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Efficient graphite ring heater suitable for diamond-anvil cells to 1300 K

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In order to generate homogeneous high temperatures at high pressures, a ring-shaped graphite heater has been developed to resistively heat diamond-anvil cell (DAC) samples up to 1300 K. By putting the heater in direct contact with the diamond anvils, this graphite heater design features the following advantages: (1) efficient heating: sample can be heated to 1300 K while the DAC body temperature remains less than 800 K, eliminating the requirement of a special alloy for the DAC; (2) compact design: the sample can be analyzed with in situ measurements, e.g., x-ray, optical, and electrical probes are possible. In particular, the side access of the heater allows for radial x-ray diffraction (XRD) measurements in addition to traditional axial XRD.

I. INTRODUCTION

The generation of homogeneous high temperatures at static high pressures has been a great challenge over the past several decades.1,2 The multi-anvil press has earned its reputation in achieving homogeneous high temperatures up to 3000 K,3 yet is routinely limited to pressures <28 GPa, although remarkable efforts have gone up to 50 GPa.4 Breakthroughs in diamond-anvil cell (DAC) technology have led to high temperatures at ultrahigh pressures.5,6 In combination with laser heating, temperatures >1500 K and pressures >100 GPa have been achieved in DACs, however, temperature gradients can be extreme.1,7,8 Much of the recent progress has been to minimize large temperature gradients (>100 K/μm) inherent in the laser-heated DAC,2,9 including heating from both sides, adjusting the laser into multimode,2 and flat-top laser geometry,10 thus achieving a more uniform sample heating (<20 K/μm). However, the small uniformly heated spot (typically <30 μm, although in principle could be as large as 50 μm) still imposes great difficulty for many applications: e.g., elemental partitioning,9 high-temperature elasticity,11–13 high-temperature rheology,14 and melt structure.15 Meanwhile, internal resistive heating has made striking progress16–19 to achieve stable, homogeneous temperatures greater than 2000 K up to 70 GPa, yet in practice, intensive and difficult sample loading procedures discourage wider applications.

In contrast to laser heating, external resistive heating around the diamond anvils provide homogeneous heating in the sample region under high pressure.20 Most resistively heated DACs employ coiled resistive wire heater assemblies in a cavity surrounding the diamond anvils,21–24 including commercial ones designed by EasyLab or Beta. These heaters are limited to temperatures less than 900 K due to inefficient radiative heating since there is no direct contact between the diamond and heater. Many designs have subsequently been proposed to extend the temperatures up to 1500 K, but are limited to either pressures under 10 GPa,20,25 require a special alloy for the DAC body,26,27 a complex heating assemblage,24,28–34 or are restricted to a particular DAC design (e.g., HeliosDAC by EasyLab). In addition, only a few heaters30,35 allow access for radial XRD measurements.

In this study, we modify a previous design employing graphite foils30,31 with a ring-shaped graphite heater (Fig. 1(a)). We have successfully generated temperatures up to ~1300 K at a pressure of ~50 GPa. This technique will open doors to studying material properties, particularly melting, transport, and elasticity at high temperatures and pressures. To assess the new design, we have tested calibrated materials at both room pressure and high pressure as well as confirmed the melting curve of H2O water ice VII up to 23 GPa.

II. HIGH-PRESSURE, HIGH-TEMPERATURE SYSTEM

Graphite is an ideal material to use for heating as it is a good thermal and electrical conductor with conductivities of ~100 W/(m·K) and ~105 S/m, respectively. Additionally, graphite can be either soft and flexible or hard and machinable. As the anvils are diamond, we also take advantage of diamond’s thermal and electrical conducting qualities: diamonds conduct heat well (>1000 W/(m·K)), however, are good electrical insulators (~10−13 S/m).

The central part of this design which makes it unique and efficient, is the direct coupling of a machined, ring-shaped graphite heater that fits over the tip of each anvil, approximately 0.7 mm from the culet (Fig. 1). The cone-shaped ring heater (3.5 mm OD, 2 mm ID, 0.8 mm thick) is machined from a 4.7 mm rod of EC-16 grade graphite (http://www.graphitestore.com/) and is cut such that it fits directly on to the pavilion of the anvil. The diamond anvil is affixed on the tungsten carbide (WC) seat with a high-working temperature graphite adhesive (Graphi-bond 551RN). Subsequently, the heater is affixed onto the diamond with an electrically insulating MgO-based adhesive (Ceramabond 571). Early tests show that the cone shape of the ring heater fits...
nicely on a 16-sided culet faceted pavilion without much efficiency lost as compared to a smooth (unfaceted) pavilion. To apply the current to the ring heater, a piece of soft, malleable graphite foil $\sim 1.4$ mm in thickness (Alfa Aesar, 99.8% pure, metals basis) is placed at an end of two machine-notched molybdenum rods. The soft nature of the graphite foil molds itself in between the two ring heaters and allows a single current to be applied to each ring heater allowing for even heating of the sample with a single power supply. More importantly, the pressed graphite foils provide the graphite heaters with good contact on the diamonds at high temperature, which is essential for efficient heating of the sample. Two type-R thermocouples (TC) are cemented onto the pavilion of the diamond to measure temperature.

