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TITLE:

An Externally-Heated Diamond Anvil Cell for Synthesis and Single-Crystal Elasticity Determination of Ice-VII at High Pressure-Temperature Conditions

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KEYWORDS:

Resistive heater, diamond anvil cell, ice-VII, single crystal, single-crystal X-ray diffraction, Brillouin scattering

SUMMARY:

This work focuses on the standard protocol for preparing the externally-heated diamond anvil cell (EHDAC) for generating high-pressure and high-temperature (HPHT) conditions. The EHDAC is employed to investigate materials in Earth and planetary interiors under extreme conditions, which can be also used in solid state physics and chemistry studies.

ABSTRACT:

The externally-heated diamond anvil cell (EHDAC) can be used to generate simultaneously high-pressure and high-temperature conditions found in Earth's and planetary interiors. Here we describe the design and fabrication of the EHDAC assemblies and accessories, including ring resistive heaters, thermal and electrical insulating layers, thermocouple placement, as well as the experimental protocol for preparing the EHDAC using these parts. The EHDAC can be routinely used to generate megabar pressures and up to 900 K temperatures in open air, and potentially higher temperatures up to ~1200 K with a protective atmosphere (i.e., Ar mixed with 1% H_2).

Compared with a laser-heating method for reaching temperatures typically >1100 K, external heating can be easily implemented and provide a more stable temperature at ≤900 K and less temperature gradients to the sample. We showcased the application of the EHDAC for synthesis of single crystal ice-VII and studied its single-crystal elastic properties using synchrotron-based X-ray diffraction and Brillouin scattering at simultaneously high-pressure high-temperature conditions.

INTRODUCTION:

The diamond anvil cell (DAC) is one of the most important tools for high pressure research. Coupled with synchrotron-based and conventional analytical methods, it has been widely used to study properties of planetary materials up to multi-megabar pressures and at wide ranges of temperatures. Most planetary interiors are under both high-pressure and high-temperature (HPHT) conditions. It is thus essential to heat the compressed samples in a DAC at high pressures in situ to study the physics and chemistry of planetary interiors. High temperatures are not only required for the investigations of phase and melting relationships and thermodynamic properties of planetary materials, but also help mitigate pressure gradient, promote phase transitions and chemical reactions, and expedite diffusion and recrystallization. Two methods are typically utilized to heat the samples in DACs: laser-heating and internal/external resistive heating methods.

The laser-heated DAC technique has been employed for high-pressure materials science and mineral physics research of planetary interiors[1,2]. Although increasing number of laboratories have access to the technique, it usually requires significant development and maintenance effort. The laser heating technique has been used to achieve temperatures as high as 7000 K[3]. However, long-duration stable heating as well as temperature measurement in laser-heating experiments have been a persistent issue. The temperature during laser heating usually fluctuates but can be mitigated by feed-back coupling between thermal emission and laser power. More challenging is controlling and determining the temperature for assembly of multiple phases of different laser absorbance. The temperature also has a considerably large gradient and uncertainties (hundreds of K), although recent technical development effort has been used to mitigate this issue[4-6]. Temperature gradients in the heated sample area sometimes may further introduce chemical heterogeneities caused by diffusion, re-partitioning or partial melting. In addition, temperatures less than 1100 K typically could not be measured precisely without customized detectors with high sensitivity in the infrared wavelength range.

The EHDAC uses resistive wires or foils around the gasket/seat to heat the entire sample chamber, which provides the ability of heating the sample to ~900 K without a protective atmosphere (such as Ar/H_2 gas) and to ~1300 K with a protective atmosphere[7]. The oxidation and graphitization of diamonds at higher temperatures limit the highest achievable temperatures using this method. Although the temperature range is limited compared with laser-heating, it provides more stable heating for a long duration and a smaller temperature gradient[8], and is well suited to be coupled with various detection and diagnostic methods, including optical microscope, X-ray diffraction (XRD), Raman spectroscopy, Brillouin spectroscopy and Fourier-transform infrared spectroscopy[9]. Therefore, the EHDAC has become a useful tool to study various material properties at HPHT conditions, such as phase stability and transitions[10,11], melting curves[12], thermal equation of state[13], and elasticity[14].

The BX-90 type DAC is a newly developed piston-cylinder type DAC with large aperture (90° at maximum) for XRD and laser spectroscopy measurements[9], with the space and openings to mount a miniature resistive heater. The U-shaped cut on the cylinder side also provides room to release the stress between the piston and the cylinder side caused by temperature gradient. Therefore, it has recently been widely used in powder or single-crystal XRD and Brillouin measurements with the external-heating setup. In this study, we describe a reproducible and standardized protocol for preparing EHDACs and demonstrated single-crystal XRD as well as Brillouin spectroscopy measurements of synthesized single-crystal ice-VII using the EHDAC at 11.2 GPa and 300-500 K.

PROTOCOL:

1. Ring heater preparation

1.1 Fabricating the ring heater base

1.1.1. Fabricate the ring heater base by a computer numerical control (CNC) machine using pyrophyllite based on the designed 3D model. The dimensions of the heater are 22.30 mm in outer diameter (OD), 7.94 mm in inner diameter (ID) and 2.25 mm in thickness. Sinter the heater base in the furnace at 1523 K for >20 hours.

1.2 Wiring

1.2.1 Cut Pt 10 wt% Rh wire (diameter: 0.01 inch) into 3 equal-length wires (about 44 cm each).

1.2.2 Carefully wind each Pt/Rh wire through the holes in the heater base, leave about 10 cm wire outside of the heater base for connection to the power supply. When wiring, make sure that the wire is lower than the gutters of the base. If it is higher than the gutter, use a proper flat-head screwdriver to press it down.

1.2.3 Wind more wires on the 10 cm extension wires to reduce the electrical resistance and thus the temperature of the extension wires during heating.

1.3 Adding insulators

1.3.1 Use two small ceramic electrical insulating sleeves to protect the wires extending outside the ring heater base. Mix cement adhesive (e.g., Resbond 919) with water at a ratio of 100:13. Fix those tubes to the ring heater base using the cement mixture.

NOTE: The cement needs 4 hours to be cured at 393 K or 24 hours at room temperature.

1.3.2 Use the high-temp braid sleeving to protect the outside wires.

1.3.3 Cut two mica rings using a CO_2 laser cutting machine. To electrically insulate the wire, attach one mica ring to each side of the heater by UHU tac.

2. EHDAC preparation

2.1 Gluing diamonds

2.1.1 Align the diamonds with backing seats with mounting jigs. Use black epoxy to glue the diamond to the backing seat. The black epoxy should be lower than the girdle of the diamond to leave some space for the high-temperature cement.

2.2 Alignment

2.2.1 Glue mica or place the machined pyrophyllite rings under the seats to insulate the seats and DAC thermally. Put the seats with the diamonds into a BX-90 DAC. Align two diamonds under the optical microscope.

2.3 Preparing the sample gasket

2.3.1 Place the rhenium gasket, which is smaller than the hole of the ring heater, between the two diamonds and pre-indent the gasket to approximately 30-45 μm by gently tightening the four screws of DAC. Drill a hole at the center of the indentation by electrical discharge machine (EDM) or laser micro-drilling machine.

2.4 Mounting thermocouple

2.4.1 Fix two small pieces of mica with the cement mixture on the seat of the piston side of DAC to electrically insulate the thermocouples from the seat. Attach two K-type (Chromega-Alomega 0.005'') or R-type (87%Platium/13%Rhodium–Platium, 0.005”) thermocouples to the piston side of the DAC, ensuring that the tips of the thermocouples touch the diamond and close to the culet of the diamond (about 500 μm away). Finally, use the high-temperature cement mixture to fix the thermocouple position and cover the black epoxy on both sides of the DAC.

2.5 Heater placement

2.5.1 Cut the 2300 °F ceramic tape in the shape of the heater base by CO_2 laser drilling machine and place it on both sides of DAC (piston and cylinder sides). If it is very easy to move around, use some UHU tac to fix it.

2.5.2 Place the heater in the piston side of the BX-90 DAC. Use some 2300 °F ceramic tape to fill the gap between the heater and the wall of the DAC.

2.6 Gasket placement

2.6.1 Clean the sample chamber hole of the gasket using a needle or sharpened toothpick to get rid of the metal fragments introduced by the drilling. Use ultrasonic cleaner to clean the gasket for 5-10 min.

2.6.2 Put two small balls of adhesive putty (e.g., UHU Tac) around the diamond on the piston side of the DAC to support the gasket. Align the sample chamber hole of the gasket to match the center of culet under the optical microscope.

3. Synthesizing single-crystal ice-VII by EHDAC

3.1 Loading sample

3.1.1 Load one or more ruby spheres and one piece of gold into the sample chamber.

3.1.2 Load a drop of distilled water in the sample chamber, close the DAC and compress it by tightening the four screws on the DAC to quickly seal the water in the sample chamber.

