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The moissanite anvil cell: a new tool for high-pressure research

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Abstract

Use of high-quality single-crystal moissanite as anvils has made possible a versatile high-pressure apparatus complementary to the diamond anvil cell (DAC) for high-pressure studies to at least the half-megabar pressure range. High-pressure research has been revolutionized by the DACs as a result of the great strength and transparency of diamond. However, the technique often suffers from interference by the diamond spectra and is limited by small anvil sizes. Other gem anvils, such as sapphire and cubic zirconia, have not been able to reach beyond 26 GPa. With gem-quality synthetic moissanite as anvils, we pressurized samples to close to 60 GPa. Moissanite anvils can be made two to three orders of magnitude larger than conventional diamonds, thus providing new opportunities for studies of material properties at high pressures with analytical techniques that are limited to small samples.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

High-pressure research has undergone explosive growth during the past two decades as a result of the development of new high-pressure devices [1–11]. Advances in diamond anvil cell (DAC) methods have pushed high-pressure research into the megabar pressure range [2–4], revealing rich phenomena in materials [5]. Deformation of the diamond anvil at high pressure [6] sets a limit on the pressure, and the small sample volume rules out certain types of study (e.g., neutron diffraction) at very high pressures. Multi-anvil devices, employing tungsten carbide anvils, can accommodate much larger sample volumes than DACs but are limited to pressures below 30 GPa [7]. The maximum pressure has been extended to 35–37 GPa with sintered diamond anvils [8].

To combine the highest pressures possible with larger sample volumes, a different approach is needed, one that dictates the use of harder materials as anvils. In previous attempts with cubic zirconia and sapphire anvil cells, pressures of only 16.7 and 25.8 GPa, respectively, could be reached [9, 10]. Recently, synthetic single-crystal moissanite (SiC) has been introduced as a new type of synthetic gem crystal [11]. Its high hardness (Knoop scale 3000, compared with 2000 for sapphire and 1500 for cubic zirconia) and excellent optical properties (e.g., transparent to visible light) makes it an ideal candidate for use as an anvil material. The moissanite anvil provides the possibility of fabricating large anvil devices (for example, on the order of one inch), since high-quality large crystals can be grown by synthetic techniques. Using these cells, we have recently passed the half-megabar mark [1], making the moissanite anvil cell (MAC) an ideal device for producing high pressures on relatively large sample volumes.

In contrast to diamond and other gemstones, moissanite has many polytypes (up to 150) [12] characterized by different stacking sequences of close-packed (hexagonal) layers A, B, and C. The most common type is 6H (stacking sequence ABCACB); most of the available large single crystals are essentially pure 6H. It is stable at temperatures to 1700 °C in air and 2000 °C in vacuum (in comparison, the diamond is stable to ∼700 and 1700 °C, respectively, under these conditions). A moissanite anvil was heated to 1100 °C in air for 36 h without damage, and temperatures close to 4000 °C have been reached in laser heating experiments [1, 13]. Recently, an *in situ* x-ray diffraction study on moissanite powder at 20 GPa up to 1300 °C was performed, and no phase transition was detected [18]. However, the transformation between 6H to other polytypes is still possible at certain high-P–T conditions. The instability of 6H might be a limitation of MAC studies at extreme pressures and temperatures.

A cone-cut method for anvil fabrication has been developed during the course of this work. It differs from the traditional 8- or 16-sided facet-cut, brilliant-cut, or other similarly cut stones generally in use with diamond and other gem anvils. Using this cone-cut method, the culet of moissanite anvils can be fashioned to a near circle. A systematic study, however, with differently cut (cone and facet) anvils would be useful to compare their relative performance. More importantly, the cone-cut method opens a way to strengthen the anvil itself by using traditional confinement rings. Preliminary results are encouraging: 38.5 GPa was achieved with 0.5 mm culet anvils, and 30 GPa with 1.00 mm anvils. Here we report experimental applications of the MAC performed at the Geophysical Laboratory during the past two years.

