Dielectric observation of disordered-states transformation of ice VII at around 10 GPa

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Keywords: high pressure, dielectric, ice VII.

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[Introduction]

Ice has 18 polymorphs. They are classified into two groups, disordered and ordered ice, by cite occupancies of their hydrogen atoms and these occupancies take 50 % and 100 % in disordered and ordered ice, respectively. The disordered and ordered states make a variety of ice polymorphs, and one of the most notable structural and phisical properties of ice.

Ice VII is a high-pressure disordered phase in a wide pressure region, from 2 to 60 GPa, at room temperature. Pressure dependence of the disordered state of ice VII has long been studied, a dielectric measurements showed that the disordered state of ice VII is dominated by orientation (or rotation) of H_2O in lower pressure region (below 5 GPa) [1]. In much higher pressure region (above 40 GPa), hydrogen-atom translation mainly induced by a quantum effect on O-H...O bond dominates the disordered state of ice VII [2,3]. Recent DFT simulation showed that dominant dynamics of ice-VII disorder state changes from the H_2O rotation into H translation at around 15 GPa [4], where a number of measurement anomalies were reported in Raman scattering, X-ray diffraction, and electrical conductivity measurements [e.g. 5,6,7]. Pruzan et al., who first reported an anomaly from their Raman scattering in [5], supposed a scenario of the transformation of ice-VII disordered state to explain the found anomaly; FWHM of symmetry stretching mode of H_2O had a minimum at around 11 GPa [1].

In order to confirm the transformation between the disordered states derived from H_2O rotation and H translation, a dielectric measurement would be an effective experimental method considering a time scale of each dynamics [8], although there are some technical difficulties to conduct high pressure dielectric measurements of ice [9].

[Experiments]

We recently overcame the difficulties by using a newly developed Bridgeman-type high pressure cell [9], and we measured dielectric properties of ice VII up to 12.1 GPa in 3 mHz – 2 MHz frequency region and at room temperature. Sample pressure was estimated from *in situ* ruby fluorescence measurement.

[Results and Discussion]

Two dielectric relaxations were observed at 4.5 GPa as shown in Figure 1, and the one of them in higher frequency region is assigned to H_2O rotation from previous study; the dynamics of water rotation is weakened with increasing pressure, and this pressure dependence leads a pressure shift to lower frequency. The other dielectric relaxation, on the other hand, shifts to higher frequency region with increasing pressure. This means corresponding dynamics was activated under high pressure, and then the two dynamics merged at around 10 GPa on frequency axis. Dielectric constant and DC conductivity, which was simultaneously measured with dielectric properties of iceVII, had minimum and maximum with the marging. These electric properties can be explained by Jaccard's theory with the assumption that the lower frequency relaxation is derived from H translation. Therefore this experiment strongly supports the proposed disorder transformation of ice VII at around 10 GPa [1,4].

In the presentation, I will show results on high-pressure dielectric measurements of ice VII up to 12 GPa with technical developments of the newly developed high pressure cell.

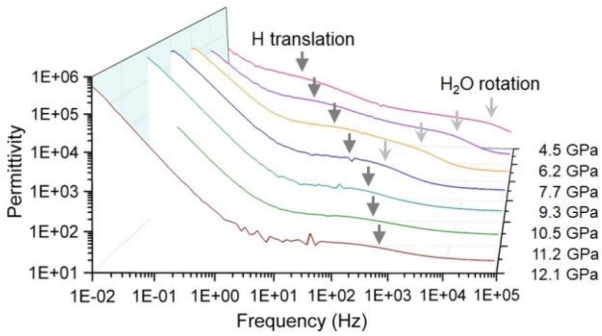

Figure 1. Pressure dependence of dielectric constant of ice VII

Acknowledgments: This work was supported by JSPS KAKENHI 18H05224 and 18J13298.

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