	Experiment title: Is there a plastic phase in ice VII at high pressure and high temperature ?	**Experiment number**: HS-3939
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Report:

In this experiment we have investigated the structure of ice VII under high pressure and high temperature in the domain 0-25 GPa and 600-1000 K, i.e. close to the melting line. The measurements were motivated by recently published computer simulations by Takii et al. [1] and Aragones & Vega [2] which claim that ice VII transforms into a plastic phase at high temperature, before melting (Fig. 1). In this phase, the H_2O molecules can more or less freely rotate around the oxygen, i.e. this is a dynamical transition to a "rotor-phase", as found in other molecular solids at low pressure such as NH_3 and CH_4. The timescale of rotations is typically in the ps range. Although x-ray diffraction pattern of such a phase can hardly be distinguished from "ordinary" ice VII due to the low scattering power of hydrogen, the simulations predict a measurable volume change between normal and plastic ice VII. The existence of a plastic phase would resolve the long-standing problem of the melting line of ice VII at high P/T. Some previous experiments obtained by visual observation in a diamond anvil cell [3] reported a melting line at considerably higher temperatures than expected from the extrapolation of the low P/T melting line and the possible existence of a "new ice phase" between the melting line and ordinary ice VII. Although these data are very controversial, they provide in fact considerable support to the computer simulations.

In our measurements HS-3939 we have carried out x-ray diffraction using externally heated DACs which is the only method which gives structural data under well defined and homogeneous temperatures. Our measurements can be regarded as a full success, despite the technical difficulties related to the extremely high chemical reactivity of the sample under such extreme conditions (to give an example, at ~1000 K, the ruby or $SrB_4O_7:Sm^{2+}$ pressure markers are dissolved within a few seconds as soon as ice VII melts, usually followed by a failure of the anvils). In total 4 DACs were preloaded in our laboratory with high purity water and various pressure markers. All cells were loaded with $SrB_4O_7:Sm^{2+}$ [4] and a two of them had additionally a small piece of gold for which the equation of state is well known [5]. Temperatures were measuremed with a K-type thermocouple glued to the diamond anvil. External heating was achieved using our own setup reaching a maximum temperature of 950 K. At the highest temperatures the DACs were flooded with Ar to avoid excessive corrosion. XRD pattern from H_2O and Au were collected using a monochromatic x-ray beam (0.414 Å) focussed to 20 x 20 μm^2 and a 2D image plate (MAR345). The DAC opening allows for collecting diffraction lines up to 2θ=35°, i.e. d>0.7 Å. Althought the patterns of ice were strongly textured, the data quality was sufficient to derive lattice parameters with the required precision. Two of the loadings failed during isobaric heating (at ~ 700 K) prior to reaching the interesting P/T domain. Neverthless these runs helped to find out an experimental protocol (gasket material and dimensions, P-T path) which was succesful in the two other loadings.

Results obtained

From the data we obtained on the two successful loadings we confirm that the melting line has a kink at ~750 K / 16 GPa (Fig. 2). We have measured the equation of state on an isotherm at 850 K and find a small but detectable difference of ~0.5% in the molar volumes in the plastic area compared to the P/T domain of "ordinary" ice VII, i.e. the extrapolation of the low temperature melting line. Such a volume jump is agreement with the prediction of Ref. [2]. In a second loading we have attempted to reach 1000 K but unfortunately were able to collect only a few pressure points before the anvils broke.

The current dataset gives hence strong evidence of a plastic phase in ice VII, but the amount of data is too limited to draw a detailed phase diagramm, i.e. we are limited to 3 points at the melting line, 1 full isochore, and a maximum temperature 950 K. Additional beamtime to reach higher temperatures would be highly desirably.

References

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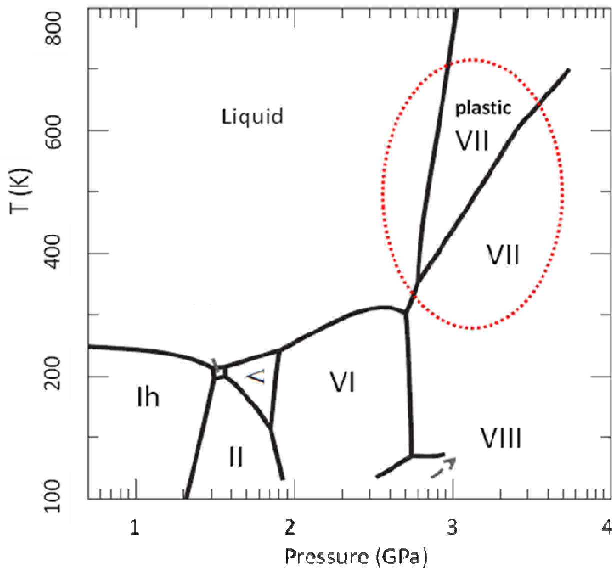

Figure 1: Phase diagram of H_2O according to computer simulations of Refs. [1,2]. Note the prediction of a plastic ice VII phase at high temperatures, next to the melting line, and the kink in the melting line produced by it.

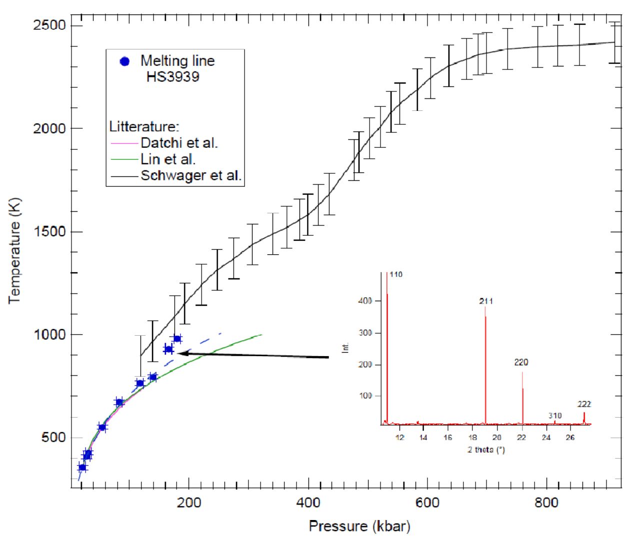

Figure 2: Melting line of water as determined from HS-3939 (dots) compared to previous melting lines obtained in externally heated DACs (Datchi et al., PRB 61, 6535 (2000); Lin et al., J. Chem. Phys. 121 8423 (2004), and obtained in laser heated DACs (Schwager et al., J. Phys.: Cond. Matter 16, S1177 (2004) & Schwager and Boehler, High Press. Res. 28, 431 (2008). Note the apparent kink in the melting line and the possible existence of a plastic phase below of it which would reconcile all set of measurements. Inset: diffraction pattern of ice VII obtained in HS-3939 in the "plastic" phase.