2. Spectroscopy and x-ray diffraction

Spectroscopic measurements were performed with conventional Mao–Bell cells using micro-optical spectrometer systems [3, 4, 14, 15]. The excitation radiation normally was the 514.5 nm line of a Coherent Innova 90C Ar-ion laser at a power in the region of 150 mW.

In the experiment that reached the highest pressures, an anvil with a 300 μm culet without a bevel and a bevelled anvil with a 300 μm culet and a 10° bevel 100 μm in diameter were mounted in a conventional Mao–Bell cell. The gasket was made from a T301 stainless steel sheet of original thickness of 320 μm. It was pressurized to 10 GPa, resulting in about 80 μm indented thickness. Ruby powder (<1 μm in size) was spread on the surface of the gasket placed between the two anvils. The R_1 and R_2 ruby fluorescence peaks were recorded to determine the pressure [14, 15]. The highest pressure reached was 52.1 GPa [1]; this appears to be the highest calibrated static pressure generated in a high-pressure device without the use of diamond. Recently, a pair of bevelled anvils (150 μm culet and 10° bevel with a 50 μm diameter plate) was used to achieve a higher pressure of 58.7 GPa. Representative ruby fluorescence spectra are plotted in figure 1. One of the moissanite anvils broke when the pressure was increased further. The observations of a non-damaged anvil at such a pressure indicates that higher pressure is still possible for moissanite anvils.

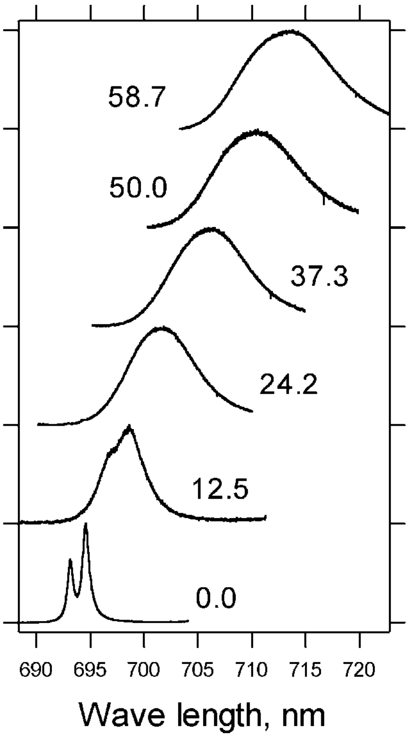

Figure 1. Ruby fluorescence spectra observed in a MAC. The highest pressure achieved was 58.7 GPa.

The Raman spectrum observed from moissanite is shown in figure 2. There are the strong peaks at 149.6, 766.9, 788.4, 964.7 cm^{-1}, relative weak peaks at 142.8, 265.5, 504.7, 514.6 cm^{-1}, and the second-order peaks in the range of 1398.3–1702.8 cm^{-1}. No scattering is observed above $\sim$1900 cm^{-1}. Therefore, moissanite anvils provide a spectra window in different frequency ranges relative to diamond.

DACs play a major role in high-pressure research. However, it is difficult to study the high-pressure behaviour of diamond itself, since the signal from the anvil diamonds seriously interferes with the diamond sample. Such is the case whenever the measured parameters are close to those of diamond. First-order Raman studies on diamond up to 10 GPa in hydrostatic pressure medium and 43 GPa in non-hydrostatic conditions were reported [1], and recently we have measured the second-order Raman spectra of diamond up to 10 GPa. A detailed description of research on diamond using MACs, as well as other gem anvil cells, is also reported in this Special Issue [13].

The MAC is also suitable for x-ray diffraction experiments, although x-ray absorption of moissanite is larger than for diamond, making the MAC only generally workable with synchrotron x-ray sources [1]. Because large anvils are available, the MAC can be used for x-ray diffraction studies on a large amount of sample: it is especially useful for light elements and their compounds; further information is given in another report in this Special Issue [16].

3. Neutron diffraction

In previous experiments, we limited our studies to anvils with culet sizes of less than 4 mm. Thus, the largest sample in the high-pressure environment was in the range of 1–10 mm^3.

