A diamond anvil cell for IR microspectroscopy

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A large optical-aperture membrane diamond anvil cell designed for infrared spectroscopy is described. The cell offers definite advantages compared to existing systems. Other possibilities concerning x-ray diffraction analyses with the cells are mentioned. © *1995 American Institute of Physics.*

I. INTRODUCTION

Infrared spectroscopy is at the present time comparatively less used than other methods in very high-pressure studies. The problem of interfacing a diamond anvil cell (DAC) with an infrared spectrometer, or an interferometer, was discussed for instance by Ferraro[1] and Johannsen.[2] Only the main conclusions will be recalled here. The standard beam diameter of a commercial spectrometer, on the sample stage, is several mm. The gasket hole of the DAC, whose diameter is ~0.2 mm, acts like a diaphragm and the largest part of the incident beam is stopped. Investigations are, however, possible without focusing optics,[3–5] but, as a rule, a focusing device vastly improves the signal-to-noise ratio and, specifically, is an absolute necessity in the case of crystal samples compressed in a pressure-transmitting medium. Various devices have been used as focusing optics: KBr, CaF_2, NaCl lenses and beam condensers consisting of aspherical mirrors[1] or on-axis Cassegrain-type beam condensers.[6] This latter device, which is used in the present work, is the most convenient for optical adjustments. Moreover, it gives access to a broad spectral range. This arrangement requires sufficiently large optical apertures which are unfavorable as regards the mechanical characteristics of the DAC. The DAC which is described here has been designed as a best compromise between the opposite requirements of large optical aperture and good mechanical stability.

It was originally designed for infrared spectroscopy. After a description of the cell, its performances and possibilities will be illustrated by some examples. Other uses in x-ray diffraction will also be mentioned.

II. DESCRIPTION OF THE SYSTEM

A. The pressure cell

The pressure cell described here was designed and built to meet precise requirements simultaneously, regarding its optical characteristics and its high-pressure performance. The optical path of the Cassegrain optics requires that:

(1) The optical aperture on both sides must be 2×38°, which is that of the Cassegrain mirror used here.
(2) The length of the cell must be less than twice the working distance, here: 2×24 mm. The cell was built with a total length of 40 mm.

On the other hand, operation at high pressure, allowing optical observation and avoiding adjustment modifications, leads to the following constraints:

(3) The variation of the force acting on the anvils must be remotely controlled.
(4) The parallelism of the anvils must be preserved under load.

These two last requirements can be solved using a variable-pressure cell with an internal membrane ram.[7] With this thrust generating mechanism the system has certain decisive advantages viz, fine pressure monitoring capability and good mechanical stability. Optical requirements [(1) and (2)] are opposed to the mechanical requirements [(3) and (4)]. To reconcile them the following solutions were adopted:

Requirement (1) made it necessary to use a membrane with a small ratio of outer to inner diameter around 1.5 compared to 2.6 usually adopted in existing devices.[7] This leads to a lower yield of the system which may be compensated by a larger working gas pressure in the ram.

Requirement (2) usually contradicts (4): in order to be properly guided the piston length to diameter is normally greater than unity. The piston of our cell (Fig. 1) has a diameter which is 50% more than its length, however, due to the specific piston-cylinder assembly, combined with the hemispherical tungsten carbide seat on the body, we have checked that requirement (4) was fulfilled at least under loads of 0.5 ton which is the upper value achieved here.

Finally, it should be noted that the present cell uses only three machined parts to hold and compress the diamond-tungsten carbide seats assembly, which makes its construction relatively simple. The cell body (3, Fig. 1), the piston (2), and the screw cap (1) are all made of maraging steel (Marval 18 from Aubert et Duval) treated to full hardness (52 RC). The cylindrical surface is ground and the piston-cylinder clearance is ~20 μm.

