk (grain interior) conduction, and the lower-frequency (10-2-102 Hz) mechanism of impedance spectra is attributed to sample-electrode interface polarization effects at a given temperature, pressure and oxygen fugacity condition. From Fig. 5, it is clear that the τC characteristic time constant (or relaxation time, which can be expressed as $R \times C$ can be used to discriminate different conduction mechanisms of a sample. The high-frequency branch of impedance semicircular arc that stands for the bulk conduction process has a relatively low relaxation time, while the lowerfrequency branch of impedance small tail that represents the sampleelectrode polarization effects has a relatively high relaxation time. With increasing temperature, the electrical conductivity of sample increases and the obvious semi-conductor characteristics is observed at high temperature conditions. [Fig. 6](#page-4-0) shows the dependence relation of the real part (Z) , the imaginary part $(Zⁿ)$, the magnitude $(|Z|)$ and the phase angle (θ) of complex impedance on the frequency.

A representative relationship between electrical conductivity of sample and the inverse temperature under conditions of 1.0-3.0 GPa and a NNO oxygen buffer is illustrated in [Fig. 7.](#page-4-0) The obtained fitted results for electrical conductivity are listed in [Table 2.](#page-5-0) In most cases, the electrical conductivity was obtained in the process of decreasing temperature after the peak temperature was reached. However, in a few runs, the measurements of conductivity were conducted along with decreasing and increasing temperature in order to test the hysteresis. We found no large hysteresis that indicates nearly equilibrium state at each given physical and chemical measurement conditions. The relationship between the electrical conductivity of garnet single crystal and temperature were found to satisfy the Arrhenius linear relation,

$$
\sigma = \sigma_0 \exp(-\Delta H/RT) \tag{10}
$$

where σ_0 is the pre-exponential factor that is approximately independent temperature (S/m), ΔH is the activation enthalpy (eV), and R is the gas constant (8.3144 dm³ \times kPa/mol/K). The relationship among

Fig. 5. Nyquist Z' vs. additive inverse Z" plots of the impedance for almandine-rich garnet with the frequency range from 10^{-2} Hz to 1 MHz, obtained under the conditions of 3.0 GPa, 973–1273 K and a NNO buffer. Z' and Z" represents the real part and imaginary part of complex impedance, respectively.

Fig. 6. Bode diagram for almandine-rich garnet with the frequency range from 10^{-2} Hz to 1 MHz, obtained under the conditions of 3.0 GPa, 973-1273 K and a NNO buffer. The dependence of real part (Z'), the imaginary part (Z"), magnitude (|Z|) and phase angle (θ) of complex impedance on frequency are shown in Figs (a), (b), (c) and (d), respectively.

activation enthalpy (ΔH) , activation energy (ΔU) and activation volume (ΔV) can be represented by the following equation,

$$
\Delta H = \Delta U + P \times \Delta V \tag{11}
$$

4. Discussion

It is well known that the electrical conductivity of iron-bearing mineral and rock is highly sensitive to the redox conditions. Thus, when we try to apply laboratory-based conductivity data to calculate the upper-mantle profile, it is crucial to take account of the influence of oxygen fugacity $fO₂$ in the upper mantle. The petrological studies suggest that the oxygen fugacity of the upper mantle lies between IW $(iron + wüstite)$ and FQM (Fayalite $+$ Quartz $+$ Magnetite) buffers, and that the transition zone and lower mantle $aO₂$ is possibly near to IW buffer [\(Xu et al., 2000b\)](#page-7-0). And furthermore, in consideration of a nearest FQM oxygen fugacity value in the upper-mantle top listed in [Fig. 1,](#page-1-0) a NNO buffer is selected to explore the pressure effect on the electrical conductivity of almandine-rich garnet. Fig. 7 shows the influence of temperature and pressure on electrical conductivity. The activation

energy (
$$
\Delta E
$$
) and activation volume $\left(\Delta V = \left(\frac{\partial \Delta H}{\partial \Delta P}\right) = -\frac{\partial \left(\frac{\partial \ln \sigma}{\partial \partial P}\right)}{\partial \Delta P}\right)$ were

determined at conditions of 1.0-3.0 GPa, 973–1273 K and a NNO oxygen buffer, yielding values of 1.29 \pm 0.12 eV and 2.01 \pm 0.57 cm³/mol, respectively. The present experimental results are in good agreement with those of anhydrous single crystal olivine, albite, K-Na feldspar solid solution reported by [Xu et al. \(2000a\)](#page-7-0) and [Hu et al. \(2011, 2013\)](#page-6-0) in terms of negative pressure dependences, and however, there exist some different pressure dependences of silicate perovskite and ilmenite at lower mantle conditions reported by [Shankland et al. \(1993\)](#page-7-0), [Katsura](#page-7-0) [et al. \(1998\)](#page-7-0) and [Zhang et al. \(2006\)](#page-7-0) in terms of positive pressure dependences, respectively. The electrical conductivity of almandinerich garnet decrease with increasing pressure is due to more difficult formation of vacancies at high pressure.

