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# High-Temperature Experiments using a Resistively-Heated High-Pressure Membrane Diamond Anvil Cell

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## Abstract

A reliable high-performance heating method using resistive heaters and a membrane driven diamond anvil cell (mDAC) is presented. Two micro-heaters are mounted in a mDAC and use electrical power of less than 150 W to achieve sample temperatures up to 1200 K. For temperature measurement we use two K-type thermocouples mounted near the sample. The approach can be used for *in-situ* Raman spectroscopy and x-ray diffraction at high pressures and temperatures. A W-Re alloy gasket material permits stable operation of mDAC at high temperature. Using this method, we made an isothermal compression at 900 K to pressures in excess of 100 GPa and isobaric heating at 95 GPa to temperatures in excess of 1000 K. As an example, we present high temperature Raman spectroscopy measurements of nitrogen at high pressures.

## I. INTRODUCTION

High-temperature experiments at high pressures in a diamond anvil cell (DAC) are very important to the study of materials at the extreme conditions that exist in planetary interiors or during high-energy density processes. Such work requires accurate control over the thermodynamic state variables, pressure and temperature, for extended periods of time. To achieve high temperatures there are two widely utilized methods available: resistive heating and laser heating. Both techniques have specific advantages and disadvantages. Using laser heating, one can achieve temperatures on the order of several thousand degrees Kelvin (1). However, it is required that the sample itself be able to absorb the incident laser beam or a heat absorber has to be loaded in the sample chamber that will indirectly heat the sample. When a heat absorber is used to indirectly heat the sample, questions about chemical reactions between the sample and the heat absorber always arise. The obvious advantage of this method is the high temperature and the localized, very fast heating of the sample. However, it is difficult to maintain and measure the temperature below 1200 K using this method (2). For steady and stable high temperature experiments below 1200 K, the resistive heating of a DAC has been used. Over the past few decades, improvements have been made to reach higher working temperatures using resistive heating, but there are always limiting issues. In case of simple external heating experiments, either by wrapping a DAC body with a heating coil or placing a mini heater near sample area, the sample pressure typically drops as temperature ramps up. One approach to address the issue of losing pressure has been to fabricate the DAC using special metals like Re and Inconel, which have relatively low thermal expansion at high temperature (3). Although this approach has merit, the cost of fabrication and material are prohibitively high. Various approaches to improve

heating efficiency, heating stability, and extending pressure and temperature ranges during external heating of a DAC are compared in Table I. The maximum temperature reached appears to be inversely correlated with the pressure limit of each type of external heating experiment, assuming similar anvil design and gasket materials. The high temperature capability of the internal heating method using a Re strip inside the sample chamber (4) is limited temperature range due to possible chemical reactions of sample and pressure medium with Re. The chemical reaction can be reduced or eliminated by coating the strip with chemically inert material to the sample and Re itself. A graphite heater can heat a sample very effectively due to better thermal contact but the stability of heating appears limited and often the gasket fails prematurely (5).

Table I. Comparison of heating methods using a diamond anvil cell

Authors	Year	Temperature (°C)	Pressure	Heating	Type	Samples
Boehler et al. (9)	1986	<1000	<15 GPa	Fe wire	I	Fe ( $\alpha$ - $\epsilon$ , $\alpha$ - $\gamma$ ), W
Schiferl (3)	1987	~400-700	5-13 GPa	HT oven-expensive (Re)	E	O <sub>2</sub>
Bassett & Shen (10)	1993	-190~1200	~2.5 GPa	Mo wire	E	H <sub>2</sub> O, brucite, muscovite
Fei et al. (11)	1994	~700	<86 GPa	Mo wire, Inert gas flow	E	FeO
Dubrovinsky et al. (5)	1998	~1200	<68 GPa	Graphite heater	E	Fe, Al <sub>2</sub> O <sub>3</sub>
Balzaretti et al. (12)	1999	~1100	<4 GPa	Gasket heating (Re)	E/I	$\alpha$ -Si <sub>3</sub> N <sub>4</sub> , $\gamma$ -Al <sub>2</sub> O <sub>3</sub>
Zha & Bassett (4)	2003	~2700	<10 GPa (50 GPa)	Internal heating (Re)	I	SiO <sub>2</sub> (Raman: qtz-coe)
Dubrovinskaya et. al (2)	2003	~1000	<92GPa	Whole-cell – special alloy cell	E	Fe <sub>0.95</sub> Ni <sub>0.05</sub> , TiO <sub>2</sub>
This work		950	105 GPa	Dual micro heaters	E	CO <sub>2</sub> (6), N <sub>2</sub>

