Pressure and temperature response of proton conductivity of ice VII and VIII, and their phase relations

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1. Introduction

Between ~2 and ~60 GPa, it has generally been accepted that only two solid H2O phases—a high temperature, proton disordered, cubic ice VII and a low temperature, proton ordered, tetragonal ice VIII are stable. However, based on X-ray diffractions and spectroscopic studies, it was pointed out that a phase transition or some structural change occurs at around 14 GPa [1-5]. In this study, we measured pressure and temperature responses of proton resistance of ice VII and VIII at 2-40 GPa and 263-300 K by using an AC impedance analysis method. We discuss the cause of the obtained P-T responses of proton conductivity and the phase relations of solid H2O.

2. Experimental

Platinum or gold electrodes were placed around a hole of a rhenium gasket combined with cubic boron nitride powder. Distilled and deionized H2O was loaded into the hole and pressurized by diamond anvils having flats of 0.35 mm in diameter. The electrodes were connected to a LCR meter. In our impedance spectroscopy measurements, an 1 V ac voltage signal was introduced into the system and the response of the system to this signal is expressed by complex impedance Z = R + Xi, where R and X are the real part and imaginary part of Z, respectively. The frequency ranged from 20 Hz to 1 MHz. We fitted the R-X plot with a function of a semicircle and obtained a bulk proton resistance of the sample at different pressures and temperatures. By use of size of the sample between electrodes measured at each pressure, the resistance value was converted into conductivity. Pressure at room temperature was determined based on a Raman shift of the diamond anvil. At target pressure, temperature was controlled by putting the whole cell into a freezer. Sample temperature was determined based on a type K thermocouple stuck on the table side of the anvil. Powder X-ray diffraction patterns were also obtained at a KEK-PF-AR-NE1 beamline on some runs.

3. Results and discussion

During increasing pressure at room temperature, the proton conductivity became smaller by the one order of magnitude at 2.2 GPa due to VI-VII transition. After taking a local minimum at ~3 GPa, it increased with pressure and took a local maximum at ~10GPa, which is greater by the one order of magnitude of that at 3 GPa. Then, it decreased with pressure. At 20 GPa, it was almost identical to that at 3 GPa. Then, it was almost constant up to 40 GPa. By powder XRD measurements at high pressure and room temperature, a slight splitting of diffraction lines of cubic VII was observed above 10 GPa, which is almost consistent with [4]. Therefore, the anomaly of high conductivity at ~10 GPa should be caused by the pressure induced structural change of VII [4].

Low temperature experiments at constant load revealed that the lower temperature it was, the lower conductivity the sample had. The conductivity of proton ordered VIII was lower than that of proton disordered VII. This indicates that proton concentration variation rather than proton mobility (mean free path) variation is dominant in the conductivity variation with temperature. Thus, we cannot interpret the high conductivity state due to appearance of modulated incommensurate phases [1], which have the degree of order higher than proton disordered VII.

On VII-VIII boundary with temperature at constant load, we did not observe a clear discontinuity and large variation of temperature dependency of the conductivity. Namely, the anomaly of high conductivity at ~10 GPa exists also in the VIII stable region. This is consistent with anomaly of pressure variation of c/a ratio of VIII [2, 3] and some structural change suggested from pressure variations of Raman spectra of VIII [2, 5], which were observed at 10-15GPa and lower temperature than that of this study.


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