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Melting of Diamond

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Abstract. *Radiation from a Q-switched YAG laser, focused on the (100) face of a single crystal diamond anvil in a high-pressure diamond cell, caused a portion of the diamond anvil face to melt. Potassium bromide mixed with graphite was under pressure between the anvils when melting occurred. The diamond surface melted at pressures greater than ~120 kilobars and graphitized at lower pressures. Evidence for the melting and graphitization of the diamond was obtained by optical and scanning electron microscopy.*

The nature of the phase diagram of carbon at high pressures and temperatures (Fig. 1) is of interest to a wide variety of researchers in such fields as physics (*1*), astronomy (*2*), and geology (*3*). Dickey *et al.* (*4*) have proposed that, under the high-pressure and high-temperature conditions of the lower mantle of the earth, carbon is liquid and may therefore be an important factor in mantle dynamics. However, successful application of the phase diagram to this type of study is difficult because of the lack of consistent experimental and theoretical data in some regions of the diagram. We studied carbon at high pressures and temperatures in an effort to better understand the role of carbon in the earth's mantle and the interiors of other planets and to obtain fundamental information on the physics of this element.

Not only are the locations of the carbon phase boundaries at higher pressures and temperatures in question, the characteristics of the carbon phases themselves, especially the liquid phases, are not well understood (*5*). Ferraz and March (*6*) have suggested the existence of a two-liquid system; Grover (*7*) has questioned whether diamond melts directly to a liquid. Whittaker (*8*) suggested that graphite does not melt directly, but instead first forms an intermediate "carbyne" phase. Bundy (*9*) reported on the melting of diamond formed in situ from boron-doped graphite. We previously found evidence for melting when graphite was used as the starting material (*10*). We now report evidence for melting when diamond is used as starting material.

Our laboratory has been developing techniques for the mapping of the equilibrium carbon phase diagram. We use a diamond anvil cell (*11*) for generating static pressures up to 450 kbar (45 GPa). The apparatus is well suited for this study because it allows the introduction of laser radiation for heating while the sample is under pressure (*12*). The static pressure distribution in an ungasketed diamond cell is approximately Gaussian, with the maximum at the center of the anvil surface when the diamonds are well aligned. This allows the investigator to make observations at a variety of pressures in the same sample. Use of the diamond anvil cell also permits spectroscopic analysis of the sample under pressure (*13*). Techniques are being developed for the rapid measurement of temperature with the quasi-blackbody radiation emitted by the sample during laser heating.

An intimate mixture of potassium bromide and graphite (6:1 by volume) was loaded into a diamond anvil cell. Potassium bromide was used as a pressure medium that is transparent to infrared radiation. The sample was compressed to more than 120 kbar (12 GPa) (Fig. 2A) and heated with light from a Q-switched YAG laser (λ = 1.06 μm) by focusing the beam through one of the diamonds to a 10-μm spot at the sample. The original intent of the experiment was to observe the melting behavior of graphite at high pressure (*10*). However, the focused laser was inadvertently run at a very high power density (~10 GW/cm^2) across the sample from a low-pressure region to a high-pressure region, thus "damaging" the anvil face (Fig. 2B)

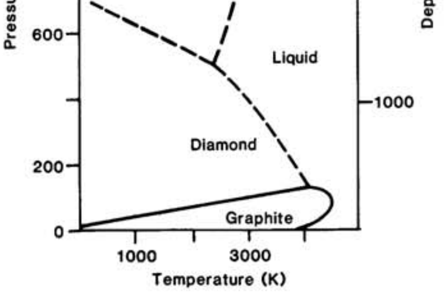

Fig. 1. Pressure-temperature diagram for carbon, showing regions of phase stability (*5*). Corresponding depths in the earth's interior are given at right.

We then examined the nature of the damage in detail. A Laue x-ray diffraction photograph of this face indicates that it has the (100) crystallographic orientation. The feature resulting from the laser damage, which we found has the topography of a furrow, begins at a stress fracture in the crystal in a region that contains graphite (Fig. 2B). Graphite may play an important role in absorbing energy from the laser and in initiating melting. The furrow extends toward the region of highest pressure in the cell. After unloading the sample, we observed the damaged anvil by transmitted light microscopy (Fig. 3). The furrow is opaque in the lower pressure region and transparent in the region of higher pressure, with a very narrow transition zone. The opaque portion of the groove is interpreted to be graphitized diamond.

Next, we examined the damaged anvil with various scanning electron microscope techniques to determine the nature of the transparent portion of the groove. Figure 4 presents a secondary electron stereopair of images taken to determine the surface morphology of the furrow. These are interpreted to indicate that the transparent region consists of a depression with a raised smooth ridge on each side. Use of a backscattered electron imaging mode designed to enhance topography confirmed this morphology (Fig. 5). The smooth curved surfaces observed in the groove and on the ridges strongly suggest that the material was molten. These features could not have been produced by fracturing, graphitization, or oxidation. Fracturing would not produce such smooth surfaces, graphitization would not produce transparent material, and oxidation would result in missing rather than redistributed material.