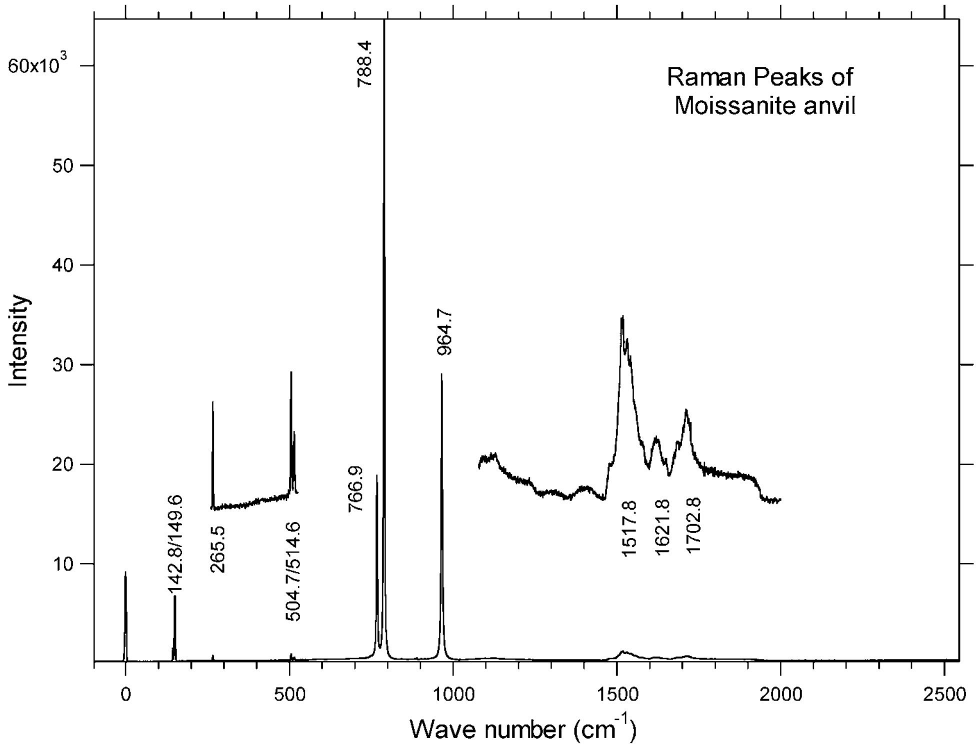

Figure 2. The Raman spectrum of moissanite. Strong, narrow peaks at 142.8, 265.5, 504.7, 514.6 cm^{-1} appear. The weaker peaks are shown in the inset with an expanded scale (×10).

This sample size is still too small for high-quality neutron powder diffraction measurements. Therefore, we have chosen to begin neutron studies with the MAC using single-crystal diffraction techniques because it provides much more intense diffraction. A single crystal can be grown in a MAC as well as a DAC. Figure 3 shows a single crystal of the $C_1D_2O–D_2$ clathrate with a volume of 0.4 mm^3 grown in a 2.0 mm culet MAC.

The cell used for the neutron diffraction is a wide-access 'panoramic' cell (figure 4). It has a long piston–cylinder configuration that ensures alignment stability. Three windows, each with 105° equatorial and 68° azimuthal opening angles, are cut open at the equatorial position of the cylinder, except for three thin 15° webs connecting the cylinder to its end. These windows are major exits for diffraction from the sample, although in addition, a total 34° window is located at the bottom of this cell. Such cells with suitable diamond anvils have been recently used in nuclear resonant inelastic x-ray scattering (NRIXS) measurements up to 153 GPa [17].

Preliminary neutron diffraction studies have been performed at both the SXD beamline, ISIS, Rutherford Appleton Laboratory, Didcot, UK, and the SCD beamline, LANSCE, Los Alamos National Laboratory, Los Alamos, USA. A 1 mm diameter neutron beam and Ti/Zr alloy (67.7 mol% Ti, 32.2 mol% Zr) were used. The Ti/Zr alloy does not diffract neutrons at all, so a very clean background can be observed. At LANSCE, we located a 1.4 mm^3 diamond in the sample hole; the (400) peak was found in 30 min. At ISIS, high-quality single-crystal neutron diffraction patterns have been obtained from a DKDP (KD_2PO_4) crystal with a volume of 0.56 mm^3 in a MAC at 1.0 GPa.

