High-temperature diamond-anvil pressure cell for single-crystal studies

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The miniature, single-crystal, diamond-anvil pressure cell of Merrill and Bassett [Rev. Sci. Instrum. **45**, 290 (1974)] has been adapted for x-ray crystallographic studies at sustained temperature and pressures up to 450 °C at 30 kbar.

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INTRODUCTION

Crystallographic studies under nonambient conditions are essential to an understanding of the solid state. A knowledge of atomic structures at high temperature and pressure is especially crucial to realistic modeling of geological processes. Advances in high-temperature crystallography at room pressure and in high-pressure crystallography at room temperature[1] have been rapid and encouraging. Simultaneous application of high temperature and pressure to a single crystal in an x-ray diffraction experiment, however, has proved to be more difficult. The only published report of such a study is by Fourme,[2] who designed a pressure cell that could sustain a temperature of 250 °C on a specially modified precession camera. Fourme's device is not generally adaptable to other single-crystal x-ray equipment.

The major experimental difficulties that must be overcome in a high-temperature, high-pressure, single-crystal experiment include the following:

(1) The crystal must remain in a fixed orientation with respect to the high-pressure cell in order to maintain crystal alignment.

(2) The crystal must be in a hydrostatic environment to prevent nonhydrostatic crystal strain.

(3) The crystal must be heated as uniformly and to as high a temperature as possible without heating the x-ray diffraction equipment significantly above room temperature.

(4) The cell must be easily adapted to standard, single-crystal x-ray devices, including precession cameras and four-circle diffractometers.

(5) A procedure for calibrating both temperature and pressure of the sample is essential.

This report presents plans for construction and operational procedures for a simple and relatively inexpensive, high-temperature, diamond-anvil high-pressure cell (hereafter referred to as the *PT* cell) that meets all the above criteria.

I. CONSTRUCTION OF THE *PT* CELL

The following design is based on the widely used high-pressure, single-crystal x-ray cell of Merrill and Bassett.[3,4] The cell consists of five major components: triangular steel supports, boron carbide disks, pyrophyllite insulating rings, a resistance heater, and two gem-quality diamond anvils. Each of these components is described below.

A. Triangular steel supports

Triangular steel supports are identical with those used in the modified Merrill and Bassett cell described by Hazen and Finger,[4] as illustrated in Fig. 1. These two supports act as the framework that holds the diamonds rigidly together in proper alignment. Any type of stainless steel may be used in the construction of these pieces; the prototype cell was machined from a type-303 stainless steel rod. A critical aspect of these supports is the precise alignment of the three guide pins. The two triangular pieces should be parallel and should fit smoothly without binding so that the cell may be assembled easily and the diamonds remain in proper alignment.

B. Boron carbide disks

Disks [Fig. 2(A)] of boron carbide ("Norbide," Norton Company, Industrial Ceramics Division, Worcester, Massachusetts) are ground from Norbide 0.25-in-thick plate stock. These disks are used in place of the beryllium disks in the room-temperature cell because of the softening of Be metal at temperatures above 100 °C. Unlike the Be disks in room-temperature experiments, there are no holes in the center of the disks, and there is no optical access to the sample chamber. This restriction is necessitated because boron carbide, which has a lower tensile strength than Be, is further weakened by the presence of a hole. Boron carbide disks with holes cannot support the diamonds to as high a pressure as disks without holes.

C. Diamond anvils

The two diamond anvils are identical with those used in the room-temperature device. Each diamond is approximately 10 points (1/10 carat) in weight, with an anvil face of 0.5–1.0 mm in diameter. The diamonds should have no flaws, though less expensive yellow diamonds are satisfactory.