There were no approaches that effectively dealt with all three of the issues collectively. We use vacuum heating to prevent oxidation of diamond and DAC metal body parts, and to sustain stable heating to over 1200 K. We also fill the space between the diamond anvils and heating coil with copper block lined with a thin ceramic ring or a high thermal conductivity ceramic paste to improve thermal conduction.

One of the greatest advantages of using a mDAC is uniform delivery of force through the inflated membrane, which applies load to the sample/gasket assembly, making contact with bottom of cylinder. The membrane is under constant He gas pressure during the high temperature experiment and provides a continuous constant load, independent of temperature. The uniform pressure loading of the membrane prevents uneven gasket thinning, which is one of the main causes of failure, leading to abrupt anvil fracture.

We coupled our membrane pressurization system to an external micro-heater system under vacuum including W-Re alloy as gasket material, leading to an improved reliability heating capability as well as substantially increased pressure/temperature ranges.

## II. HIGH TEMPERATURE EXPERIMENTAL SETUP:

### The membrane driven DAC:

Without a membrane, screws are typically used to generate pressure in a DAC. Using the screws to raise the sample pressure, the applied torques often shift the position of the sample in its holder and there is a tendency to induce uneven deformation of gasket. This can be a cause for an unexpected failure of the gasket. We use a membrane so that the inflation of the membrane delivers force through larger contact area at the bottom of the piston of a DAC. The membrane will likely minimize or completely eliminate the lateral force components applied to the table/bottom of the diamond anvil. This will compress and thin the gasket evenly. A gasket material with high tensile strength at high temperature will also help to reach extreme pressures. In increments of 1 psi we can pressurize the membrane to evenly apply force over the whole surface of the piston (a sketch of the DAC cell is shown in *Fig. 1*), which permits smooth and accurate control of the sample pressure. *Figure 2* shows a plot of a typical sample pressure measured using a standard in situ pressure calibrant, as a function of the He gas pressure of the membrane. The advantages of using a membrane for external heating are the precise pressure control and minimal perturbation of the cell to raise the sample pressure. When screws are used, there is always a noticeable thermal fluctuation caused by thermal contact of the drive mechanism, hand tool or gearbox, through the screws.

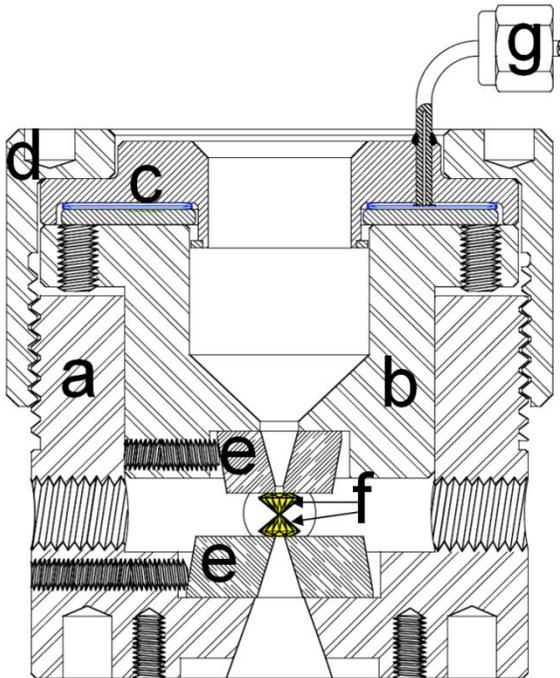


FIG. 1 Membrane Diamond Anvil Cell sketch. **a**-cylinder, **b**-piston, **c**-membrane, **d**-membrane cap, **e**-tungsten carbide seats, **f**-diamonds, **g**- gas (He) connector.