3.2 Pressurizing sample to obtain powder ice-VII

3.2.1 Determine the pressure of the sample by measuring the fluorescence of ruby spheres using a Raman spectrometer.

3.2.2 Carefully compress the sample by turning the four screws and monitor the pressure by ruby florescence until it reaches the stability field of ice-VII (>2 GPa). Watch the sample chamber under the optical microscope during compression. Sometimes the coexistence of water fluid and crystallized ice VI is visible if the pressure is close to the phase boundary of water and ice VI.

3.2.3 Continue compressing the sample chamber until it reaches the pressure in the stability field of ice-VII. In order to melt the ice-VII later, the target pressure is usually between 2 GPa and 10 GPa at 300 K.

3.3 Heating sample to obtain single crystal ice-VII

3.3.1 Put the EHDAC under the optical microscope with a camera connected to the computer. Thermally insulate the DAC with the microscope stage, without blocking the transmitted light path of the microscope.

3.3.2 Connect the thermocouple to the thermometer and connect the heater to a DC power supply.

3.3.3 Monitor the melting of ice-VII crystals upon heating to a temperature that is higher than the melting temperature of high-pressure ice-VII determined by the phase diagram of H_2O.

3.3.4 Quench the sample chamber to allow the liquid water to crystallize, and then increase the temperature until some of the smaller ice crystals are molten. Repeat the heating and cooling cycles a few times until only one or a few larger grains remains in the sample chamber.

3.3.5 Measure the pressure of sample after the synthesis.

4. Synchrotron X-ray diffraction and Brillouin spectroscopy collection

4.1 Synchrotron X-ray diffraction

4.1.1 Check if the ice-VII sample synthesized is polycrystalline or a single crystal by synchrotron-based single-crystal XRD[15]. If it is a single crystal, the diffraction pattern should be diffraction spots instead of powder rings.

4.1.2 Obtain step scan single-crystal XRD images to determine the orientation and lattice parameters of ice-VII.

4.1.3 Collect the XRD of pressure marker, gold in the sample chamber to determine the pressure.

4.2 Brillouin spectroscopy

4.2.1 Mount the EHDAC on a specialized holder which can be rotated within the vertical plane by changing the χ angles. Connect the thermocouples to the thermocouple meter and connect the heater to the power supply.

4.2.2 Perform Brillouin spectroscopy measurements every 10-15° χ angle at 300 K for a total χ angle range of 180° or 270°[16]. Then heat the sample to high temperatures (e.g., 500 K) and repeat the Brillouin spectroscopy measurement.

REPRESENTATIVE RESULTS:

In this report, we used the fabricated resistive micro-heater and BX-90 DAC for the EHDAC experiment (**Figure 1** and **Figure 2**). **Figure 1** shows the machining and fabrication processes of the ring heaters. The standard dimensions of the heater base are 22.30 mm in outer diameter, 7.94 mm in inner diameter and 2.25 mm in thickness. The dimensions of the ring heater can be adjusted to accommodate various types of seats and diamonds.

We heated the compressed H_2O sample in an EHDAC at about 6 GPa up to 850 K to synthesize single crystal ice-VII. The ice-VII synthesized from the liquid H_2O after several cycles of heating and cooling was a large single crystal (**Figure 3**). The synthesized single crystal ice VII was utilized for the synchrotron XRD and Brillouin spectroscopy at HPHT. The temperature-power relationship is determined during experiments (**Figure 4**). The single-crystal XRD data were collected as a set of step scans by rotating the omega angle from -110° to -71° at 0.5°/step. The single crystal ice VII had little lattice stress and retained its good quality after compression and heating, as indicated by the sharp Bragg diffraction peaks in synchrotron-based single crystal XRD images (**Figure 5**). The diffraction pattern can be indexed with a cubic structure (space group $Pn\overline{3}m$, Z = 2) with unit cell parameters $a = b = c$ = 3.1375(6) Å at 11.2(1) GPa, 300 K and $a = b = c$ = 3.1605(3) Å at 11.2(4) GPa, 500 K. The crystallographic orientation of the single-crystal ice-VII are determined to be (-0.105,0.995,0) at 300K and 500 K. The sound velocities and elastic moduli were obtained by high-pressure and high-temperature Brillouin scattering measurements (Fi**gure 6**). The obtained elastic moduli are: C_{11} =89.73(1) GPa, C_{12} = 55.72(1) GPa and C_{44} = 56.77(1) GPa, K_s = 67.8(1) GPa and G_{VRH} = 34(6) GPa at 11.2(4) GPa and 300 K; C_{11} =82.42(1) GPa, C_{12} = 49.02(1) GPa and C_{44} = 52.82(1) GPa, K_s = 63(1) GPa and G_{VRH} = 30(5) GPa at 11.2(4) GPa and at 500 K.

FIGURE AND TABLE LEGENDS:

Figure 1 Fabrication of ceramic ring heater base and a micro heater with Pt/Rh wires. (**A**) 3-D model of the heater base (**B**) Milling the pyrophyllite heater base by the CNC machine. (**C**) Heater bases sintered in the furnace at 1523 K. (**D**) Heater with Pt/Rh wires and insulators (mica, insulating tube and high-temp braid sleeving).

Figure 2. Preparation of EHDAC for high-pressure and high-temperature experiments. (**A**) BX-90 DAC with thermocouple installed. (**B**) Zoom-in view of the placement of thermocouples near the diamond culet. (**C**, **D**) The placement of micro-heater in the EHDAC. (**E**) EHDAC on the cell holder with the heater connected to a DC power supply and thermocouples connected to a thermometer.

Figure 3. Synthesis of single crystal ice-VII in an EHDAC at about 6 GPa up to 850 K. (**A**) Polycrystalline ice-VII crystallized from the supercooling water at high pressure and high temperature. (**B**) Growth of polycrystalline ice-VII by decreasing the temperature. (**C**) Growth of a large single-crystal ice-VII and melting of other smaller crystals after multiple heating and cooling cycles. (**D**) Growth of one single-crystal ice-VII to fill the sample chamber by further decreasing the temperature.

Figure 4. The temperature-power relationship of the EHDAC experiments. Solid squares represent the temperature-power data in this study, which can be linearly fitted (solid line). This is consistent with the relationship (dashed line) in previous work[7].

Figure 5. Single crystal XRD pattern of ice-VII at 11.2 GPa and 500 K. Diffraction peaks of single crystal ice-VII were marked by black boxes. Red labels correspond to Miller indices (*hkl*) of the diffraction peaks. Other single-crystal peaks are from single-crystal diamond anvils used in the EHDAC.

Figure 6. Sound velocities of single crystal ice-VII at 11.2(1) GPa, 300 K and 11.2(4) GPa, 500 K (**A**) Representative Brillouin spectra of ice-VII at χ angle = 260 ° (**B**) Sound velocities of ice-VII as a function of rotational χ angles. Solid symbols represent the measured velocities by Brillouin spectroscopy. Dashed lines represent the calculated velocities from the best-fit single-crystal elasticity model.

DISCUSSION:

In this work, we described the protocol of preparing the EHDAC for high pressure research. The cell assemblies including a micro-heater and thermal and electrical insulating layers. Previously, there are multiple designs of resistive heaters for different types of DACs or experimental configurations[7,17-20]. Most of the heaters are machined by individual investigators or purchased from industry which are typically designed for other purposes. Fabricating micro-heaters in a normal machine shop can be time consuming and not always reproducible. In most occasions, unfortunately, the micro-heaters of different designs from individual groups are not optimized and thoroughly tested. The heaters supplied from industry typically are not designed and optimized for EHDAC experiments. Custom designed and machined heaters are mostly pricy due to the requirement of bulk order by industrial machine shops. Therefore, the infrastructure development of heaters for EHDAC experimentation would benefit the entire community with standardized and thoroughly tested heater assemblies, and well documented preparation procedures. In addition, the design and standardization of thermal and electrical insulating layers can help improve the success rate and temperature stability of the EHDAC experiments. The new EHDAC setup allows routine high-temperature DAC experiments for the broad high-pressure community[13].

We have also designed other variations of heaters. The thickness of the heater can be increased to 4.65 mm for the BX90 EHDAC, when backing plates (or seats) with stepped thickness are used. We also designed heaters with varying thickness along the radial direction. They are thinner at the center and thicker near the rim, thus can be used in the EHDAC with short diamonds anvils of Boehler-Almax (BA) design. The DAC with BA diamonds has large opening angles, which is optimal for high-pressure single-crystal XRD experiments.