The greatest restriction on the temperature range of the diamond cell is the thermal instability of diamonds

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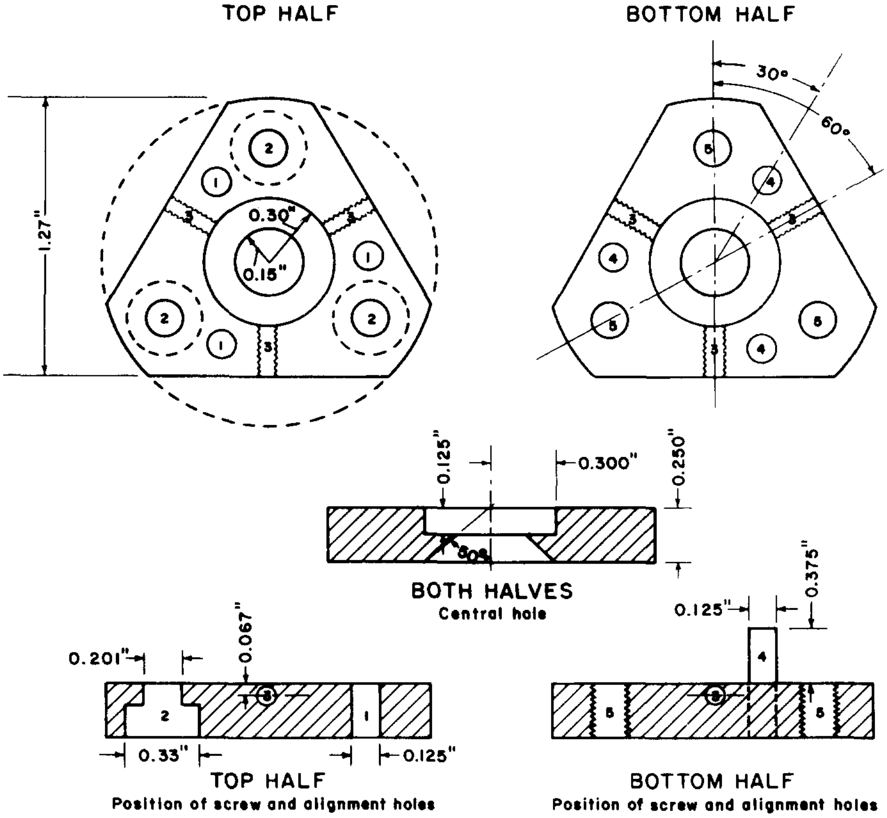

FIG. 1. Triangular steel supports. Both halves have three-fold symmetry. (1) 0.318 cm hole for guide pin. (2) Well for Allen cap screws; i.d. = 0.51 cm, o.d. = 0.84 cm. (3) Tap for No. 3-48 screw. (4) Guide pin, 0.318 cm diameter. (5) Tap for No. 10-32 screw.

themselves. At approximately 700 °C diamonds oxidize in air, and at temperatures as low as 800 °C in an inert atmosphere they graphitize (H. K. Mao, personal communication). If temperatures much above 600 °C are desired, then an alternative anvil material may be required.

Lasers have been employed successfully in heating polycrystalline samples in diamond-anvil pressure cells to 3000 °C.[5] Diamonds are transparent to the light energy of the laser, whereas the powdered sample is made absorbent by mixing black material. Laser heating cannot be applied to a single-crystal experiment, however, because of difficulties in maintaining a uniform temperature in the sample while varying the orientation of the pressure cell.

D. The resistance heater

A miniature resistance element is used to concentrate heat at the sample without excessive heating of the surrounding instrumentation. In this device a resistance heater of 0.32-cm diameter is placed around the diamonds and the gasketed sample. The heating element is a 0.033-mm-diam. platinum–platinum-10-rhodium thermocouple wire with the junction in the center of the four-loop winding (Fig. 3). The furnace is operated in the manner described by Ohashi and Hadidiacos[6] in which power is applied to the winding during half of the cycle of the alternating current power source. The electromotive force of the thermocouple junction is sensed during the other half of the cycle and is thus used to to control power to the furnace.

The winding is supported by a pyrophyllite ring (Fig. 3) in which the wire is mounted by Sauereisen high-temperature ceramic cement (Sauereisen Cements Company, Pittsburgh, PA). Both the Pt and Pt10Rh leads are doubled and exit the cell in a four-hole ceramic tube. These wires are redoubled and connected to copper-alloy, thermocouple-compensating extension wires, which serve as the power leads. The single-strand heating element thus occurs only in the vicinity of the sample. The entire heating element—consisting of the four-loop winding, doubled and redoubled leads, pyrophyllite ring support, and ceramic tubing—is a self-contained assembly that is removable from the pressure cell.