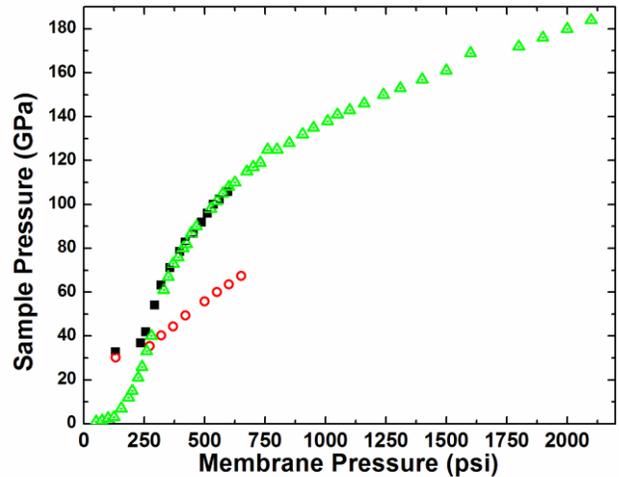


FIG. 2 A plot showing sample pressures as a function of He gas pressure in the membrane. solid black squares represent data measured using anvils of 300  $\mu\text{m}$  culet with 100  $\mu\text{m}$  bevel at 400  $^{\circ}\text{C}$ ; solid green triangles data measured at room temperature using the same size anvils and open red circles represent data measured using 300  $\mu\text{m}$  culet size anvils at 400  $^{\circ}\text{C}$ . W-Re alloy was used as a gasket and pre-indented to 24 GPa.

### The heaters:

The basic framework of the micro-heater is a ceramic ring made of aluminum oxide graded at the maximum working temperature at 1650 °C – with a diameter of 22 mm and a height of 4 mm to fit easily around the diamond anvils and between the anvil seats. A Pt-Rh alloy with a nominal melting temperature of 1850 °C, is used as a heating wire, which is spiraled inside of the ceramic ring as shown in *Fig. 3a*. The heater wire is covered with Cotronics RESBOND 920, a ceramic paste with high thermal conductivity (40 W/m )K. The result is a heater with a resistivity of about 1Ω. This is one of the 2 resistive heaters delivering 60-70% of the power for the sample heating. The heater is mounted on the “bottom” part of the cell – cylinder, see *Fig. 3b*.

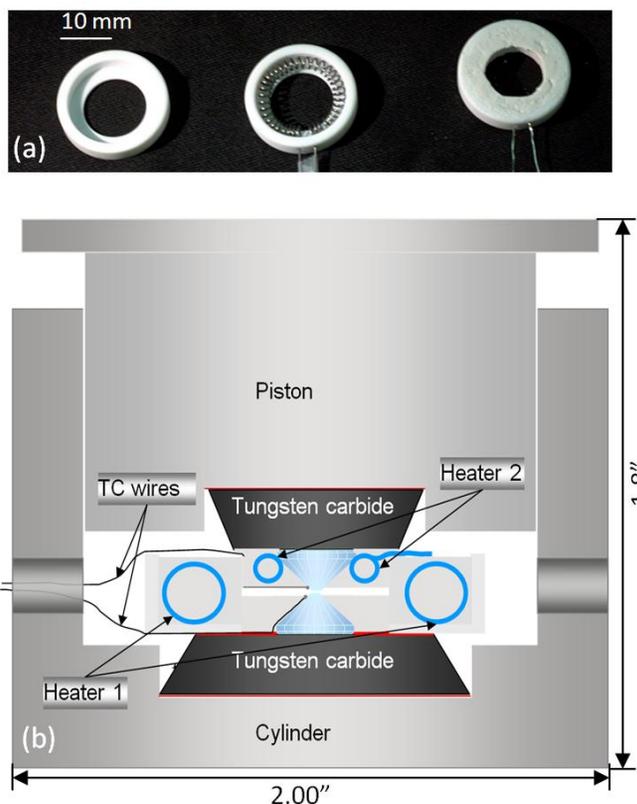


FIG. 3. a) from left to right: Al<sub>2</sub>O<sub>3</sub> based ceramic ring, the ring with the Pt-Rh heating wire in it, the finished heater; b) dual heater assembly

the thermocouple can be affixed to the anvil with high thermal conductivity ceramic paste that also serves as heat conductive medium between the diamond and the heater. On the piston side (smaller heater) the thermocouple is affixed onto the surface of the top diamond with thermally conductive ceramic paste. During experiments, we measured the difference between the two thermocouples to be less than 10 K at 900 K.