There are some pros and cons of this technique. The highest achievable temperature is typically limited to 900 K in the open air due to the oxidation and graphitization of diamonds compared with laser-heated DAC. However, higher temperatures above 1200 K have been achieved for a BX90 EHDAC housed in a newly designed and fabricated water-cooled enclosure with protective atmosphere/vacuum and membrane for pressurization. The thermal gradient in the sample chamber of the EHDAC is smaller and the temperature can be stable for a long time (several hours to days) with an easy feed-back control between power and temperature. In this work, the temperature was stable at 500°±2 K for about one day for each Brillouin scattering data collection and multiple heating-cooling cycles can be achieved. Another challenge for the EHDAC is that the pressure sometimes would increase significantly upon heating especially at low pressures (<20 GPa). This could be mitigated by untightening the screws for pressurization before heating or tuning the membrane gas pressure during heating when a membrane pressurization system is used.

There are several critical steps for the EHDAC experimentation. Regarding the placement of the thermocouple for accurate temperature measurements, the thermocouple should be first electrically insulated from the metallic seats and body of the DAC. The junction of the thermocouple should be secured to touch the surface of the diamond's pavilion and <1 mm away from the culet, in order to determine the temperature of the sample. Regarding heater preparation, ensuring good thermal insulation surrounding the micro-heater is critical, and it is necessary to wind more spare wires around the wires extending from the heater to reduce the electrical resistivity and thus the temperature of the extension wires during heating.

Here we showcased the utilization of the EHDAC to synthesize single-crystal ice-VII of good quality from liquid H_2O at HPHT. Combined with the accurately determined single-crystal orientation by single crystal XRD, the elastic moduli with small uncertainties were determined from Brillouin scattering measurements. The elastic moduli at 300 K of ice-VII were close to the previous data[21,22] and the elastic moduli at 500 K was the first HPHT Brillouin results of single-crystal ice-VII reported. The sound velocities and elastic moduli decease as a function of temperature at 11.2 GPa (**Figure 6**). Experiments at different pressures and temperatures should be performed to understand the temperature effect on the elastic moduli of ice-VII at elevated pressures. In this case, the EHDAC can be used to synthesize high-pressure phases with low melting temperature, and can also be used to simulate the HPHT conditions in the Earth's and planetary interiors. Combined with various detection methods, such as synchrotron XRD and Brillouin spectroscopy, physical properties of planetary materials in deep interiors of planets or moons can be obtained and compared with the geophysical models.

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DISCLOSURES:

The authors declare no conflict of interest.

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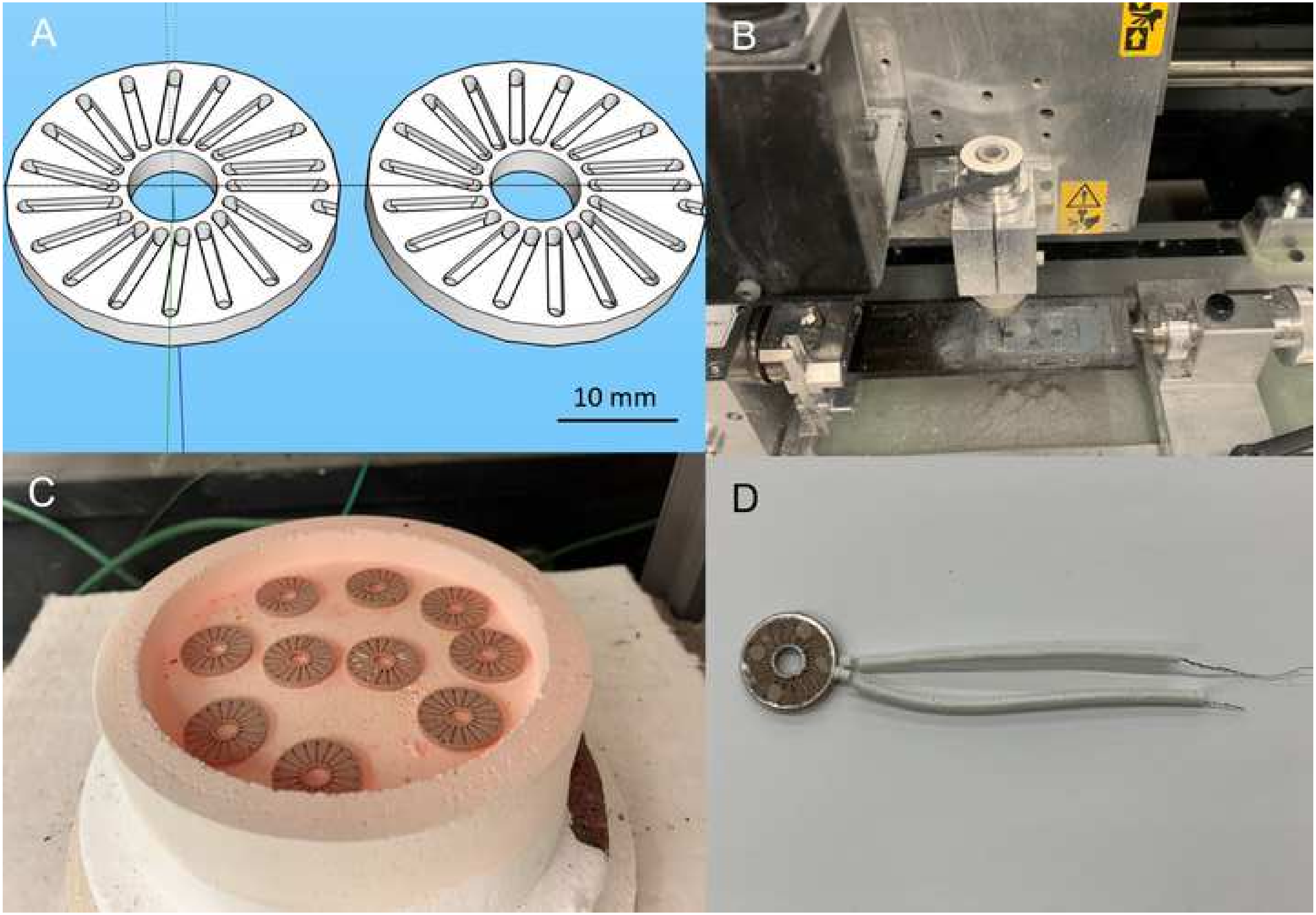
Figure 1



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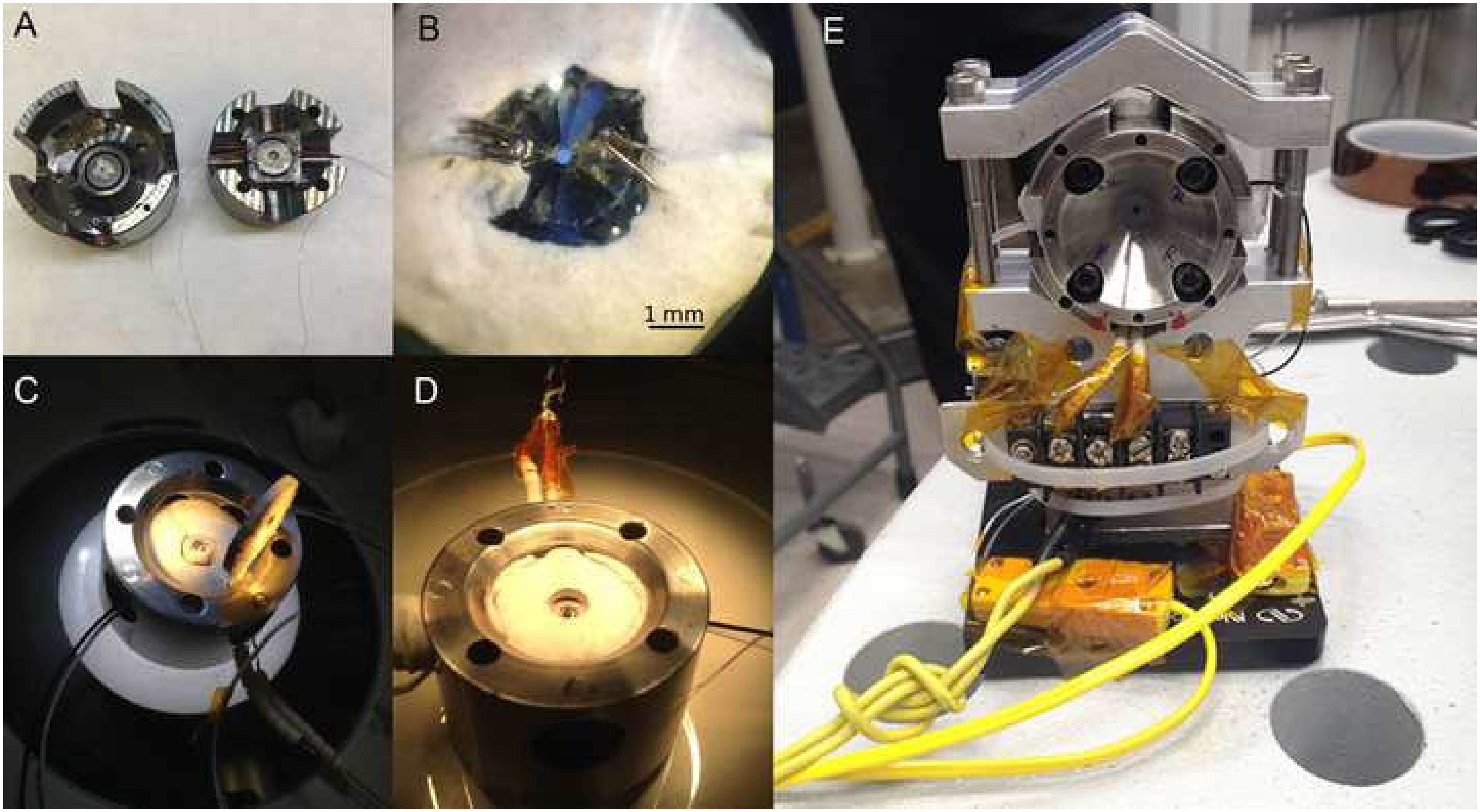