E. Pyrophyllite insulating rings

Two pyrophyllite rings fit around the boron carbide disks and the heating element to add thermal insula-

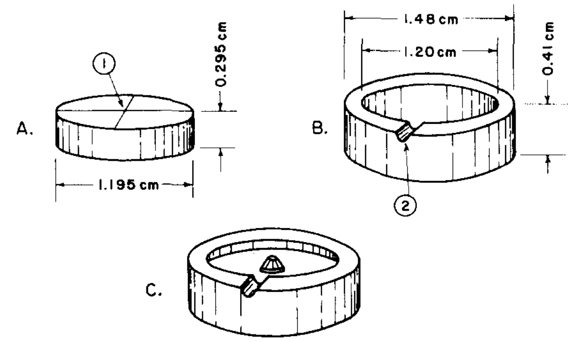

FIG. 2. Diamond anvil assembly. (A) The boron carbide disk; *1* is an inscribed point to aid in diamond centering. (B) The pyrophyllite insulating ring; *2* is a semicylindrical slot for 1.6-mm-diam. ceramic tubing. (C) Diamond anvil assembly.

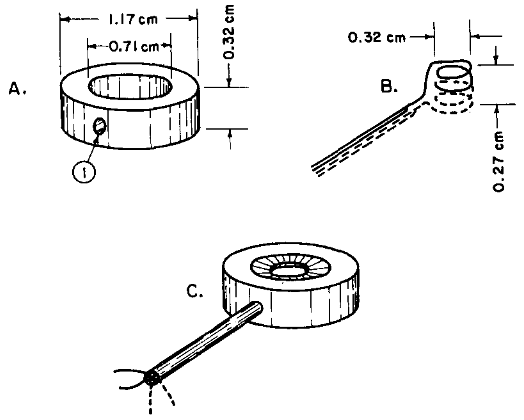

FIG. 3. Resistance heater assembly. (A) The pyrophyllite support; *1* is a hole for 1.6-mm-diam. four-wire ceramic tubing. (B) The winding is made of 0.033-mm-diam. wire, four turns at 19 turns per centimeter. Solid line is Pt; dashed line is Pt10Rh. (C) The assembled heater; Sauereisen cement holds the winding in place.

tion to the cell [Fig. 2(B)]. After they are machined, these pieces are hardened by firing at 800 °C for 2 h in a nitrogen atmosphere.

F. Other components

In addition to the five major components described above, the following pieces are required for assembly of the *PT* cell:

(1) Two mica-sheet insulating washers (0.25 mm thick; i.d. = 0.85 cm; o.d. = 1.34 cm) fit into the circular wells of the triangular supports to provide additional thermal insulation.

(2) Three Allen Cap screws 2.0 cm long are used to clamp the two halves of the cell together.

(3) Two Belleville spring washers (Fig. 4) 0.9 cm in diameter are inserted next to each of the three screw heads. These washers are important in applying force to the diamonds. Without these washers, which are outside the triangular supports and thus cooler than other cell components, the three screws relax owing to heating at high temperature, and the pressure is reduced.

(4) A metal gasket 2.5 mm in diameter is constructed from Inconel 750X foil (International Nickel Company) 250 μm thick. The gasket hole is approximately 300 μm in diameter. This cylindrical hole, which is closed at either end by the two diamonds, defines the size and shape of the sample chamber.

II. ASSEMBLY OF THE *PT* CELL

The assembly of the *PT* cell is illustrated in Fig. 4. Each diamond is mounted at the center of a boron carbide disk with an epoxy-type cement. The diamonds should be flat against the polished disk surfaces to ensure that anvil faces are parallel in the assembled cell. The disks plus diamonds are placed inside the two insulating pyrophyllite rings [Fig. 2(C)], which are in turn placed in the circular wells of the triangular steel supports. The three set screws that hold the disks in place (Fig. 1, circle 3) should be adjusted so that the two diamond anvil faces are parallel and concentric when the two halves of the cell are placed together. Each half of the *PT* cell is then further insulated by applying Sauereisen high-temperature cement to spaces around the pyrophyllite rings. The gasket hole is centered over the lower diamond and secured to it by a small dot of epoxy cement. The heater assembly is placed around the diamond and gasket of the lower cell half and is fastened to the insulating pyrophyllite disk with Sauereisen cement. The single-crystal to be studied may now be loaded.

