ESRF	**Experiment title:** Superionic water at high pressures and temperatures	**Experiment number**: HC4677
Beamline: ID27	**Date of experiment**: from: 23/02/2022 to: 26/02/2022	**Date of report**: 14/03/2022
Shifts: 9	**Local contact(s)**: Gaston Garbarino, Mohamed Mezouar	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Gunnar Weck* (CEA)

Alexis Forestier* (CEA)

Sandra Ninet* (IMPMC, Sorbonne Université, CNRS UMR 7590)

Frédéric Datchi* (IMPMC, Sorbonne Université, CNRS UMR 7590)

Report:

Scientific background and objectives of the experiment

Warm dense water ice is at the center of a great interest due the unusual properties of its superionic (SI) phases and to its rich polymorphism. These newly discovered phases stability regions and thermodynamic properties are needed to accurately model planetary interiors. The protonic mobility associated to superionic state should play a role in the magnetic field of icy giant planets such as Uranus and Neptune [1].

A transition from bcc symmetric ice X to fcc-SI ice was first predicted in ab-initio calculations [2-4]. Recently, fcc-SI ice was observed above 160 GPa by coupling multi-shocks compression with X-ray diffraction [5]. Subsequently, two static studies using synchrotron XRD in laser heated diamond anvil cells (DAC) have confirmed the existence of fcc-SI ice and disclosed its stability field [6,7]. However, these two static studies significantly differs, ours being in good agreement with dynamic compression and numerical simulations [2,4,5]. At lower pressure values, another SI state was evidenced below the melting curve, sharing the same oxygen bcc sublattice that of ice X [8,6]. The stability field and detailed properties of these forms of warm dense ice remains actively debated.

Discrepancies on reported transition curves could originate from the difficulties to detect the appearance of the novel superionic phase due to strong temperature gradient in the sample cavity. Developing a sample assembly with boron-doped diamond heaters proved to be a good strategy to reduce temperature gradients in the heated ice and so obtain a large volume of the novel phase under well determined P-T conditions. In our first study, only one absorber was implemented (HC-3952 and ref. 7). In the present experiment, two boron-doped diamond absorbers were implemented, providing full confinement of the probed warm ice volume in the heated "capsule". The objectives of this experiment were to precisely measure the transition line between bcc insulating and fcc-SI ices up to 200 GPa, and to collect thermodynamic data on the novel warm fcc-SI ice: bulk modulus, transition line slope and volume discontinuity at transition and thermal expansion.

Experimental details and results

Five diamond anvil cells were prepared: one with 300 µm anvil culet diameters, two with 150 µm, one with 100 µm and one with 70 µm. Each anvils were first machined by focused ion beam (FIB) with a central circular pit to provide sufficient space for the boron-doped diamond heaters on both sides of the sample cavity. 1.5 µm-thick Al_2O_3 layers were deposited on each anvil to provide thermal insulation between the C:B heaters and the diamond anvils. Then, C:B heaters were installed on each anvils and fixed using a sub-micrometer thin layer of UV curing glue. Pure H_2O was loaded in the DACs cavity, and samples were characterized using Raman spectroscopy. Figures 1(a) and (b) shows a sketch of the sample assembly and a picture of an anvil before H_2O loading.

Samples were studied on the ID27 beamine at the ESRF under two-side YAG laser heating while temperature was measured by optical pyrometry. During X-ray diffraction recording, care was taken to balance temperatures at both sides of the sample and to keep it as stable as possible. Temperature increments of 100 K were used for accurate determination of the boundary line, performing both ascending and descending temperature ramps. A large number of X-ray diffraction data could be collected at various pressure ranging from 30 GPa to 200 GPa. The transition from ice X to fcc-SI could be unambigously observed with more than 3 reflexions from the novel fcc-SI phase up to 200 GPa with excellent quality data as visible in figure 1(c). Previous static measurements were limited to ~160 GPa [6,7].

We are currently analysing the data in details in order to refine the boundary line between ice X and the fcc-SI. Since we have been able to finely track the evolution of the fcc-SI phase reflexions with increasing temperature beyond the boundary line, we will be able to extract thermodynamic properties of the fcc-SI such as volume jumps at transition and thermal expansion as planned. Data should also provide interesting information on the transition kinetics.