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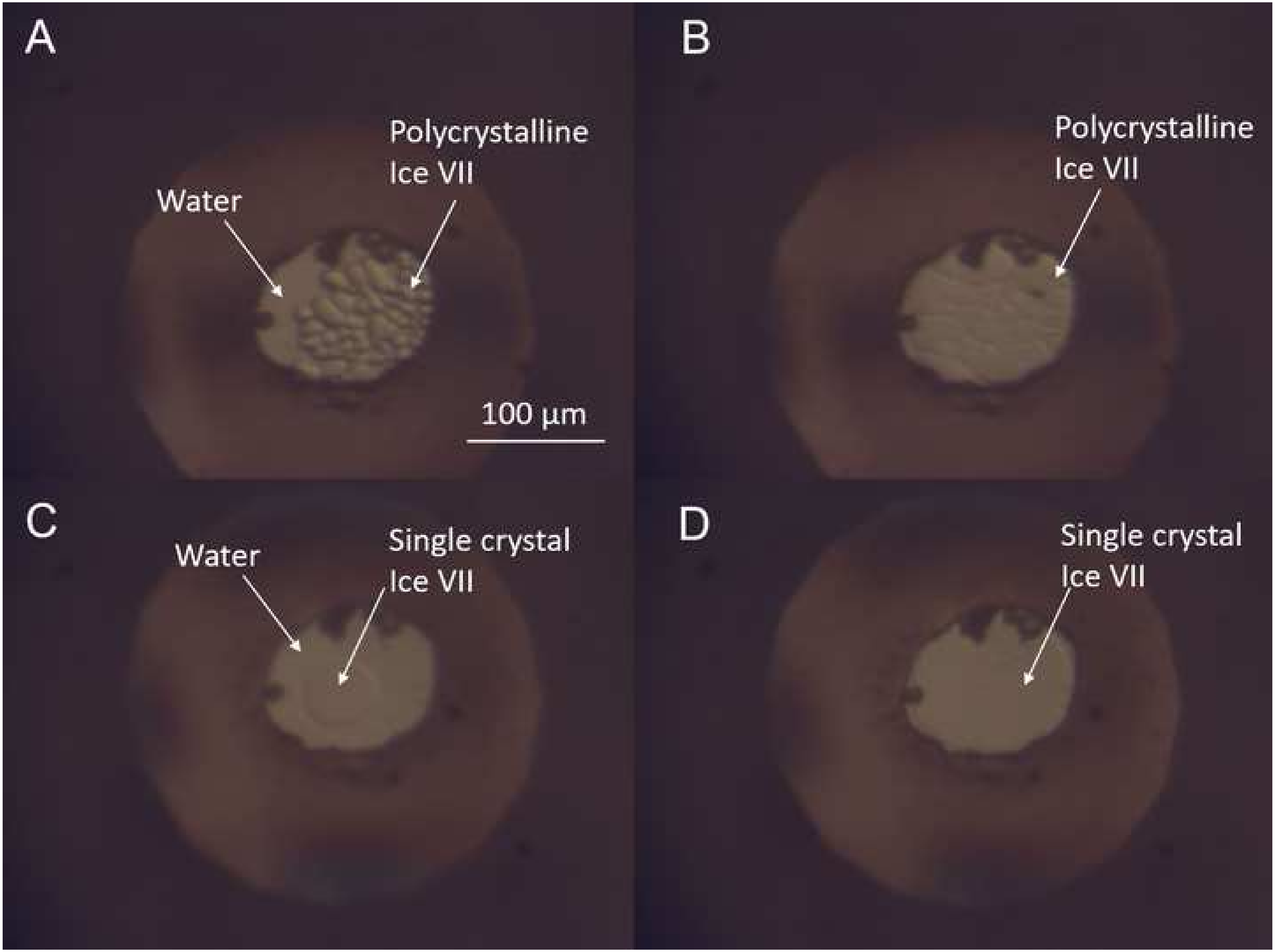
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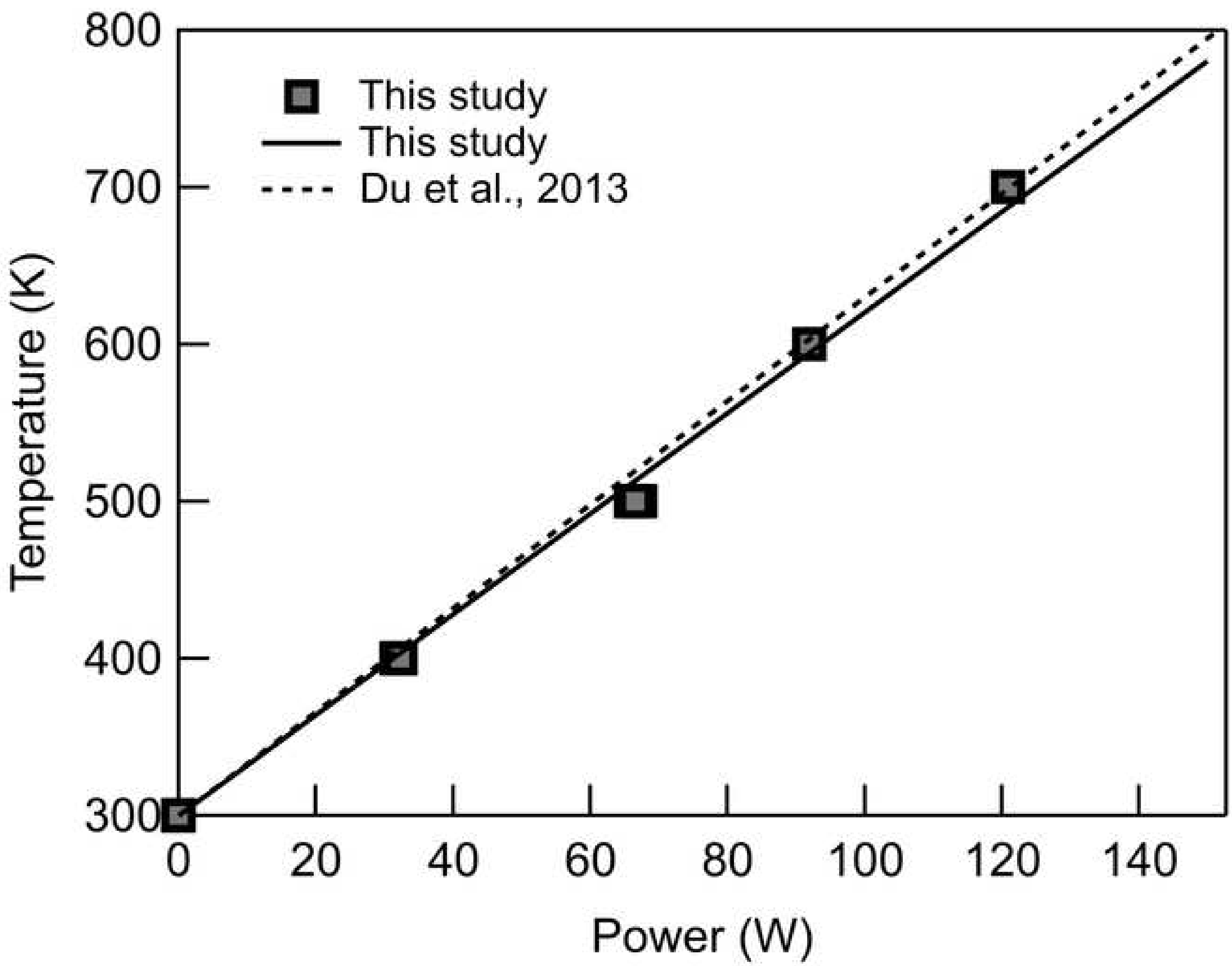
100 µm
B
Polycrystalline Ice VII
C
Water
Single crystal Ice VII
D
Single crystal Ice VII