[Fig. 8](#page-5-0) shows the relationship between electrical conductivity and oxygen fugacity at 3.0 GPa over the temperature range of 873 to 1273 K and corresponding to five different oxygen buffers including

Fig. 7. Logarithm of electrical conductivity versus reciprocal temperature for the almandine-rich garnet under conditions of 1.0-3.0 GPa and with a NNO oxygen buffer. The open circles represent the conductivity of sample during the period of heating cycles at 3.0 GPa. The calculated electrical conductivity of almandine-rich garnet at atmospheric pressure is also shown by virtue of parameters of the Arrhenius relation.

Table 2

Fitted parameters of Arrhenius relation for the electrical conductivity of almandine-rich garnet.

 $Fe₃O₄ + Fe₂O₃$, Ni + NiO, Fe + Fe $₃O₄$, Fe + FeO and Mo + MoO₂. At</sub> a given pressure of 3.0 GPa, the relation between the electrical conductivity of anhydrous samples and oxygen fugacity can be described as:

Log₁₀
$$
\sigma = (2.67 \pm 0.05) + (0.054 \pm 0.003) \times \log_{10} f_{O_2}
$$

 $+ \frac{(-5446 \pm 68)}{T}$ (12)

The oxygen fugacity exponent (q) is 0.054 \pm 0.003. We interpret this result assuming that the oxygen fugacity dependence of electrical conductivity is due to the dependence of number density of charge carrier on oxygen fugacity. The defect chemistry of anhydrous almandine-rich garnet indicates that the concentration of the ferric iron-related defects [X] depends on the chemical environment as:

$$
[X] \propto f_{O_2}^q \times \alpha_{MeO}^s \tag{13}
$$

where q and s are constants that are dependent on different defect types; f_{0_2} is the oxygen fugacity; α is the ionic activity, and MeO is the metal oxide. Similar to other dominant rock-forming minerals such as dry wadsleyite and ringwoodite in the transition zone [\(Huang et al., 2005\)](#page-6-0), the values of q and s for typical defects of anhydrous almandine-rich garnet are summarized in Table 3.

The observed values of exponential factors of q (0.054) are very close to the exponents (0.061) obtained by [Dai et al. \(2012\)](#page-6-0) for dry pyrope-rich garnet at conditions of 1.0-4.0 GPa, 873–1273 K, and controlled oxygen buffers (Fe₃O₄ + Fe₂O₃, Ni + NiO, Fe + Fe₃O₄, Fe + FeO and $Mo + MoO₂$). And it is very close to the results (0.050)

Fig. 8. Effect of oxygen fugacity on electrical conductivity of almandine-rich garnet under conditions of 3.0 GPa, 973-1273 K and controlled oxygen buffers (Fe₃O₄ + Fe₂₋ O_3 , Ni + NiO, Fe + Fe₃O₄, Fe + FeO and Mo + MoO₂).

obtained by [Dai and Karato \(2009b\)](#page-6-0) for dry wadsleyite in the mantle transition zone under conditions of 15 GPa, 873–1273 K, and with three solid buffers (Ni + NiO, Mo + MoO₂ and Re + ReO₂). However, it is substantially lower than the exponent of 0.182 determined by [Constable and Duba \(1990\)](#page-6-0); [Constable et al. \(1992\);](#page-6-0) [Constable and](#page-6-0) [Roberts, 1997; Constable and Duba, 2002\)](#page-6-0) for dry San Carlos olivine, Red Sea olivine, dunite and lherzolite under conditions of atmospheric pressure, temperature of 873–1773 K and controlled oxygen fugacity by continuously changing a ratio mixture of $CO + CO₂$ gas buffer across sample cavity. [Karato and Wang \(2013\)](#page-7-0) recently put forward and developed the novel models for the concentration of point defects in olivine (Mg,Fe) $_2$ SiO₄ or orthopyroxene (Mg,Fe)SiO₃, depending on the chemical environment under chemically neutral conditions for either Fe_{Mg} $\mathcal{H} = \left[\text{H}^\prime \text{Mg} \right]$ (p = 1/4, q = 1/8, and r = -1/2) or $\left[\text{Fe}^\prime \text{Mg} \right] = \left[\text{V}^\prime \text{Mg} \right]$ (p = 0, $q = 1/6$, and $r = -1/3$). However, the value of $q(0.054)$ for almandine-rich garnet is less than simple model predicted, suggesting the involvement of other charge neutrality conditions, such as $[Fe^{\dagger}_{Mg}] = [V_0^{\dagger}]$ ($p = 0$, $q = -1/6$, and $r = 1/3$) and $[Fe^{\dagger}_{Mg}] = [e^{\dagger}]$ $(p = 0, q = -1/6,$ and $r = -2/3$), or that chemical equilibrium was