The heating assembly is integrated with a modified symmetric DAC (Princeton University Machine Shop) (Fig. 2), an OmniDAC (EasyLab), and a panoramic DAC (Syntek), although the design can be easily substituted into a DAC of choice once a few minor modifications are made. To allow for the addition of the two Mo rods that supply current and thermocouple leads, two cuts, performed by electric discharge machining (EDM), are made into the piston of the symmetric DAC as shown in Fig. 2. We have not observed a decrease in the performance or the overall alignment of the DAC from the EDM cuts.

A stainless steel gas membrane can is machined to support and align the Mo rods to the center of the sample region. The membrane can also seal argon with 1% hydrogen ($\text{Ar} + 1\% \text{H}_2$) or pure Ar gas to prevent the whole cell assembly (e.g., DAC, heater, and anvils) from oxidation or graphitization. The inflatable gas membrane is used to smoothly control the sample pressure at high temperatures, bypassing the usual mode of screws for compression (Fig. 2). The membrane can is subsequently mounted into a water-cooling jacket (not shown) during the heating experiments, which turns out to be essential in keeping the temperature of the DAC body $<800$ K, thus negating the need for special high-temperature alloys.

III. TEMPERATURE CALIBRATION AT AMBIENT PRESSURE

To test the efficiency of the ring-shaped graphite heater, a series of experiments are conducted at ambient pressure up to a temperature of $\sim 1300$ K. A type-R thermocouple junction is placed between the two diamond anvils to measure temperature of the diamond culets. In addition, another type-R thermocouple is cemented to the pavilion of one diamond anvil.
within 0.3 mm from the culet, and this agrees with the temperature of the diamond culets to within 10 K up to 700 K, after which it falls off the anvil and thus is no longer able to measure a valid temperature. The temperature of one of the diamond’s table and tungsten carbide seat is also measured by inserting a type-K thermocouple at the back of the cell during heating.

In separate experiments, standards of Au foil and NaCl powder are loaded into a Re gasket, and heated under ambient pressure, and the melting temperatures measured. Melting is observed visually when the standards turned into spherical droplets as observed by optical microscopy. Temperature versus power curves are shown in Fig. 3 and show a nice linear relationship between the experiments, suggesting excellent reproducibility. Diamond culets are heated to $\sim 1300$ K with a modest power input of 300 W. Meanwhile the temperature of the WC seats in contact with the DAC, and thus the highest temperature of the DAC body itself, does not exceed 800 K. The exterior of the DAC does not reach a temperature greater than 500 K at the highest temperatures in this study, provided it is water-cooled.

To attain these high temperatures, it takes $\sim 10$–$15$ min to reach a steady-state temperature. By changing the electric power (or current), the temperature is increased from, for example, 800 K to 900 K continuously and steadily. The same is true for decreasing temperatures as well. Once the steady state temperature is reached, the temperature fluctuates to within a few degrees. In addition, this temperature-power calibration is reproducible to within 5% after a change of one or both ring heaters as long as the heater dimensions are the same. If the heaters are not changed and only a reapplication of glue/epoxy occurs (due to loosening at temperatures $> 900$ K), the temperature-power calibration remains the same to within our measurement uncertainties.

Despite the high temperatures and long heating durations, we have not observed degradation of the graphite heater or graphitization of the diamond anvils during our experimental runs provided we supplied sufficient Ar or Ar + 1% H$_2$ gas, including 2 h of heating at 1300 K and over 10 h of heating at 800 K at pressure. Outside of the DAC, the heater continues to perform well: we held the temperature at 2000 K, as measured by spectroradiometry, in a sealed chamber flushed with pure Ar gas or Ar + 1% H$_2$ for 2 h. The heater temperature remained stable during these tests and did not exhibit any noticeable degradation after heating. In fact, the only time we observed severe degradation of the heater was when the temperature exceeded 2500 K after 1 h of heating.

### IV. APPLICATIONS

#### A. Melting of H$_2$O ice

To test the new design at high pressures, we measured the melting curve of water ice VII up to 23 GPa (Fig. 4). We loaded deionized water into a Re gasket or gold-lined Re gasket, reloading the water sample and gasket for each melting point measurement. Ruby spheres were used as pressure calibrant as well as a motion detector. Melting is detected by visual observation either by disappearance of ice crystals or sudden movement of the ruby sphere. Melting points are measured up to 23 GPa, and are in good agreement with previous measurements using similar techniques.