The single crystal is mounted in the center of the gasket hole with a small amount of silicone vacuum grease as "glue." This grease keeps the crystal in a near-constant orientation with changes in temperature and pressure, yet does not cause crystal strain as observed in stronger glues such as epoxy-type cements. The gasket hole is filled with a pressure fluid, and the two halves of the cell are closed together. In high-temperature experiments to 30 kbar, Cargill index of refraction oil (R. P. Cargill Laboratories Inc., Cedar Grove, NJ) has proved a satisfactory pressure medium. This liquid neither evaporates because of heat nor becomes too rigid owing to pressure under the conditions tested to date.

The fully assembled *PT* cell may be attached to a modified goniometer head[4] and used on both single-crystal cameras and four-circle diffractometers. The

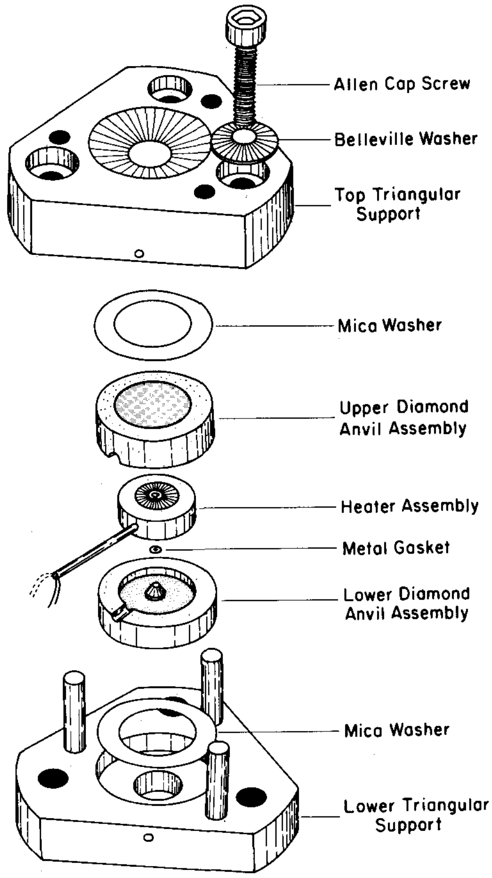

FIG. 4. Exploded view of the *PT* cell assembly. Pyrophyllite components are stippled. See also Figs. 1–3.

goniometer cradle for the *PT* cell was constructed from pyrophyllite that was then fired in nitrogen at 1100 °C for 12 h. This cradle is a good thermal insulator compared with the standard metal support.

The *PT* cell, when assembled, is similar in appearance (except for power leads) to the room-temperature cells illustrated previously.[3,4]

III. OPERATION OF THE *PT* CELL

A. X-ray photography

The *PT* cell is used in much the same way as the room-temperature device. The cell fits on a standard precession camera; only the beam stop needs to be modified to fit around the assembly. As in the cell with beryllium disks, MoKα radiation should be used owing to high absorption of longer wavelengths. Major diffraction effects on x-ray films include diamond streaks, boron carbide powder rings, and sharp diffraction maxima from the single crystal under study (Fig. 5).

B. Four-circle diffractometry

Operational procedures for the *PT* cell are much the same as those for the room-temperature cell.[7–9] The most important difference is that provisions must be made in the automation routines to prevent the twisting, and consequent binding, of the power leads. A second difference is that without optical access to the sample the crystal must be centered in the beam using the procedures outlined by King and Finger,[8] by which eight equivalent orientations of a given reflection (i.e., four at $+2\theta$ and four at -2θ) are measured. As in room-temperature diamond-cell experiments, the measured intensity data must be corrected for absorption by boron carbide and diamond components of the cell, as well as the crystal itself.[7]

C. Calibration of temperature and pressure

The temperature controller is calibrated for each different heating assembly at room pressure by mounting a reference crystal in the gasket hole with no pressure medium. The thermocouple reading at several temperatures is calibrated against the known thermal expansion of the reference crystal. The prototype cell was calibrated against the expansion of NaCl, MgO, and CaF_2. All three calibrations agreed within ±5 °C at temperatures to 450 °C, the highest temperature attempted. The temperature of subsequent experiments is set by presetting the feedback controller to the desired thermocouple electromotive force.

