氏　　　　名	王　冉
授与した学位	博　士
専攻分野の名称	理　学
学位授与番号	博甲第　　　６８５０　　　号
学位授与の日付	２０２３年　３月　２４日
学位授与の要件	自然科学研究科　　　　地球惑星物質科学専攻 （学位規則第４条第１項該当）
学位論文の題目	Electrical conductivity and Seebeck coefficient of mantle minerals （マントル鉱物の電気伝導度とゼーベック係数）
論文審査委員	教授　神﨑　正美　　教授　芳野　極　　　教授　田中　亮吏 准教授　山﨑　大輔　　教授　James Tyburczy

学位論文内容の要旨

Knowledge of physical properties of mantle constituent minerals is essential to understand the composition, structure and dynamics of Earth's interior. Electrical conductivity measurement of mantle minerals is a widely applied approach to interpret the electrical anomalies in the deep Earth. Seebeck coefficient is a thermoelectric parameter to indicate the species of charge carriers. Combination of both parameters help to precisely investigate the intrinsic and extrinsic properties of mantle minerals. I conducted measurements and simultaneous modelling on electrical conductivity and Seebeck coefficient of olivine, garnet, wadsleyite and hydrous minerals to quantitatively study the contributions of different conduction mechanisms to the total.

We established a new method to measure the Seebeck coefficient of mantle minerals under high pressure and high temperature condition. The temperature difference was produced by an isolated dual heating system and the electromotive force (EMF) was monitored by independent probes set on top and bottom of the sample. Thus, I can easily obtain the Seebeck Coefficient: $S=-\Delta V/\Delta T$, where ΔV is the EMF and ΔT is the temperature difference of top and bottom of the sample. Seebeck Coefficient of Si wafers were conducted to check the reliability of our method. And the results show good consistency with previous studies at room pressure which also indicates a negligible pressure dependence of Seebeck Coefficient of Si.

Simultaneous modelling on electrical conductivity and Seebeck coefficient of mantle minerals were conducted to quantify the contributions of different conduction mechanisms to the total. Olivine, garnet, wadsleyite and hydrous minerals were chosen as the targe materials to study the contributions of each conduction mechanism to the total. Small polarons and Mg vacancies dominate the conduction mechanism of dry olivine at low and high temperatures. Small polaron conduction makes more contributions to the total with increasing the total iron content. Protons and proton vacancies dominate the conduction at low temperatures in Fe-free and Fe-bearing wadsleyite, respectively. Incorporation of more water in Fe-bearing wadsleyite can effectively enhance the ionic conduction. Proton vacancies dominate the conduction at low temperatures in diaspore and ε-FeOOH while small polarons also make contributions to the total conduction in diaspore since a considerable amount (0.82 ± 0.08 wt.%) of Fe_2O_3 is contained in the crystal.

論文審査結果の要旨

Ran Wang has studied electric properties of the mantle minerals in the earth's interior during 5-years PhD course. Since Seebeck effect can create the electromagnetic interaction at the core mantle boundary of planets, it is important to determine the Seebeck coefficient of mantle minerals for understanding the planetary dynamo, redox state and isotope fractionation between core and mantle. Furthermore, determination of the Seebeck coefficient of minerals made it possible to constrain the type of charge carrier combined with electrical conductivity data. However, experimental measurements on the Seebeck coefficient have not measured under high pressure using dual heating system because of experimental difficulty. He firstly measured the Seebeck coefficients of major mantle minerals under high pressure for the first time in the world.

Measurements on olivine with various Fe contents at 3 and 5 GPa up to 1400 K shows that the Seebeck coefficient and electrical conductivity systematically increases with increasing Fe content. Modelling demonstrated small polarons dominate the total conduction within the measuring temperature range and contribution of Mg vacancies becomes dominant with increasing temperature. Seebeck coefficient measurements of Fe-free and-bearing wadsleyite with various amounts of water were conducted at 15 GPa up to 1000 K. Fe-free wadsleyite shows a negative Seebeck coefficient, while Fe-bearing wadsleyite show a positive value, requiring different type of H-related charge carrier between Fe-free and -bearing wadsleyite. Measurements of electrical conductivity and Seebeck coefficient of hydrous mineral showed negative Seebeck coefficient, suggesting that proton is not a dominant charge carrier in hydrous minerals. These results not only make it possible to constrain redox reactions due to the Seebeck effect at the core-mantle boundary, but also make it possible to more accurately constrain the amount of water in the mantle from electrical conductivity.

Ph D. defense for Ran Wang was held on 14th February. We considered that this thesis is the first report on Seebeck coefficient of main mantle minerals under high pressure and gives a new insight on electrical charge of the mantle minerals. The presentation was made in English. After some correction based on comments given by committee members, we judged that this thesis is suitable to be accepted as a dissertation of Doctor of Philosophy in Okayama University.