The second smaller heater is made using the same type of Pt-Rh alloy wire with smaller diameter. This is built around the “top” diamond – mounted on piston part of the cell – also using the RESBOND 920, both to attach and electrically insulate the wires from the seat. A thin, very low thermal conductivity layer is applied between the heater body and the seat to enhance the heating of the diamonds. This heater has a resistance of ~1.2Ω and is capable of delivering a maximum power of ~30W.

### Temperature readouts:

We use two K-type thermocouples mounted on the anvil pavilion and close to the tips of the diamond anvils to measure the temperature. To ensure good thermal contact between the thermocouple and the diamond, one of the thermocouples is mounted inside a copper disk that is pressed around the anvil. Alternatively,

## Assembly:

The mounting of the heaters is very simple and one of the advantages of this heater assembly is that they can be mounted in any type of DAC with an opening for the electrical connectors. However, the mDAC has a major advantage. It enables almost perfect isobaric conditions for temperatures varying from 300K to 1200 K, and it allows remote operation, which is useful at synchrotron x-ray facilities. Since the mDAC was the cell type we choose, we present the cell assembly specific to the mDAC.

One of the heaters is mounted on the cylinder part of the DAC (Fig. 3). To achieve the highest possible temperature it is very important to make the best possible thermal-coupling between the heater and the diamonds. We press 2mm thick copper disks on the diamond to ensure the best thermal contact possible, at the same time it is important for the disks not to touch the seat for two reasons: avoiding the grounding of the thermocouple and creating a thin air (vacuum) layer between to avoid heat loss via Cu-seat contact. To further avoid heat loss, a thin insulating layer of mica is placed between the diamond seat and the cell, and between the heater ring and the seat. The heater is then glued with aluminum-nitride based cement to the copper ring, once again the criteria for choosing the glue is stability at high temperatures and high thermal conductivity.

For practical purposes the copper disk can be replaced with high thermal conductivity ceramic paste, like the aluminum-nitride based one or even the Resbond 920, without noticeable decrease in the system performance below 1000 K.

## Vacuum chamber:

To prevent the oxidation of metal components of the cell, including the heater wire and gasket and to prevent graphitization of diamonds, the entire mDAC assembly is placed inside a vacuum chamber (Fig. 4.). The usual vacuum during operation was less than 0.5 mTorr. The cell mount in the jacket is fabricated using MACOR for low thermal conductivity, reducing heat loss to the vacuum jacket vessel through conduction. Pressure in the sample chamber is controlled by varying the pressure in the membrane through a thin feed-through connection. The chamber is about 10 cm long and made of stainless steel with a similar external diameter as can be seen on

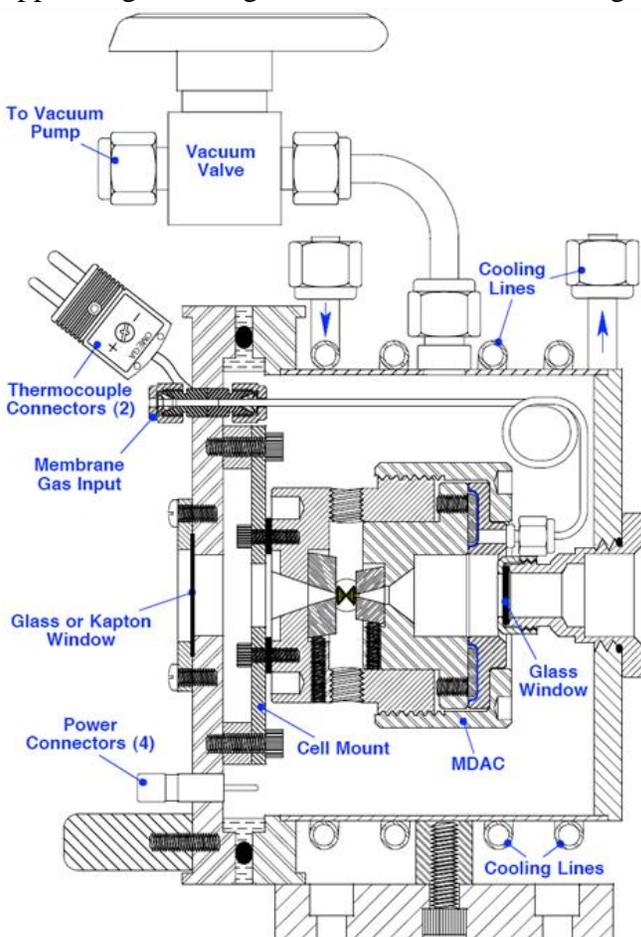


FIG. 4 A schematic drawing of the vacuum chamber with the mDAC mounted inside.