Pressure at high temperature is estimated by measuring the cubic cell edge of CaF_2. Calcium fluoride is an excellent x-ray scatterer and forms flat triangular (111) cleavage plates that remain parallel to one diamond face. This calibration crystal, which is mounted in each run, thus provides an internal standard. The equation of state of CaF_2 at high temperature and pressure is well known. The unit-cell edge of calcium fluoride at a known temperature provides a precise pressure calibration.[10] The unit–cell edge of calcium fluoride may be measured to better than 1 part in 5000 on a four-circle diffractometer if the procedures of King and Finger[8] are followed. The implied precision of pressure calibration ($\Delta V/V = 0.0005$) is ±0.5 kbar.

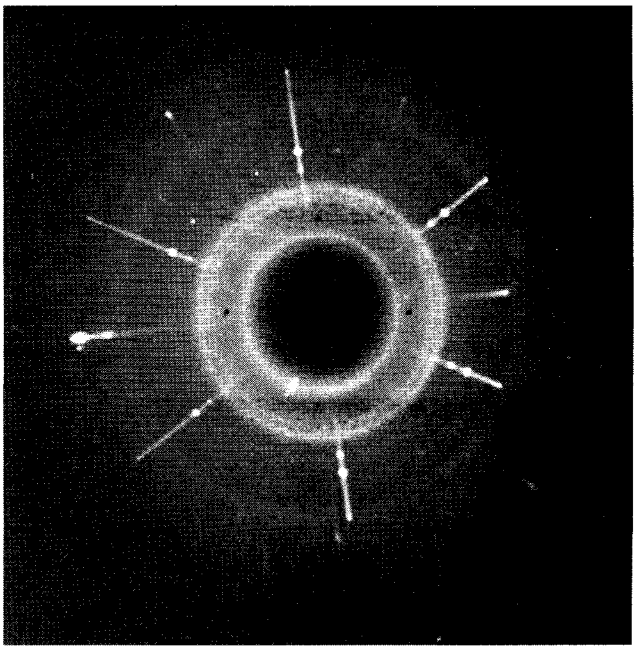

FIG. 5. Orientation photograph of a crystal of calcium fluoride (cubic) in the *PT* cell. Diffraction effects include strong, diffuse streaks from the diamond anvils, boron carbide powder rings, and sharp diffraction maxima from the CaF_2 crystal, which is oriented with (111), the three-fold axis of symmetry, perpendicular to the anvil faces. The photograph was taken with Mo white radiation, 45 kV, 15 mA, 30 min exposure, Polaroid type-57 film.

IV. APPLICATIONS

The *PT* cell may be used for a wide variety of x-ray diffraction studies of crystals. Of great interest are crystal structures of minerals at the elevated temperatures and pressures of formation. The highest sustained temperature (450 °C) and pressure (40 kbar) correspond to depths within the earth of approximately 30 and 120 km, respectively. Conditions within much of the earth's crust, as well as pressures to well within the upper mantle, are now reproducible in single-crystal experiments.

The *PT* cell is valuable for studying the many reversible phase transitions that are nonquenchable. Changes in symmetry associated with these transitions may be easily mapped as a function of temperature and pressure with either x-ray photography or diffractometry. Furthermore, details of symmetry and atomic positional changes can be determined for the high-temperature and -pressure phases that were previously inaccessible to single-crystal techniques.

The *PT* cell will be employed extensively in equation-of-state studies for both minerals and materials that are fluid under ambient conditions. Of special interest are the equations of state of methane, ammonia, and other crystallized gases that compose a large volume of the Jovian planets. Recent experiments at the Geophysical Laboratory[11] have demonstrated that these gases, as well as the inert gases, when solidified, form single crystals in the diamond-anvil pressure cell. These crystals are excellent for unit-cell and structure determination. The extension of this work to high temperature and pressure will greatly enhance understanding of the structure and bonding in these extremely soft solids.

In summary, the *PT* cell may be used to study routinely high temperatures and pressures as variables in crystal-chemical studies of structure and bonding.

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