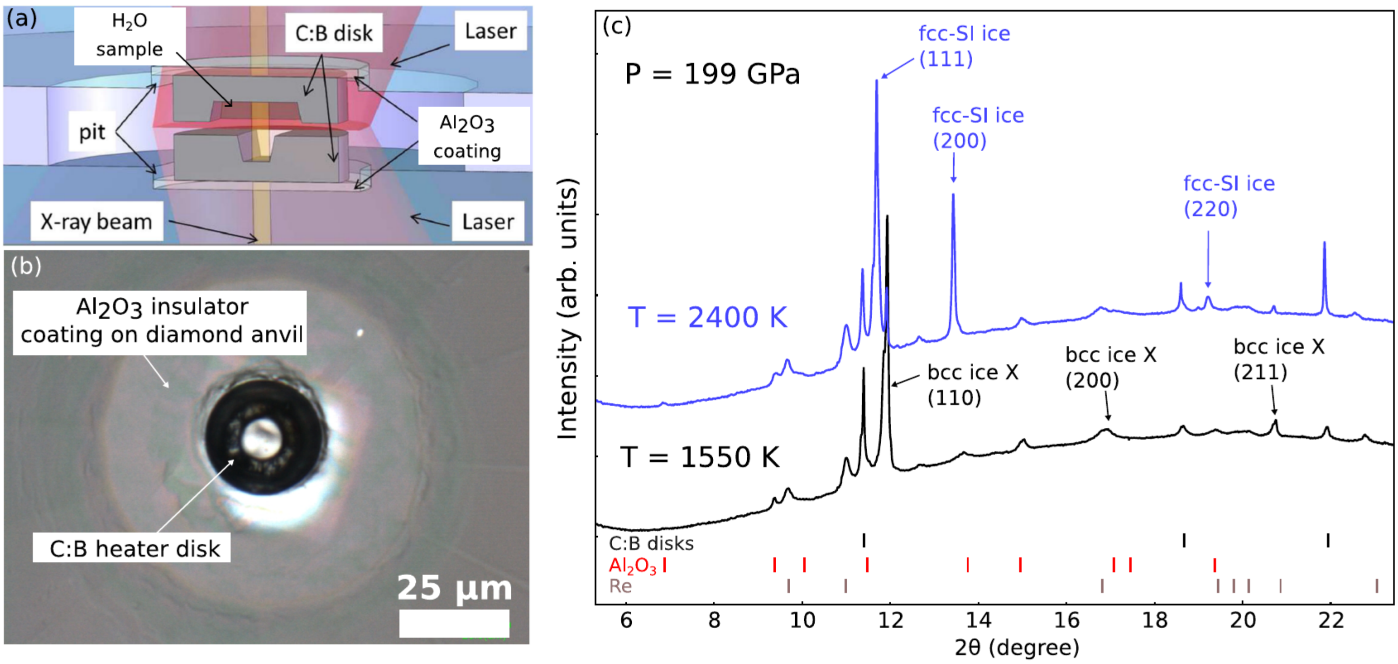

Figure 1: (a) Sketch of the DAC pressure chamber showing the confined H_2O sample in the "capsule" made of two face-to-face boron-doped (C:B) diamond heaters. (b) Picture of a 70 µm diameter anvil with the C:B heater installed inside the FIB-machined pit. (c) X-ray diffraction diagrams obtained at 199 GPa, showing the transition from bcc symmetric ice X to fcc-SI ice upon heating to 2400 K.

References

[1] KM Soderlund, S. Stanley. Phil. Trans. R. Soc. A 378, 20190479 (2020) ; [2] H. Wilson et al. Phys. Rev. Lett. 110, 151102 (2013) ; [3] J. Sun et al. Nat. Com. 6, 8156 (2015) ; [4] B. Cheng et al. Nature Physics 17, 1228 (2021) ; [5] M. Millot et al. Nature 569, 251 (2019) ; [6] V. Prakapenka et al. Nature Physics 17, 1233 (2021) ; [7] G. Weck et al. Submitted Phys. Rev. Lett. ; [8] J.A Queyroux et al. Phys. Rev. Lett., 125, 195501 (2020)