Figure 4


This study
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Du et al., 2013
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Figure 5

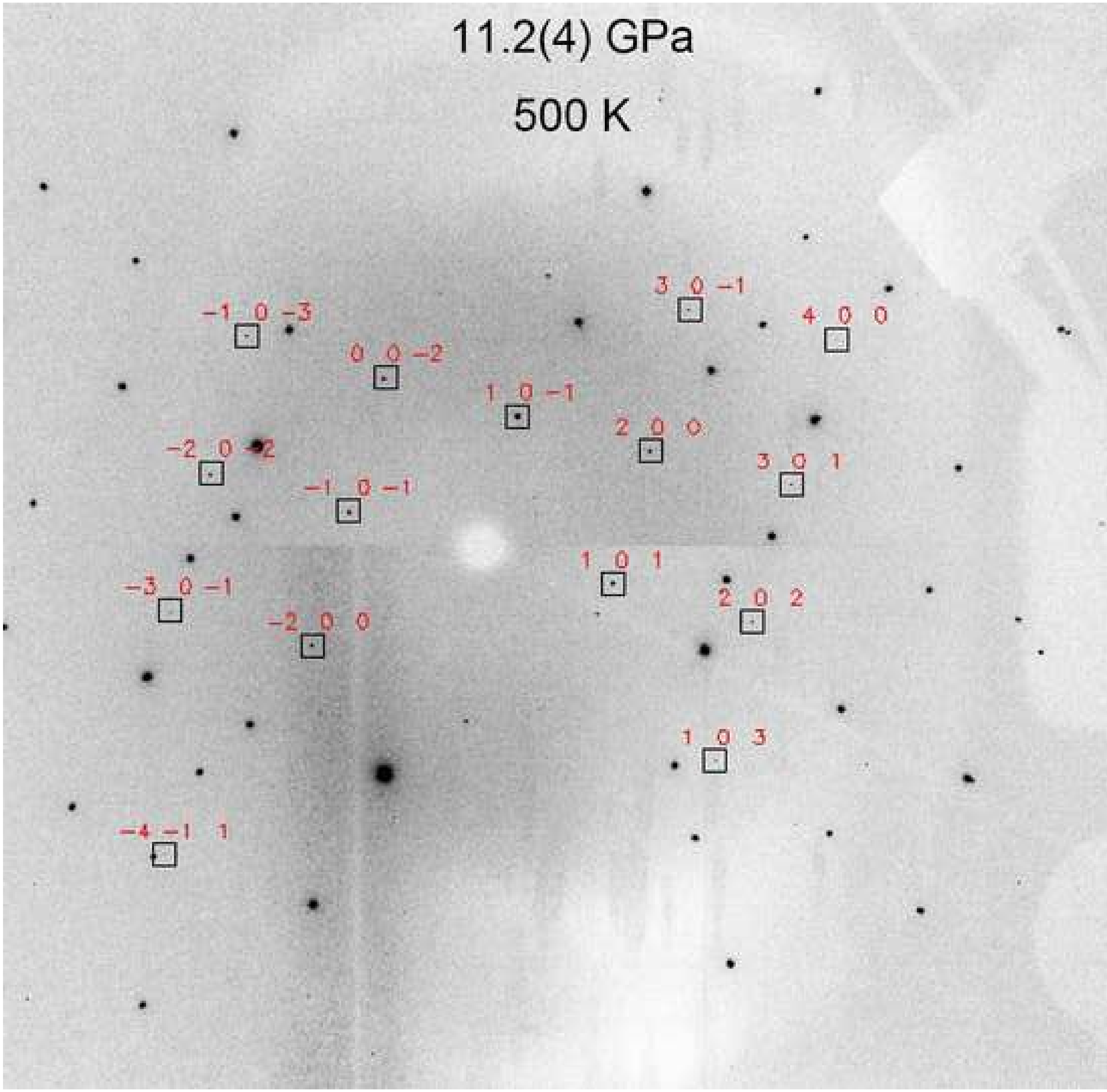
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Figure 6

Click here to access/download;Figure;Figure 6.tif

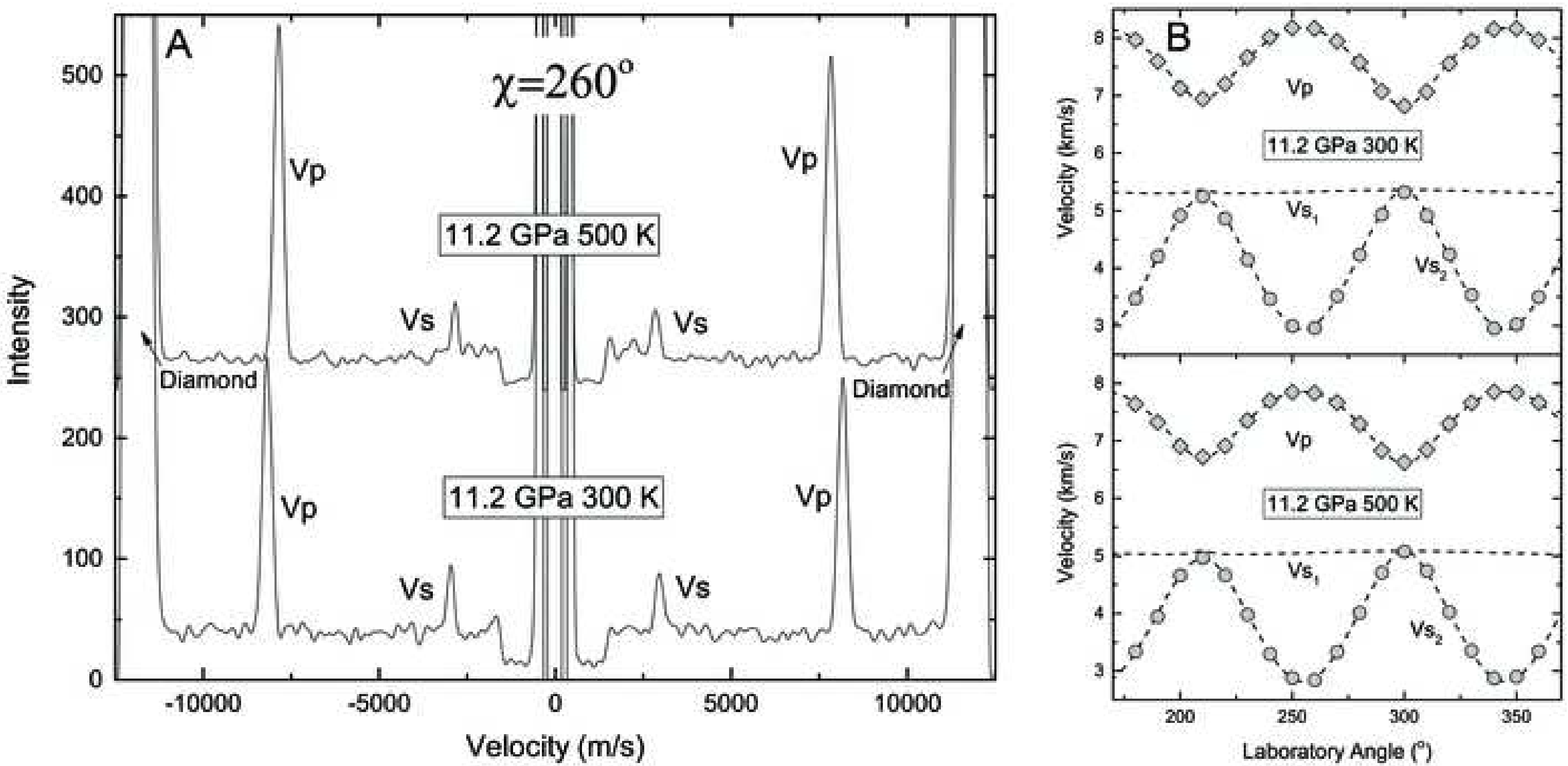


Table of Materials

Click here to access/download;Table of Materials;Table of Materials.xlsx

Name of Material/ Equipment	Company	Catalog Number	Comments/
Au	N/A	N/A	for pressur
Deionized water	Fisher Scientific	7732-18-5	for the star
Diamond anvil cell	SciStar, Beijing	N/A	for generat
K-type thermocouple	Omega	L-0044K	for measuri
Mica	Spruce Pine Mica Comp	N/A	for electric
Pt 10wt%Rh	Alfa Aesar	10065	for heater
Pyrophyllite	McMaster-Carr	8479K12	for fabricat
Re	Sigma-Aldrich	267317	for the gask
Resbond 919 Ceramic Adhesive	Cotronics Corp	Resbond 919-1	for insulatir
Ruby	N/A	N/A	for pressur
Ultra-Temp 2300F ceramic tape	McMaster Carr Supply	390-23M	for thermal

/Description

e calibration

ting material of ice-VII synthesis

ing high pressure

ing high temperature

al insulation

ing the heater base

ket of diamond anvil cell

ng heating wires and mounting diamonds on seats

e calibration

l insulation

Dear editors and reviewers,

Thanks a lot for your constructive comments and suggestions concerning our manuscript entitled " Externally-heated diamond anvil cell for synthesis and single-crystal elasticity determination of ice-VII at high pressure-temperature conditions " [JoVE61389]. Following your instruction, we have prepared a point-to-point response (blue colored text) to the comments of editors and reviewers and described how the manuscript has been revised accordingly. A summary of the major changes was also included to highlight the revisions that we have made to address the comments.