The diamond anvils are type IIa stones (nitrogen free) whose infrared absorption bands lie in the range 1800–2650 cm^{-1} (two-phonon spectrum of the diamond). For the present studies the anvils had a standard Drukker shape with culet diameter ~0.5 mm, 2 mm height, and 3 mm table diameter while the access holes in the tungsten carbide seat are 1.3 mm in diameter. For easy optical adjustments of the sample position with the infrared setup, the cell was designed in such a way that the diamond culets were close to the geometrical center of the main body. The gaskets used in this work were 301 stainless steel preindented to a thickness

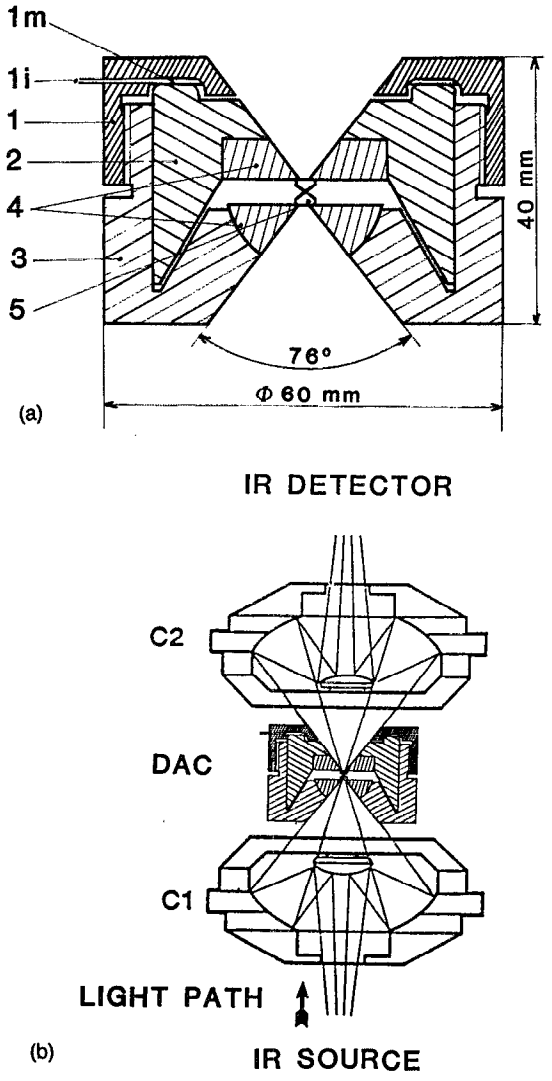

FIG. 1. The membrane diamond anvil cell designed for infrared microspectroscopy. (a) The cell: (1) cap with membrane chamber (1 m) and gas inlet (1i) of the ram, (2) piston, (3) lower body, (4) WC diamond seats, (5) anvils. (b) Schematic diagram of on-axis Cassegrain optics used with the diamond anvil cell for infrared microspectroscopy: C1 and C2 Cassegrain mirrors. The scale is given by the cell's dimensions.

of 40 μm. The sample cavity was then machined by drilling the center of the indentation to a diameter ~0.15 mm. Prior to filling the cavity, several ruby grains were placed in the hole to enable pressure measurement using the R_1 line shift and the five power law.[8] With liquid samples the cavity was filled with a syringe. In the case of crystals the pressure-transmitting medium was a mixture of ethanol-methanol or liquid argon loaded at liquid-nitrogen temperature. The effective multiplication factor (internal pressure/ram pressure) of the press with this size of anvils was found to be around 3000, depending somewhat on the compressibility of the sample.

B. Interfacing of the cell with an infrared microscope

As mentioned above, the DAC described in the previous section was designed for use with beam condensers consisting of on-axis Cassegrain mirrors (insert of Fig. 1). We used a commercial system (Perkin–Elmer FT-IR microscope), the opposed Cassegrain mirrors of which have 5× magnification, 0.6 numerical aperture and a working distance of 24 mm. With this system the infrared beam spot diameter on the sample is 0.1 mm. A variable knife-edge aperture, placed at the conjugate point of the sample, after the output Cassegrain mirror, allows us to select a desired area (20×20 μm or more) of the sample for infrared analysis. The DAC was mounted on an X, Y, Z micropositioner on the sample stage. In the present work the microscope was equipped with a MCT detector and coupled to a Perkin–Elmer 1600 interferometer. The spectral range of the system extends from 500 to 4000 cm^{-1}. It is to be noted that for investigation in the far infrared region, a similar microscope, equipped with a bolometer, should be very efficient. Specifically, the use of a synchrotron radiation source[9,10] would be in this case very powerful.

III. INVESTIGATIONS PERFORMED WITH THE INFRARED SETUP

Investigations performed, or in progress include various types of liquids and solids viz, molecular (silicone oil, CS_2), and covalent solids (GaAs). We will describe in detail the results obtained with silicone oil, but only briefly those obtained on CS_2 and GaAs.

