High-Pressure High-Temperature Amorphous Ice.

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SUMMARY. We studied behaviour of H_2O in externally heated diamond anvil cells (DACs) at pressures up to 50 GPa and temperatures to 1150 K combining visual observations, Raman spectroscopy, and X-ray powder diffraction. Above 30 GPa and 950 K, using visual observations and Raman spectroscopy we found an X-ray amorphous phase clearly distinct from liquid water. The new material reversibly transforms to Ice VII and can be obtained on cooling or compression of liquid water suggesting that the high-pressure high-temperature amorphous phase may be thermodynamically stable.

INTRODUCTION.

Properties of H_2O at elevated pressure and temperature are of fundamental importance in both condense matter physics and planetary sciences [1-9]. The pressure-temperature phase diagram of water ices is extremely complex [10] and various solids forms of H_2O have been and still are the subject of intense experimental and theoretical investigations. Ice Ih is the first system which was observed to amorphize under pressure [11]. Several glassy and amorphous ices (including low-density (LDA) and high-density (HDA) amorphous forms) were observed to exist metastably at pressures below ~1.5 GPa and low temperatures [1,2,10].

Ice VII is a stable water phase at room temperature above 2.3 GPa [10]. Melting of Ice VII has been studied over last 40 years by different techniques (for recent reviews see Refs. 10,12-14, for example). Fei et al. [12] studied melting of Ice VII in externally electrically heated DAC to about 16 GPa by monitoring the disappearance of the (110) peak in the X-ray diffraction collected using energy dispersive detector. Datchi et al. [13] followed melting of water at pressure up to 13 GPa (temperatures about 750 K) by visual observations in externally heated DACs. Dubrovinskaia and Dubrovinsky [14] extended the studied pressure range up to 37 GPa employing the whole-cell heating assemblage for pressure and temperature

generation and angle-dispersive synchrotron-based X-ray diffraction for detection of Ice VII melting event. Lin et al. [15] applied Raman spectroscopy and visual observations in an externally heated DAC to detect melting of water and reached 22 GPa and 900 K. Keeping in mind different techniques used for recognition of melting and different standards for pressure characterization (Au equation of state [12,14] or fluorescence markers [13,15] there is fair agreement between data [12-15] obtained in electrically-heated DACs (Fig. 1) (at 650 K difference in pressure is of the order of 2 GPa). Contrary, melting curve of H₂O measured in a laser-heated diamond anvil cell with visual observation of the laser-speckle pattern [16] is in odds with all so far reported data (at 15 GPa difference is at least 250 K and increases with pressure). Resolving such a controversy requires further experimental studies with accurate *in situ* measurements of pressure and temperature in diamond anvil cells.

EXPERIMENTAL.

In order to study the behaviour of pure doubly distilled deionised water at elevated pressures and temperatures we employed external electrical heating diamond anvil cell technique [14]. Uncertainties in temperature measurements with a S-type thermocouple are within 10 K at temperature of 1000 K. Pressure was determined from the equation of state of gold and/or fluorescence sensors [13,14,20] (Sm:YAG and ruby; Sm:YAG was used only at temperatures below 650 K because its possible reaction with water [13] at higher temperature). The unit cell of gold determined from (111), (200), (220), (311), and (222) diffraction lines was used in conjunction with well-established the thermal equation of state [14]. The uncertainty in measured lattice parameter of gold is not worse than 0.003 Å at pressure of ~45 GPa which corresponds to uncertainty in pressure of 0.8 GPa. Natural lowfluorescence type IIa and high-purity synthetic (for Raman spectroscopy, see below) diamonds with 250 to 350 μ m in diameter culets were used. Re gaskets were used at temperatures to 900 K. At higher temperatures on long-duration heating (dozens of minutes) Re starts to react with H_2O (shape of the hole in the gasket changes, "black clouds" start to grow at gasket-water interface, SEM and microprobe analysis reveal contamination by Re of the whole working surface of the diamonds after experiments). So, in experiments aimed studies at temperatures approaching or higher than 900 K, we used Ir gaskets which did not show any sign of reaction with water. One experiment at pressure up to 38 GPa and temperature to 1125 K was performed in Ir gasket coated by spattered gold of 1 μ m thickness and no difference with the results obtained in experiments with pure Ir gasket was found. Melting temperature of water is very sensitive to its chemical purity. In order to check that no chemical reactions occurred at high pressures and temperatures on decompression we melted ice VII at pressures between 5 and 8 GPa and within the uncertainty of our experiments we have not seen any differences between data obtained before and after high-P,T treatment.