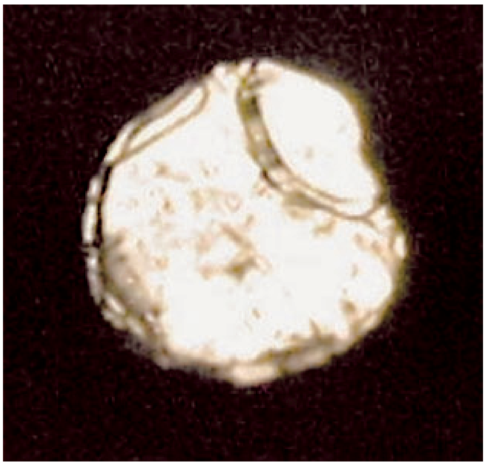

Figure 3. A single crystal of the C_1D_2O–D_2 clathrate at 1.4 GPa with a volume of 0.4 mm^3 grown in a MAC. The small part in the upper-right corner is excess D_2 fluid.

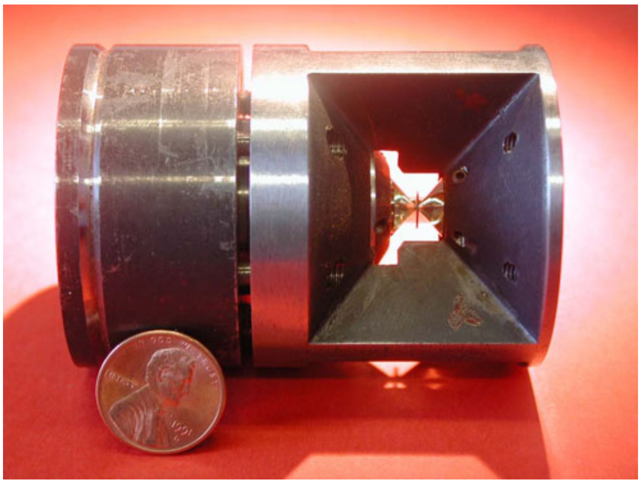

Figure 4. A wide-access 'panoramic' MAC. The size of the moissanite anvils is equivalent to eight-carat diamonds.

Studies to date have been hampered by the lack of suitable software for single-crystal neutron diffraction studies at high pressures. The quality of measurements in this area will be greatly improved with the development of these codes, which should include the following sequence of steps:

(1) initial experimental set-up,
(2) searching for diffraction from anvil 1 (back to 1 if failed),
(3) searching for diffraction from anvil 2 (back to 1 if failed),
(4) calculating all possible anvil peaks and excluding them,
(5) searching for the major peaks from the sample, indexing them, and determining the orientation matrix of the crystal (or crystals),

(6) calculating all possible diffraction of the sample, including weak peaks, and integrating all of the intensity in even very weak peaks,
(7) correcting the intensities,
(8) refining the crystal structure.

For the last two steps, the gasket material Ti/Ze does not contribute to the diffraction; however, it does absorb neutrons. On average, the intensity is reduced by about 20% if the beam passes through about 1.0 cm Ti/Zr. The situation becomes more complicated when considering a diffracted beam passing only through Ti/Zr and another one passing partly through Ti/Zr and partly through the anvil. The recorded intensities for equivalent reflections could be quite different for different orientations. Hence, the intensity correction strongly depends on the shape of the gasket.

4. Conclusions

With these developments, the MAC can now be applied to examine a variety of scientific questions. High hardness and desirable optical qualities make moissanite useful for high-pressure work. Its potential for new large volume cells is very high. We believe that the MAC will play an important role in future high-pressure research by providing a cheaper and larger substitute for diamond anvils for studies up to at least 50 GPa.

Acknowledgments

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