We tried our best to revise the manuscript by responding the reviewers' comments. We appreciate the comments and suggestions from editors and three anonymous reviewers earnestly, and hope that our responses and revisions are satisfactory.

Should you have any question, please do not hesitate to contact us.

With best regards,

Bin Chen (binchen@hawaii.edu, tel: 808-956-6908)

On behalf of all co-authors

A summary of the major changes

1) To address the comments from reviewer 1, a 3-D model was added in Figure 1.

2) To address the comments from reviewer 1 and 2, a figure of the synthesis of single crystal ice VII was added (Now Figure 3).

3) To address the comments from reviewer 1, a figure of power-temperature relationship was added in the manuscript (Now Figure 4).

4) To address the comments from reviewer 2, a statement of laser heating was modified (Line 71-74).

5) To address the comments from editors, paragraphs about critical steps within the protocol; modifications and troubleshooting of the technique; Any limitations of the technique was added in the discussion part (Line 297-325).

Editorial comments:

General:

1. Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues.

Response: We thoroughly proofread the manuscript.

2. Please include email addresses for all authors in the manuscript.

Response: Email addresses for all authors were added in the manuscript.3. Please reduce the length of the Summary to 10-50 words.

Response: The length of the summary was reduced to 50 words.

Protocol:

1. For each protocol step/substep, please ensure you answer the "how" question, i.e., how is the step performed? Alternatively, add references to published material specifying how to perform the protocol action. If revisions cause a step to have more than 2-3 actions and 4 sentences per step, please split into separate steps or substeps.

Response: We made sure that we answered the "how" question and added the relevant references.

Specific Protocol steps:

1. 4.2.2: Please provide a reference for Brillouin spectroscopy here or otherwise provide more details about this procedure.

Response: A reference (Sinogeikin, Bass et al. 2006) for Brillouin spectroscopy was added in 4.2.2.

Figures:

1. Figure 5 is referenced in the Results section, but it is not present.

Response: Sorry for the confusion, we mislabeled the figure number. We have corrected it.

Discussion:

1. Please revise the Discussion to explicitly cover the following in detail in 3–6 paragraphs with citations:

a) Critical steps within the protocol

b) Any modifications and troubleshooting of the technique

c) Any limitations of the technique

Response: We added three paragraphs about the above aspects in the discussion part (Line 297-325).

Disclosures:

1. Please include at least a sentenced in the Disclosures section, providing information regarding the authors' competing financial interests or other conflicts of interest. If authors have no competing financial interests, then a statement indicating no competing financial interests must be included.

Response: The statement "The authors have no conflict of interest" was added in the disclosure section.

Table of Materials:

1. Please ensure the Table of Materials has information on all materials and equipment used, especially those mentioned in the Protocol.

Response: We made sure that the Table of Materials has information on all materials and equipment used.

Reviewers' comments:
Reviewer #1:

Manuscript Summary:
The authors provide a comprehensive description for a ring-heater design. The author also propose a novel method to make a single-crystal ice in-situ at high pressure. Those are very nice contributions and worthy of publication. I have a few minor points, hopefully to help this manuscript to access broader readership, as well as convey the important aspect of this new contribution.

Minor Concerns:

1) please provide scale-bars in Figure 1.
2) It would be helpful to show a better photo for an external-heater design, particularly its inner structure.
3) Perhaps to show a 3-D file for the design of the ring-heater, plus a 2-D cross-section would be very helpful

Response: Figure 1 was modified. A 3-D model with scale bar was added in Figure 1 to show the design of ceramic micro-heater base. We find a 2-D cross-section may not provide more information in addition to the 3-D model, so we did not show it in Figure 1.

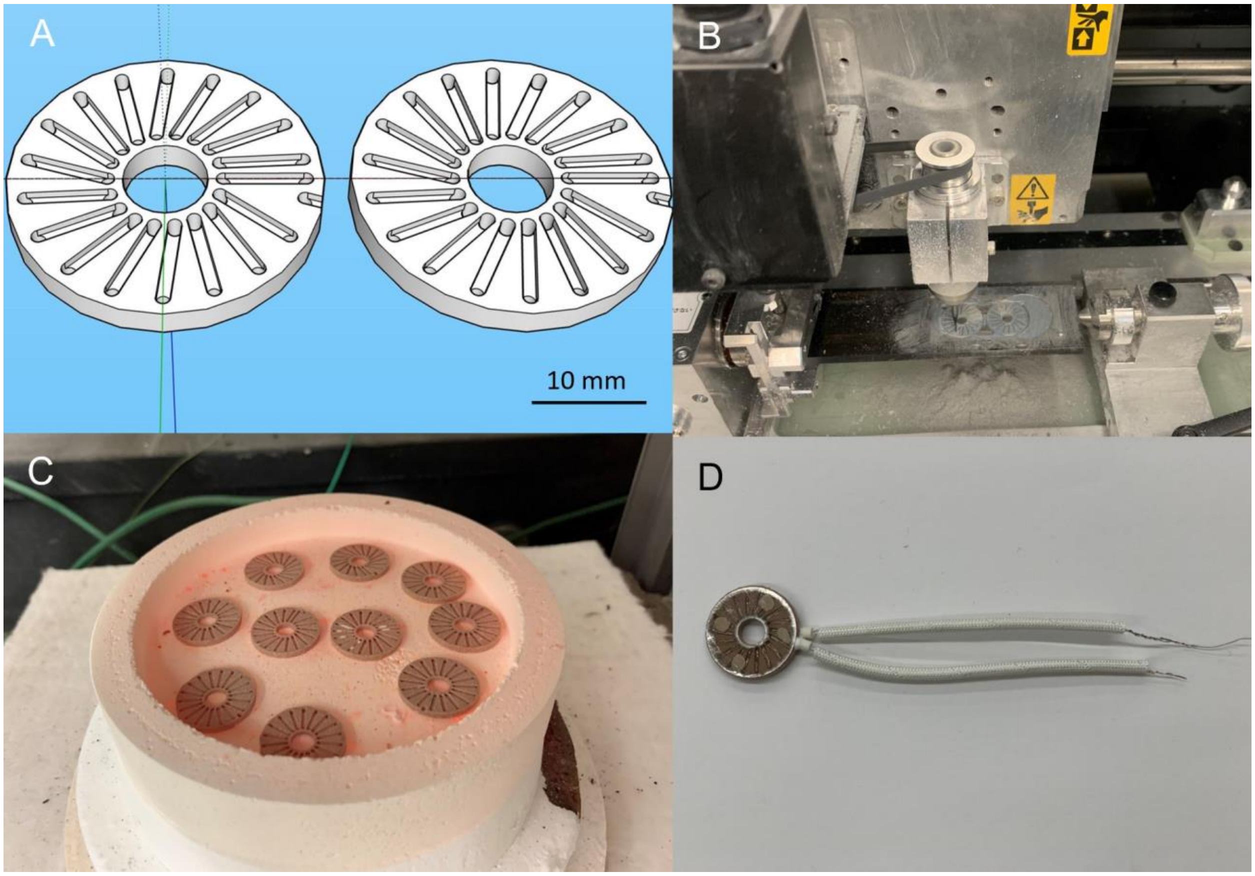


Figure 1.

4) It would nice to show a Temperature- Power relationship with this new design to compare with previous work.

Response: A temperature-power curve was added in the manuscript (Figure 4). The temperature-power relationship is similar to the one in the previous study (Du, Miyagi et al. 2013).