Raman spectra were recorded using Dilor XY (514 nm Ar laser, 1800 g/mm and 1200 g/mm grating, double-stage spectrometer, 1 cm⁻¹ resolution) and LabRam (632 nm He-Ne laser, 1200 g/mm grating, ~2 cm⁻¹ resolution) systems. High-pressure Raman studies of water ices is a challenging task due to weak signal from the sample, merging of Raman-active stretching mode of Ice VII into the second-order Raman signal from diamond anvils above 25 GPa, stresses and pressure gradients development in the ice. We overcome the latter problems by melting of samples and their slow (~10 K/min) subsequent cooling to desired temperature: even at ~50 GPa (highest pressure in this study) pressure variation in the sample cooled to room temperature is less than 1.5 GPa across the 130 μ m in diameter pressure chamber. In order to improve a signal-to-noise ratio and to collect especially weak at high temperature Raman spectra of Ice VII and liquid water, we followed the methodology proposed by Goncharov et al. [17]: we used confocal optical configuration and spatial filtering with depth of focus down to 2 μ m, as well as high purity thin (1.2 to 1.5 mm thickness) synthetic diamonds. The background spectrum collected from the part of pressure chamber free of water (it was blocked by a particle of Au or Ir on the surface of the anvil) was subtracted.

X-ray powder diffraction experiments were conducted at the ESRF on beam line ID30 and at Bayerisches Geoinstitut (BGI). At ESRF the data were collected using the MAR345 or Bruker CCD detectors and an X-ray beam of 0.3738 Å wavelength with a size of 10x15 μ m. The detector-to-sample distance varied in different experiments from 170 to 350 mm. At BGI we used FR-D high-brilliance Rigaku X-ray rotating anode generator (MoK α radiation, operating at 55 kV and 60 mA) with Osmic MaxFlux focusing optics allowing to produce a beam of about 40 μ m in diameter. Data were collected using Bruker APEX CCD area detector. The opening angle of 36° in the backing plates allowed us to collect diffraction data down to a *d*-spacing of 1.1 Å. The collected images were integrated using the Fit2D program in order to obtain a conventional diffraction spectrum.

RESULTS AND DISCUSSIONS.

Visual observations have been proved to be a reliable method to detect melting of ice VII at pressures of about 20 GPa [13-15]. At higher pressures, however, samples become thinner and visual identification of melting becomes problematic. Angle dispersive X-ray diffraction with area detector is a powerful method for studying melting [14,18]. We monitored melting by the disappearance on heating or appearance on cooling, of reflections from ice VII [14]. As the major criterion of losing of crystalline structure by Ice VII we used the appearance of a diffusion halo. As shown in Fig. 1, our X-ray data-points, extended in this study to 48 GPa, fall along the line which could be describe by Simon equation [14]

$$P = 2.2 + 1.31 \left[\left(\frac{T}{364} \right)^{3.3} - 1 \right]$$

Relatively small difference in the common pressure range (e.g. to 15 GPa in Refs. 12,13 and 22 GPa in Ref. 15) between our and previously reported melting curves of ice VII measured in externally-heated diamond anvil cells [12,13,15] can be attributed to the difference in methods of registration of melting event (e.g. X-ray diffraction with energy dispersive detector [12] versus angle dispersive in the present study) or difference in pressure measurements (Au and ruby in direct contact with water sample in our work versus Sm:YAG isolated from H₂O in Ref. 15). Significant discrepancies with data obtained in laser-heated DAC [16] remain unresolved and can be related, as proposed by Lin et al. [15], to methodology of temperature measurements in the sample while a metallic hot-plate is used as an absorber of laser radiation.



Figure 1. Phase relations between Ice VII, water melt, and high-pressure hightemperature amorphous (HPHTA) ice. Dark-red circles represent X-ray data (melting or transformation in non-crystalline phase), pink diamonds – melting according to Raman and visual observations, open hexagons – transformation of Ice II in to HPHTA ice by Raman and visual data. Red solid line is the curve which describe transformation of Ice VII in to non-crystalline phase (Eq. (1), melting curve of Ice VII to about 30 GPa). Green triangles – data on melting of Ice VII by Fei et al. [12], darkgreen dotted line – melting curve by Lin et al. [15], blue dash line – melting curve by Datchi et al. [13], dark-blue dash-dot line – melting curve according to Schwager et al. [16].

Melting manifested itself in Raman spectra by disappearance of active translational modes, changes in shape and reducing of intensity of OH-stretching modes [10,15]. The results of observations of melting of ice VII using Raman spectroscopy are summarized in Fig. 1. Spectroscopic and X-ray observations are in good agreement at pressure up to 30 GPa, although Raman data are more scattered.



Figure 2. Photographs taken upon heating of ice VII at 33(1) GPa. At 935(2) K solid phase is Ice VII (upper left). After increasing temperature to ~980 K with a speed of 2°/min we observed formation of the "cell pattern" (upper right and bottom left; time was counted since temperature reached 980 K). "Cell pattern" is preserved for dozens of minutes if temperature and pressure remain constant, although the shape of individual "cells" changes. Upon further heating above 1015 K, "cells" disappear (bottom right). Small spheres in the left part of photographs are ruby crystals.