Fig. 4. The mDAC is mounted on the front flange of the jacket using thermally insulating mounts to minimize heat loss. The window materials can be selected and replaced for both Raman spectroscopy and X-Ray diffraction measurements. When a cell is in place, the distance between the sample and the bottom of the chamber mount is 7.8 cm. To avoid overheating of the front flange, a water-cooled ring can be mounted between the front flange and the jacket body, which would extend it to about 10 cm. For Raman measurements we use a glass window on the front flange, while for X-ray diffraction Kapton tape is used. At the back of the cell there is a small glass window added as an optically transparent window that also permits the x-ray clean-up slit to be placed as close as possible to the sample. This window is critical only in X-ray diffraction experiments, though it is very useful for backlighting transparent samples for visual observation.

The mica and vacuum thermal insulating layers, the compact design of the heaters and the enhanced thermal coupling between the elements of the setup helps to keep the temperature of the mDAC relatively low. At sample temperatures of 1200-1300 K, the temperature of the cell body does not exceeds 720-770 K. Thus no special modification of the DAC is required. In addition, the efficiency of this dual heater design is proven by the power consumption. It requires only 150 W to achieve a 1200 K sample temperature.

### III. APPLICATION:

For our experiments, a W-Re (75/25) alloy proved to be the most stable gasket material at high temperatures, holding sample to pressures exceeding 100 GPa and up to 1200 K. One reason is the thermal expansion of W-Re alloy ( $4.48 \mu\text{m}\cdot\text{m}^{-1}\text{K}^{-1}$ ) at high temperature is less than the thermal expansion coefficient of Re ( $6.2 \mu\text{m}\cdot\text{m}^{-1}\text{K}^{-1}$ ), yet it is not as brittle as W alone. However, for Raman experiments there is an issue at temperatures higher than 750 °C; the

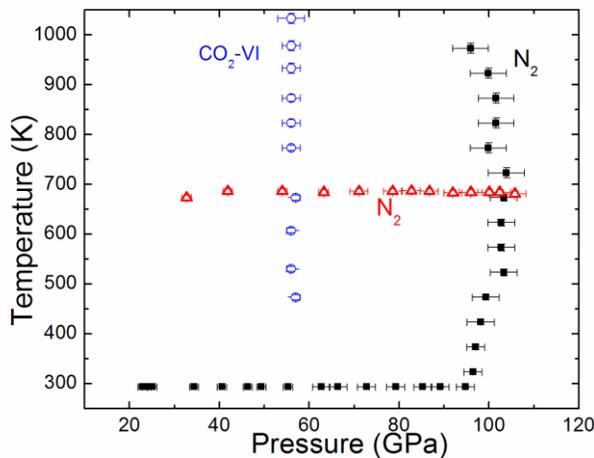


FIG. 5 A plot showing pressure and temperature conditions during experimental measurements: full squares represent P/T conditions for a quasi-isobar at  $\sim 95$  GPa for  $\text{N}_2$ , empty circles represent P/T conditions for an isobar experiment to higher than 1000 K of  $\text{CO}_2$  at around 56 GPa, half filled triangles are for an isothermal compression of  $\text{N}_2$  at around 700 K to  $>100$  GPa..