only partially obtained. In summary, all of above listed evidences including the activation energy (ΔU) 1.29 \pm 0.12 eV, the activation volume (ΔV) 2.01 \pm 0.57 cm^3/mol , the negative dependence of electrical conductivity on pressure, and as well as the positive dependence of electrical conductivity on oxygen fugacity make it clear that in our experiment the main electrical conduction mechanism of anhydrous almandine-rich garnet is the Fe²⁺ \rightarrow Fe³⁺ hopping of small polaron, which is in general agreement with those of dry Fe-bearing silicates such as olivine, orthopyroxene, clinopyroxene, augite, pyrope-rich garnet, wadsleyite, and ringwoodite that previously reported dominantly representative minerals in the Earth crust, upper-mantle and transition zone [\(Dai et](#page-6-0) [al., 2008a, b, 2010; Huang et al., 2005; Wang et al., 2006; Xu et al.,](#page-6-0) [2000a; Yang, 2012; Yang and Heidelbach, 2012; Yang and](#page-6-0) [McCammon, 2012; Yang et al., 2011; Yang et al., 2012; Zhang et al.,](#page-6-0) [2012](#page-6-0)). Because the electrical conductivity of dry garnet shows a positive relation with the concentration of point defects, the electrical conductivity increases with a higher oxygen fugacity and a higher concentration of small polaron arising from a point defect reaction. At a typical temperature and pressure in the upper mantle, the influence of oxygen fugacity is substantial. [Fig. 9](#page-6-0)

We compare the electrical conductivity of almandine-rich garnet with those of previously available results. The comparison is made at 3.0 GPa and for the same oxygen fugacity controlled by a $Mo + MoO₂$ buffer. The results show that under anhydrous (water-free) conditions, the almandine-rich garnet ($Alm_{82}Py_{15}Grs_3$) has about 3 times higher conductivity than pyrope ($Py_{73}Alm_{14}Grs_{13}$) by [Dai and Karato \(2009a\).](#page-6-0) As argued by [Romano et al. \(2006\),](#page-7-0) they investigated the electrical conductivity of synthetic pyrope $(Mg_3Al_2Si_3O_{12})$ –almandine (Fe₃Al₂Si₃O₁₂) samples and found that electrical conductivity increases by four orders of magnitude from $Py_{85}Alm_{15}$ to $Py_{20}Alm_{80}$. It has been suggested that the explanation of this discrepancy is due to the garnets investigated by [Romano et al. \(2006\)](#page-7-0) containing a large amount of water, which would have produced anomaly high electrical conductivity,

Table 3 Point defect concentrations for dry almandine-rich garnet.

Defect	q	S	Defect	q	S
$[Si_1^{\ldots}]$	$-\frac{1}{3}$	$-\frac{10}{3}$	$[V_0^{\bullet}]$	$-\frac{1}{6}$	一気
$\lceil V^{'}_{M} \rceil$	$\frac{1}{6}$	一卦	Si	ŧ	$\frac{10}{3}$
$[Mg_i^{\star}]$	ᅳᄛ	ŧ	$[h^{\dagger}]$	$\frac{1}{6}$	$-\frac{1}{3}$
[0, 0] [Fe _{Mg}]	Ė ŧ	÷–	[e']	$-\frac{1}{6}$	

Fig. 9. Electrical conductivities of dry almandine-rich garnet (black solid lines) in this study compared with the previous results. Lines are indicated as follows: 1. Present study; 2–1, 2–2, 2–3 and 2–4 represent electrical conductivities of dry and hydrous pyrope-rich (Py₇₃Alm₁₄Grs₁₃) by Dai and Karato (2009a); 3–1, 3–2, 3–3 and 3–4 represent electrical conductivities of chemical compositions from Py₈₅Alm₁₅ to $Py_{20}Alm_{80}$ garnets by [Romano et al. \(2006\)](#page-7-0). Comparison is made at P = 3 GPa and for the same oxygen fugacity controlled by a $Mo + MoO₂$ buffer.

especially in the low-temperature region (Dai et al., 2012; Yang et al., 2012). The actual contribution from almandine-rich garnet depends on not only its volume percentage but also its geometry. Although the dry almandine-rich garnet has a relatively higher conductivity than those of dominant dry rock-forming minerals such as olivine and pyroxene in the upper mantle, there exists an extremely feeble effect on the bulk conductivity because almandine-rich garnet is a relatively rare mineral phase in the cal-alkaline volcanic rocks worldwide and is impossibly interconnected. In brief, for a small quantity of volume percentage of almandine-rich garnet, its contribution is extremely feeble in a typical upper mantle and the transition zone of the Earth's mantle, but maybe its contribution becomes very important in the Central Slovakian Volcanic Filed (CSVF), the volcanic complexes of the Börzsöny and Visegrád Mts and the Cserhát and Mátra cal-alkaline volcanic rocks of the North Pannonian Basin in Eastern-Central Europe since almandine-rich garnet is relatively common (Harangi et al., 2001).

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