Silicone oil (mixture composed of polysiloxane chains with methyl and phenyl groups) may be used as pressure-transmitting medium. The stability range of the liquid extends above ~10 GPa where it transforms into a glass. However, as observed in ethanol-methanol mixture,[11] well below the glass transition pressure significant pressure gradients may be observed in such a medium due to its large viscosity under pressure.

Preliminary experiments were performed with this fluid, in order to test the cell, and to obtain information on the pressure dependence of the viscosity and the effects of the glass transition. Silicone oil (Rhodorsil 47V1000 from Prolabo) was loaded with a few ruby grains in the gasket hole. The infrared spectrum was collected, during upward and downward pressure cycles, from 600 to 3500 cm^{-1} at ~30 pressure points ranging from atmospheric pressure to 30 GPa. The absorption bands broaden with pressure. This is illustrated in Fig. 2(a), which shows the C–H stretching band (higher frequency peak at ~2960 cm^{-1} at atmospheric pressure) at 3, 15, and 30 GPa, respectively. Actually the width of the C–H band first increases linearly with pressure; for the higher-frequency peak, it is 50 cm^{-1} at atmospheric pressure, at 15 GPa the width reaches ~225 cm^{-1} [Fig. 2(b)]. On further compression this width does not vary. In the same way, at 15 GPa, a jump of the C–H higher frequencies [Fig. 2(c)] and a broadening of ~7 cm^{-1} of the R_1 ruby line were also observed. These changes may be ascribed to the glass transition, whereas the strong broadening of the C–H band with pressure, observed between ambient pressure and 15 GPa, is likely related to the rapid rise of the viscosity.

Other infrared investigations were performed with the optical arrangement described in the previous section. First of all, we studied the chemical transformation in carbon disulfide (CS_2) at 10 GPa at room temperature. At this pres-

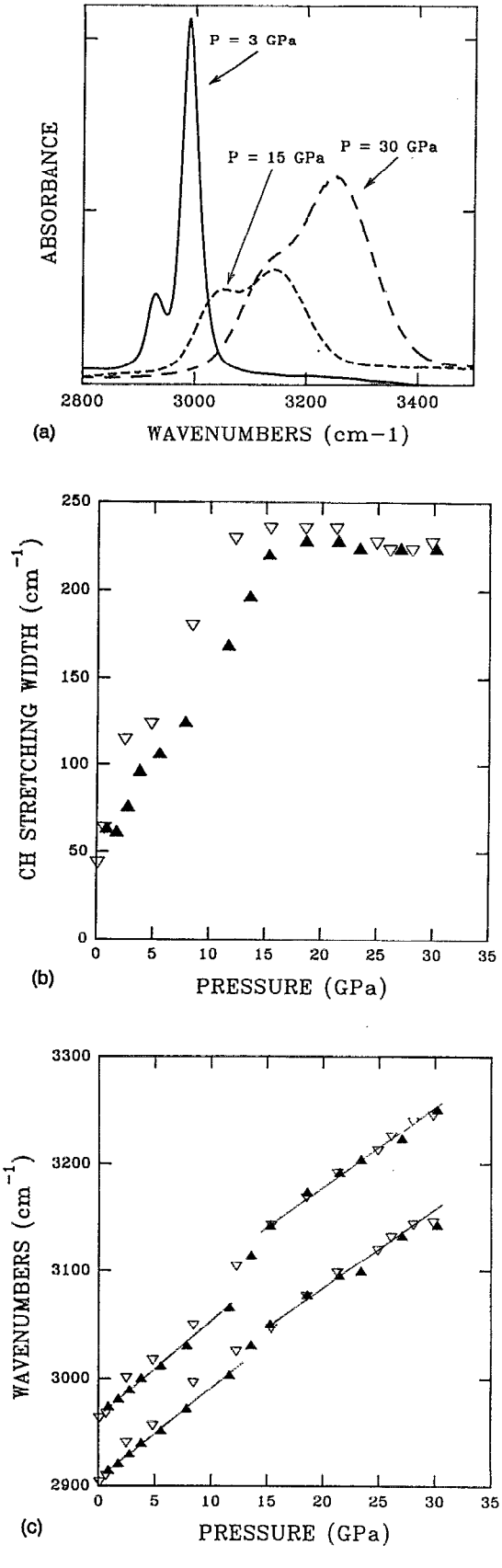

FIG. 2. (a) Infrared C–H stretching band of silicone oil at 3, 15, and 30 GPa. The band broadens up to 15 GPa and then its width remains constant. (b) Total width of the C–H band of silicone oil as function of pressure. (c) Frequencies of the C–H peaks of silicone oil as function of pressure. Filled symbols: increasing pressure runs. Open symbols: decreasing pressure runs.

sure, broad bands occurred in the range of 600–1200 cm^{-1}. These bands were found in the recovered compound and are characteristic of the new product.[12]

Another type of experiment concerned the determination of the refractive index of GaAs up to 8 GPa in the 0.07–0.6 eV range.[13] The interference method used was that described in Ref. 14. A thin plate of GaAs (~10 μm) was loaded into the gasket hole and argon was used as pressure-transmitting medium.