At pressures above 30 GPa on heating at temperatures approaching those of the expected melting, we observed the formation of a distinct pattern apparently looking like grains boundary (we called it "cell pattern") (Fig. 2). Note, that we did not observe re-crystallization of ice VII at lower pressure before melting. Raman spectra corresponding to the "cell pattern" are clearly different from those of ice VII and from the spectra of "usual" water melted at high-pressure and temperature (Fig. 3). For example, upon heating to 980 K at 33 GPa, the "cell pattern" forms while in Raman spectra translational modes disappear, and OH-stretching modes broaden and shift to higher frequencies (Fig. 3). On further heating at 1015 K the "cells" melt, the intensity of Raman OH-stretching modes rapidly decreases and spectra look like those typical for water melt at corresponding pressures and temperatures. The diffusion hallo in X-ray diffraction images collected at 33 GPa and temperature above 980 K unambiguously reveals non-crystalline state of the material at corresponding conditions (Fig. 4).



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Figure 3. Raman spectra of water collected at 33(1) GPa and different temperatures in (a) low- (translational modes) and (b) high-frequency (stretching modes) regions. Spectra at 915(10) K on heating and 965(10) K on cooling correspond to the ice VII. At 980(10) K on heating and 985(10) K on cooling we observe spectra of the new high-pressure high-temperature amorphous ice. At 1015(10) the spectrum is from melted water. For all spectra collecting time was 600 s (except upper one in *b* collected for 1800 s). Mode assignment is according to [10,15,17].

We made all pre-cautions to avoid contamination of the water sample and have no reason to relate formation of the non-crystalline phase at high pressures and temperatures to chemical reaction(s) between gasket material and/or diamond with H₂O. Our *in situ* X-ray and Raman data (Raman spectroscopy is especially sensitive to the presence of oxygen and hydrogen phases) do not provide any evidences of possible water decomposition in the studied pressure range. It means also that "cell pattern" can not be explained by formation of a new unknown liquid unmixable with water.

Our observations imply that the "cell pattern" forms when ice VII transforms to the amorphous phase (which we will call below "high pressure high temperature amorphous (HPHTA) ice"). We think that the "cells" are observed due to formation of cracks as a result of stresses generated by the difference in densities of ice VII and the amorphous phase (similarly to the system of cracks forming at the phase transition between low and high density amorphous ices at low pressure [2]. Note that estimated differences between ice VII and melt along the melting curve is 5 to 10% at pressure ~35 GPa [20]).



Figure 4. Example of 2D diffraction images collected on heating of water at high pressure and temperature. At 34(1) GPa and 930(5) K (a) the pattern corresponds to the cubic ice VII phase with lattice parameter 2.938(3) Å. At 33(1) GPa and 958(5) K (b) the crystalline phase co-exists with the X-ray amorphous phase. At 975(5) K and 33(1) GPa (c) only the diffusion hallo from non-crystalline phase was observed.

The formation of the "cell pattern" appears visually in course of transformation from ice VII to HPHT ice (e.g. on heating or decompression of ice VII at appropriate pressures and temperatures, Fig.1). On reverse paths (by compression or cooling melted water towards Ice VII) we have not seen clear "cell patterns" although perturbation of images and occasionally cracks were observed. At the same time, Raman spectra (Fig. 3) provide clear evidence that ice VII and liquid water reversibly transform into HPHTA ice. The reversibility of the transformations suggests that HPHTA ice may be a thermodynamically stable phase especially taking into account that the appearance the amorphous phase does not depend on the rate of cooling or heating (ranging in our study from 1°/hour to 10°/min) and it can be preserved for dozens of minutes if temperature and pressure remain constant.

CONCLUSIONS.

Apart very rich polymorphism of crystalline phases, water is know to have several X-ray amorphous phases at low pressures and temperatures, including low and high density amorphous ices [1,2,10]. Even liquid water is thought to exist in certain thermodynamic conditions in two distinct (low and high density) forms [1,2]. New HPHTA ice is clearly distinct from all known water phases by its Raman signature (Fig. 3), as well as pressure and temperature conditions at which it was observed. Moreover, all so far known amorphous ices are metastable and can not reversibly transform to phases stable at corresponding conditions.

Pressure-induced amorphization of solids is a complex phenomenon not fully understood yet. Experimental and theoretical studies [8,9,19] relate phase transformations and amorphization of ices VIII and XI to the non-linear behaviour and softening of some stretching and transitional modes which, in turns, lead to collapse of the hydrogen-bonded networks and mechanical instabilities. *Ab initio* molecular dynamic simulations [4] suggest that at pressures above 30 GPa and temperatures above 1000 K water becomes superionic with the oxygen *bcc* sublattice preserved, and hydrogen atoms jump among equivalent sites along the O-O separations. Apparent coincidence of the thermodynamic conditions, at which theory [4] predicts formation of superionic water and at which we found HPHTA ice, indicates that these two phenomena could be related. However, further detailed combined experimental and theoretical studies are necessary in order to uncover atomistic nature of the new high-pressure high-temperature amorphous ice.

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