#### B. In situ high-pressure and high-temperature synchrotron XRD experiments

In order to measure the pressure simultaneously at high temperature, we performed XRD experiments at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. Diamond anvils with 300 $\mu$m culets were used in this experiment. MgO powder (Alfa Aesar, 99.9%, metal basis) was loaded into 100 $\mu$m diameter sample chamber, which was drilled through a Re gasket preindent to 30 $\mu$m. A piece
of Au foil (Alfa Aesar, 99.9%, metal basis), 20 μm × 20 μm × 5 μm in dimension, was loaded as a high-temperature pressure calibrant. X-ray diffraction patterns were taken at each increment of pressure and temperature at steady state. As shown in Fig. 5, Au and MgO peaks are clearly resolved at high pressure and high temperature. Subsequently, pressure was calculated based on thermal equation of state of Au. As shown in Fig. 6, while maintaining the gas membrane pressure, the pressure of the sample remains nearly constant at ~46 GPa up to 1000 K and gradually increases to ~51 GPa at 1300 K. We held the temperature and pressure constant for an hour at 1300 K before further increasing the temperature. As we increased the temperature to 1350 K, the pressure dropped to 37 GPa and subsequently both diamond anvils failed.

V. DISCUSSION

From a practical standpoint, it is convenient to put together the ring-shaped graphite heater assembly. For experiments at temperatures below 800 K, the whole cell assembly remains intact and can be reloaded with different samples repeatedly. However, for experiments at temperatures greater than ~900 K, the diamond anvils loosen upon decompression thus it is necessary to realign and reaffix the anvils, reaffix the graphite heaters and thermocouples for subsequent experiments, but the rest of cell assembly, e.g., Mo electrodes, graphite foils are still in place and reusable. This is in contrast to previous graphite heater designs, in which the heater can only be used once. Additionally, we do not observe a significant increase in pressure as temperature is increased, at least up to 1300 K (Fig. 6) as has been reported previously. This may be due to smaller temperature gradients outside of the sample chamber or due to the steady gas membrane control applying the force on the DAC.

Thermocouples on the pavilion of diamonds are recommended to measure sample temperatures precisely, however, we also found that the culet temperature-power curve (e.g., Fig. 3) is reproducible to within 5% when steady state is reached, usually within ~10 min. Therefore, a thermocouple may not be necessary, once a reliable temperature-power curve is measured for a given heating assembly, which makes sample preparation even easier.

The gap between the two graphite heaters (Fig. 1) is large enough to allow x-rays to pass through, providing the opportunity for radial XRD measurement at high temperatures. Additionally, any other standard techniques, including axial XRD, can also be used with this design.

In several of our runs to test the limit of the current design, in addition to the run shown in Fig. 6, we did not experience gasket blowouts until temperatures exceeded 1300 K at pressure ~50 GPa. Therefore, we indentify the temperature limit as 1300 K at high pressures. The pressure limit remains to be explored and extended in future experiments.

Despite the efficiency and ease of use of the current design, there are some limitations. First, strength of the WC seat is significantly reduced at high temperatures and eventually the strength vanishes at its eutectic melting point at ~1500 K. Second, Re gaskets (and metallic gaskets in general) may become too weak to support the diamond anvils at high temperatures. Third, the diamond anvils also become more ductile at increasingly high temperatures and might eventually limit our maximum pressure and temperature range.

In order to achieve higher temperatures (>1300 K) at high pressures, cubic boron nitride gaskets are essential over metallic gaskets (e.g., Re, W) given its extreme high strength and chemical inertness, even at the extreme conditions. As for anvil materials, nanopolycrystalline diamond (NPD) may be an ideal solution for external heating. With an order of magnitude lower thermal conductivity than single-crystal diamond, this difference will further build up the temperature difference between the diamond culet and WC seat (Fig. 3), thereby allowing for higher sample temperatures. Moreover, NPD retains its high strength at high temperatures.

FIG. 5. X-ray diffraction patterns of a sample of Au and MgO before (thin line) and during heating (thick line) at high pressures. The hkl’s of both Au and MgO are noted.

FIG. 6. Pressure-temperature path of Au/MgO sample during heating. At the highest temperature of 1300 K, a pressure of ~51 GPa was reached and held constant for 1 h. The dashed line through the data points is a guide for the eye.
temperature. Additionally, this external heating can be coupled with laser heating to provide bigger and more uniform hot spots.

VI. CONCLUSION

We designed a compact and efficient heater that can be used with most DAC designs with minimal modifications. The design is unique in the use of direct coupling of a ring shaped graphite heater to the diamond anvil thus yielding efficient, reproducible, and reusable heating. Additionally, the compact nature provides easy access for both radial and axial XRD, electrical leads, and the ability to fit into many synchrotron beamlines and spectroscopic setups.

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