IV. USE OF THE CELL FOR X-RAY DIFFRACTION AT HIGH PRESSURE

Although this cell has been designed originally for infrared measurements, it could be used in other types of experiments, where a large angular aperture is necessary.

Angle-dispersive and energy dispersive x-ray diffraction techniques are currently used with DAC. The former technique requires a large optical aperture on one side of the cell. The usual DACs are generally suitable for the latter technique. However, large apertures are very useful, for instance in identifying features due to the effect of tilting the cell, or for some specific requirements as mentioned below. The cell was used to perform powder-diffraction measurements on a new high-temperature supraconductor mercury-cuprate compound ($HgBa_2Ca_2Cu_3O_8$) at the European Synchrotron Radiation Facility (ESRF, Grenoble, France).[15] Data on the lattice parameters of this compound were obtained up to 18 GPa. The x-ray setup and the imaging-plate assembly were very similar to that described earlier.[16] In the experiment the diffraction angle range was ~22°, as dictated by the diamond height (1.8 mm in this case) and the hole diameter (1.3 mm) in the outer tungsten carbide seat. A wider diffraction angle could be obtained with smaller diamond height, but at the expense of the pressure range of the DAC.

An energy dispersive setup was installed at LURE (Orsay, France) for the determination of the equation of state of $SrTiO_3$ at 2000 K up to 14 GPa.[17] In this setup the large optical aperture was used for: (i) ruby fluorescence measurement, (ii) temperature measurement for the sample thermal emission, and (iii) for the passage for the incoming x-ray beam, and the laser beam for heating. The converging and collecting optics for ruby fluorescence and temperature measurement was made of a parabolic mirror. Holes machined in the mirror, along the optical axis (or DAC axis) and at an oblique angle (~16°) allowed the passage of the beams from the x-ray source and from the CO_2 laser for sample heating. The opposite optical entrance was used to collect the diffracted x-ray beam at an angle of ~13°.

In both experiments the optical bench was equipped for ruby luminescence measurement, which was particularly useful and convenient since pressure could be changed without moving the cell from its holder.

V. DISCUSSION

In this paper we have described the design and use of a DAC, for pressure range in excess of 30 GPa, dedicated to infrared microspectroscopy. The infrared optical microscope uses the standard on-axis Cassegrain optics. The cell uses the

membrane type thrust mechanism, allowing pressure changes to be made without moving the cell body from the sample stage.

Compared to the existing systems the proposed DAC offers the following advantages:

(i) Despite the large optical aperture and a small height/diameter ratio, the various tests have demonstrated the reliability of the system. Owing to the particular piston-cylinder assembly and the membrane principle for thrust generation, good mechanical stability and excellent parallelism between diamond culets were observed after runs at least to 30 GPa. In view of the good mechanical stability achieved, we believe that pressures up to 80 GPa could easily be obtained with beveled diamond having 250 μm central flat. Lately, with 300 μm central flat standard Drukker shape anvils, pressures over 50 GPa have been reached in the course of powder-diffraction experiments performed at ESRF.

(ii) The cell permits easy adjustment and operation under the infrared microscope. This is due to the symmetrical geometry of the DAC coupled with the diaphragm principle: with an adequate optical arrangement, this type of variable pressure cell permits the observation of the sample and measurement of pressure without removing it from the bench.

(iii) The system has proven to be a versatile device: The large optical aperture of the cell makes it suitable for x-ray analyses under various conditions. In addition, the large aperture of the DAC could also be turned to advantage to improve the signal-to-noise ratio in micro-Raman spectroscopy by using an objective with large optical aperture. For instance our usual setup for micro-Raman is equipped with an objective with 0.22 numerical aperture. With the new cell a 0.4 numerical aperture could be used to improve the Raman signal by a factor 4.

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