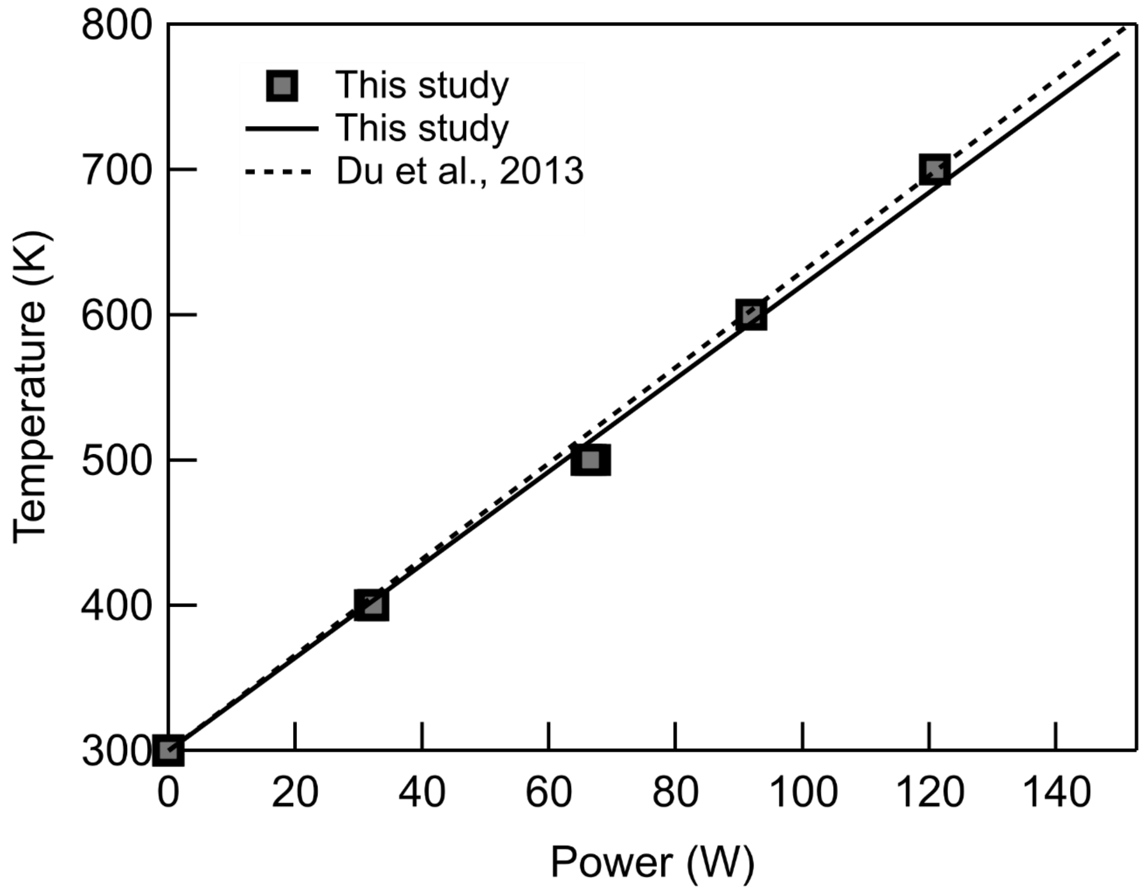


Figure 4 in the manuscript

5) It should be a lot clearer and of broader interest if authors can provide a serious of photos showing how water melts and crystallized, as well as how single crystals was made.

Response: We added Figure 3, which contains four figures to show the melting and crystallization of ice VII. The synthesis process of ice VII will also be presented in the video part.

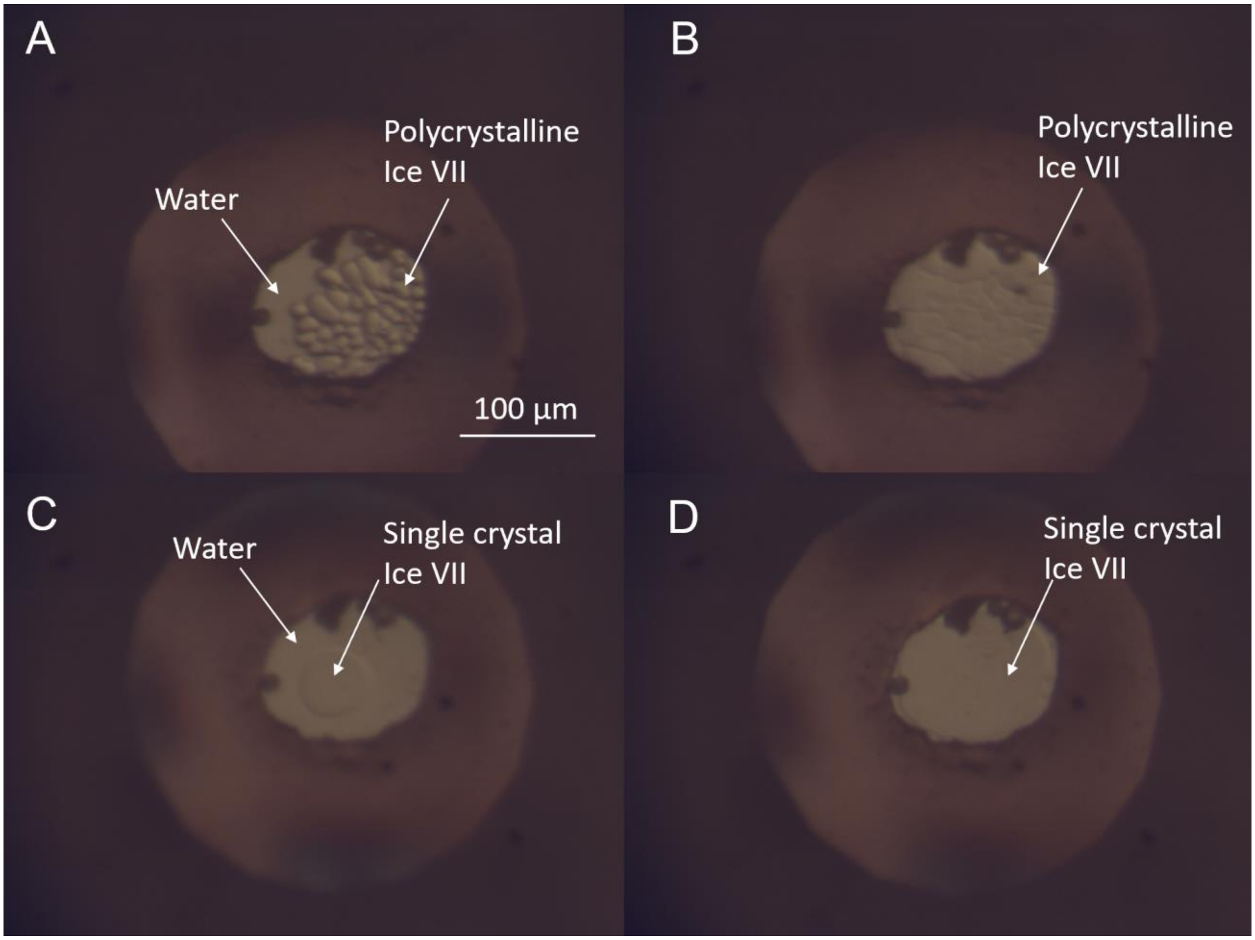


Figure 3 in the manuscript.

Reviewer #2:

Manuscript Summary:
the paper reports the protocol for improved external heating of diamond cells with large axial apertures, suitable for Brillouin-spectroscopy and single crystal X-ray diffraction. This opens new possibilities for high P-T experiments in the 10 GPa 1000K range and beyond.

Major Concerns:
none

Minor Concerns:

Some wording issues and some additional explanations at some points would help. Here is a detailed list of comments:
-> THE Externally-heated diamond anvil cell (EHDAC) can be used to generate simultaneously
Response: We corrected it.

->THE Diamond anvil cell (DAC) is one of the most important tools for high pressure research.
Response: We corrected it.

'laser heating temperature usually fluctuates'

-> Can be mitigated by feed-back coupling of thermal emission and laser power.

-> One main issue is that in multiphase assemblies the absorbance of laser light may be different for different phases

Response: We changed the statement to "The temperature during laser heating usually fluctuates but can be mitigated by feed-back coupling between thermal emission and laser power. More challenging is controlling and determining the temperature for assembly of multiple phases of different laser absorbance." (Line 71-74)

76...well suited to be coupled with various detection and diagnostic methods, including optical
77 microscope, X-ray diffraction (XRD), Raman spectroscopy, Brillouin spectroscopy and Fourier transform infrared spectroscopy.
Response: We added a reference (Kantor, Prakapenka et al. 2012) to strengthen our statement.

82 BX-90 type DAC is a newly developed
-> THE BX-90 …., also, explain about the aperture (90deg?)
Response: We changed the statement to "The BX-90 type DAC is a newly developed piston-cylinder type DAC with large aperture (90° at maximum) for XRD and laser spectroscopy measurements"

The U-cut
84 on cylinder side also provides room
-> 'U-shaped cut' ?