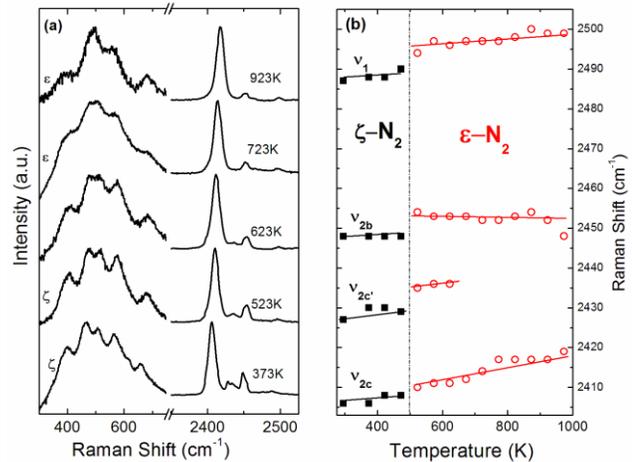


FIG. 6 A plot showing Raman data along the 95 GPa isobar of  $\text{N}_2$  a) Raman spectra of phonons and vibrons; b) Raman shift of nitrogen vibrons as a function of temperature at 95 GPa.

thermal background increases significantly and with the signal from a very thin sample weakening it becomes difficult to make accurate measurements.

We used our setup to study molecular systems at high pressures and temperatures using Raman spectroscopy for extended period of time – typical experiment length was 8-12 hours. In figure 5, we show data measured along isobars and isotherms. Each experiment lasted more than 8 hours. The full blue circles represent a temperature path of isobaric heating of phase VI of CO<sub>2</sub> (6), the full squares are temperature paths of isobaric heating of molecular nitrogen. We also performed *in-situ* measurements of different phases of nitrogen at high temperature (7). The experiment was done using the W-Re gasket material mentioned earlier with 100/300  $\mu\text{m}$  beveled diamonds. We did not see any evidence of formation of nitrides from Raman measurements. The samples were loaded placing the DAC in a vessel and filling the cell with liquefied ultra-high purity nitrogen gas at 50 psi at and  $\sim 80$  K. The initial dimensions of the sample chamber were  $\sim 50$   $\mu\text{m}$  in diameter and 15-18  $\mu\text{m}$  of initial gasket thickness. When the loaded sample was warmed to room temperature, the initial pressure was  $\sim 5$  GPa. Slowly raising the membrane gas (He) pressure, the sample pressure was increased to 95 GPa at 300 K. At each increment in pressure, Raman spectra of N<sub>2</sub> were recorded both in phonon and vibron region (not shown), the data at 300 K agrees very well with literature values (8). After reaching 95 GPa, we increased the temperature slowly, while keeping the membrane pressure constant. Along the 95 GPa isobar we collected Raman spectra of the sample in 50 K temperature steps. A few representative spectra are presented on Fig. 6(a) both the phonons and vibrons. Following the N<sub>2</sub> Raman shifts of the vibrons along the isobar (Fig. 6(b)), we see a discrete increase in the  $\nu_{2c}$ ,  $\nu_{2c'}$ ,  $\nu_{2b}$ ,  $\nu_1$ , frequencies at 525 K, and the disappearance of the  $\nu_{2c'}$  branch characteristic to the  $\zeta$  phase, the remaining peaks are characteristic of the  $\epsilon$ -N<sub>2</sub>. In the studied region we observe 2 different phases for nitrogen: one the initial  $\zeta$  phase that transforms to the  $\epsilon$ -phase which remains stable at 95 GPa up to at least 1000 K. Because our samples were very small and very thin the experimental time was quite long, extending for more than 8 hours, this demonstrates that our design is capable of sustaining extreme pressure/temperature conditions for lengthy experiments. We only present data for the isobaric heating. However, during our experiments on a large number of samples we managed to observe the non-molecular phase of nitrogen at pressures higher than 130 GPa and temperatures above 800 K.

#### IV. CONCLUSIONS:

In this paper we present our resistive heating technique, which uses a membrane driven DAC in a vacuum jacket. We used this system to explore the phase diagrams of CO<sub>2</sub> and N<sub>2</sub> above 1000 K at pressures over 100 GPa. Using this technique we were able to collect Raman spectra of weak scattering samples at high temperatures that required stability of the sample and conditions over long collection times. The technique is also suitable for synchrotron x-ray diffraction experiments. As an application of the technique we presented *in-situ* Raman spectra of molecular nitrogen up to 1000 K at 95 GPa. Finally, the setup was used to show the stability of CO<sub>2</sub> phase VI, six fold coordinated carbon dioxide up to at least 1200 K at 50 GPa. (6)

## V. ACKNOWLEDGEMENTS:

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