Response: We replaced "U-cut" by "U-shaped cut" .

EHDACs and demonstrated
88 single-crystal XRD as well as Brillouin spectroscopy measurements of synthesized single-crystal

-> Perhaps you should explain why this is not trivial - what is the main improvement above earlier EHDAC set ups - angular aperture? …
You seem to have succeeded in stabilizing temperature/reducing internal thermal gradients - or is it possible that you grow large crystallites because you have a gradient?
Please expound a little bit.

Response: We did not expect that our EHDAC has better control on thermal gradient than previous ones. The main advantage is that we standardize the heater and insulating parts for this BX90 DAC. The

BX90 + external heater is now widely used in high-pressure community (Yang, Mao et al. 2014, Lai, Zhu et al. 2018). A standard protocol will make the preparation routine and results consistent, i.e. the power curve, the temperature gradient, the thermal pressure, etc. Another advantage is that the heater can be fabricated by a CNC machine, thus with the model we provided in the paper, other labs can easily produce the same heater at low cost.

215 'The ice-VII synthesized from the liquid H2O after several cycles of heating and cooling at 6 GPa
216 was a large single crystal

-> Only one?

Response: Yes, we performed multiple heating and cooling cycles to allow the polycrystalline ice phases melt and crystallize. The heating and cooling cycles would allow smaller grains to melt first and leave one grain in the sample chamber. Then this one grain can act as a seed to grow to a large one after we slowly lowered the temperature. Figure 3 (a new figure) shows the process of growing one single crystal of ice-VII in the sample chamber under a microscope. We checked the synthesized sample using single-crystal XRD and confirmed the ice VII piece in the whole sample has the same orientation. Sometimes, we could only grow 2-3 large grains of the single crystal ice-VII, which can still be used in single-crystal XRD and Brillouin scattering measurements.

'with little lattice stress :'
-> How do you know? What is the integral R-factor for cubic, tetragonal,…
I see no other criterion to distinguish an strained from an unstrained crystal through diffraction.

Response: We only obtained the unit-cell parameters and orientation from our single crystal XRD data and did not refine the atomic positions, so there is no R-factor. The chi^2 is about 0.013 which indicates that the cubic phase is a good model. We found the single crystal spot under pressure did not elongate (implies orientation is no longer identical as single crystal) or broaden (implies pressure gradient increases inside the detected volume), thus we inferred that the crystal retained good quality.

216 ‘ and retained its good quality after compression’
217 and heating, as indicated by the sharp Bragg diffraction peaks in synchrotron-based single crystal
218 XRD images (Figure 3).

-> Explain what the other reflections in fig 3 are!

Response: They are diamond reflections from the single-crystal diamond anvils, we explained them in figure caption in Figure 5 in the updated version.

' The diffraction pattern can be indexed with a cubic structure'
-> Usually for single crystal data one indexes peaks based on the set of quadruples , coordinates and tth, for instance by using the statistics of distance vectors.
Your statement suggests that your integrated the pattern (around 360 deg? Or along radial stripes?) and used the d-spacings for indexation.

Please explain. I was under assumption that you collected single crystal diffraction data (XRD frames collected over fixed angles/small increments at different angular settings, phi/omega/chi). Also explain the diffraction measurement strategy and geometry: I assume chi was fixed, then phi or omega changed? Chi = 90deg -> phi= omega?

Response: We collected the step scans by rotating omega angle from -110 deg to -71 deg at 0.5 deg /step and we added this information in the manuscript (Line 230-231). The step scans were used to obtain the unit cell parameters and crystal orientation of ice VII for latter Brillouin scattering data processing.

The single-crystal XRD data were collected by rotating the omega angle, along the axis perpendicular to the sample stage. The Brillouin scattering data were collected by rotating the chi angle, along the axis perpendicular to the optical window of the two diamond anvils.

' (space group
219 Pn-3m, Z = 2) with unit cell parameters a = b = c = 3.1375(6) Å at 11.2(1) GPa, 300 K and a = b = c
220 = 3.1605(3) Å at 11.2(4) GPa, 500 K. '

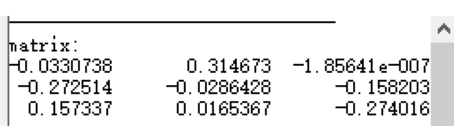
-> what is the integral R factor, what is R2, what GooF or did you not attempt structure analysis (if so, why?), what are the thermal displacement factors (of O at least).

Response: We did not do structural refinement since the rotation angle (39 deg) is limited, but we get the information (crystallographic orientation and also lattice parameters) required for the elasticity determination.

'The crystallographic orientation of the single-crystal ice-VII
are determined to be (-0.105,0.995,0) at 300K and 500 K. '

-> What is that? Is this a Miller index -1 10 0?
-> Usually the orientation of a crystal specimen is described with a UB matrix. On the other hand, I don't see that you need to report this.

Response: The crystal is grown with a plate-like shape within the narrow space between the two diamond anvils. (-0.105, 0.995,0) is the plane normal of the ice single crystal in the diamond anvil cell, which is parallel to the diamond anvil cell axis. The plane normal was used in the Brillouin data analysis to obtain various crystallographic directional cosines of the experimentally measured velocities. The orientation of a crystal is indeed usually described with a UB matrix (see the following figure for the UB matrix), we used the plane normal for simplicity to represent the orientation of the crystal synthesized in the diamond anvil cell.


matrix:

-0.0330738	0.314673	-1.85641e-007
-0.272514	-0.0286428	-0.158203
0.157337	0.0165367	-0.274016

Figure R1. UB matrix of ice VII at 11.2 GPa, 300 K

-> What is the index of refraction of ice-VII at 300 and 500K and 11 GPa?

Response: It depends on the wavelength of the light. Within X-ray wavelength, the index of refraction should be quite similar and close to 1.

Reviewer #3:

In this paper by Lai et al. entitled "Externally-heated diamond anvil cell for synthesis and single-crystal elasticity determination of ice-VII at high pressure-temperature conditions", the authors describe a protocol for preparing standardized external micro-heaters for the BX-90 type diamond anvil cells and for assembly all the components in order to perform experiments at extreme conditions of pressure and temperature. According to the authors, these EHDAC cells can be routinely used to generate pressures of the order of the megabar and temperature up to 900 K in air (up to 1200 K in protective atmosphere).

The paper is well written, the title and the abstract are appropriate. The potential applications of the protocol are clear, the materials are presented in a table and the steps are well listed and described.

However, I find that the reported scientific case does not fully cover the anticipated results. In fact, one of the issues generally encountered in EHDAC is the inability of reaching "extreme" pressure, due to thermally-induced mechanical instability of the cells. Although the authors stated that megabar experiment can be routinely performed with this cells, they are reporting a single case at 11.2 GPa and 500 K. It is my opinion that this paper would gain more interest if the authors can report some scientific case showing the real potential of this protocol.

Response: We added a reference Lai et al. 2018, in which we used the same protocol and achieved higher pressure (up to 80 GPa, 700 K) (Line 295). But the main goal of the JoVE paper is to show the protocol of this method, which we felt the synthesis of ice VII crystal is a more suitable case to show the capacity of the method to a broader audience.

I therefore recommend the publication of this work after a minor revision.

References:

Du, Z., L. Miyagi, G. Amulele and K. K. Lee (2013). "Efficient graphite ring heater suitable for diamond-anvil cells to 1300 K." Review of Scientific Instruments **84**(2): 024502.

Kantor, I., V. Prakapenka, A. Kantor, P. Dera, A. Kurnosov, S. Sinogeikin, N. Dubrovinskaia and L. Dubrovinsky (2012). "BX90: A new diamond anvil cell design for X-ray diffraction and optical measurements." Review of Scientific Instruments **83**(12): 125102.

Lai, X., F. Zhu, J. Liu, D. Zhang, Y. Hu, G. J. Finkelstein, P. Dera and B. Chen (2018). "The high-pressure anisotropic thermoelastic properties of a potential inner core carbon-bearing phase, Fe7C3, by single-crystal X-ray diffraction." American Mineralogist **103**(10): 1568-1574.

Sinogeikin, S., J. Bass, V. Prakapenka, D. Lakshtanov, G. Shen, C. Sanchez-Valle and M. Rivers (2006). "Brillouin spectrometer interfaced with synchrotron radiation for simultaneous X-ray density and acoustic velocity measurements." Review of Scientific Instruments **77**(10): 103905.

Yang, J., Z. Mao, J.-F. Lin and V. B. Prakapenka (2014). "Single-crystal elasticity of the deep-mantle magnesite at high pressure and temperature." Earth and Planetary Science Letters **392**: 292-299.