Close examination of the material in the bottom of the groove revealed additional evidence of melting. We observed small spherules, identified by x-ray energy dispersive spectroscopy as KBr, suspended in carbon in the transparent part of the furrow. Figure 6 shows the spherules of KBr. Some of the spherules remained after the sample was soaked in water, indicating that they are completely encapsulated. Stereopairs of secondary electron images confirm that some of the spherules lie below the surface of the furrow. The existence of spherules indicates that KBr and carbon liquids are immiscible.

Calculations based on the repetition rate of the laser pulses and the spacing of the resulting ridges in the furrow yield a minimum cooling rate of $\sim 10^7$ K per second. However, the actual cooling rate may be several orders of magnitude higher because diamond is such an excellent conductor of heat.

We repeated the procedure in a second experiment in which only KBr was compressed between the diamond anvils. A higher laser power was required to initiate melting because graphite was not present to absorb the laser radiation. In the resulting affected areas, which were at a pressure greater than ~120 kbar, we observed small (submicrometer) spherules in a depression. These spherules, which are transparent in visible light, were determined by x-ray emission spectroscopy to consist of carbon. They apparently were formed by the contact of immiscible carbon and KBr liquids.

In conclusion, these observations indicate that portions of two diamond anvils melted under pressure on exposure to laser radiation. To our knowledge, this is the first time that experimental evidence has been produced to show melting of carbon at high pressure when diamond is used as the starting material.

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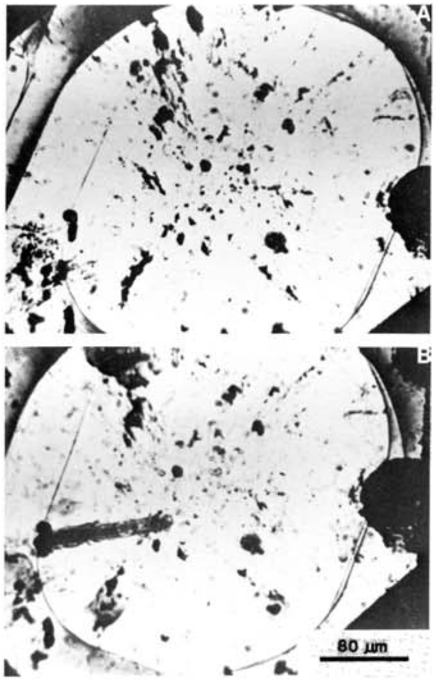


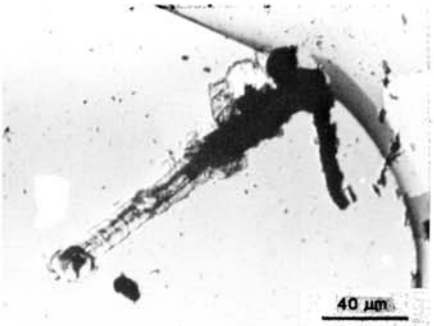


Fig. 2 (left). (A) Transmitted light micrograph of graphite (opaque) and KBr (transparent) at >120 kbar (at the center) in a diamond anvil cell before laser heating, as viewed through the upper diamond anvil. The dark curved line is a stress fracture in the anvil. (B) Transmitted light micrograph of the same sample after being subjected to heating by YAG laser radiation focused to a 10-µm spot. Note the appearance of the damaged area (furrow) on the right. Some grains of graphite at lower pressure were apparently melted and dispersed to form cloudlike features, whereas several grains that were at higher pressure have become transparent and are presumably diamond (*10*). Scale bar, 80 µm. Fig. 3 (right). Transmitted light micrograph of the damaged region of the diamond anvil face. The opaque region has a positive relief while the transparent portion has the topography of a furrow (a central depression with raised ridges). Scale bar, 40 µm.

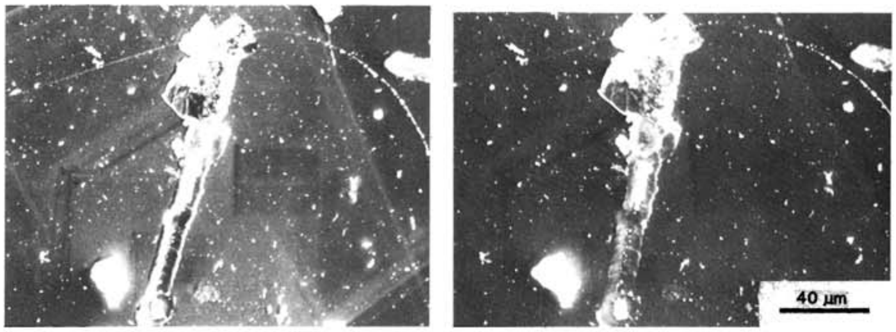
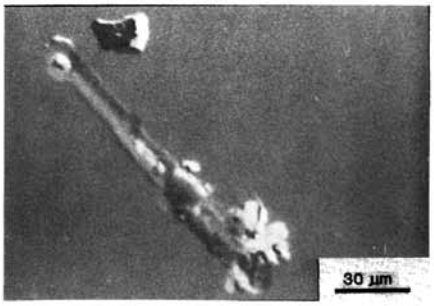


Fig. 4. Secondary electron image stereopair of the furrow. The image on the left is tilted approximately 15° on an axis in the plane of the page. The stereopair shows the topography of the furrow. Scale bar, 40 µm.



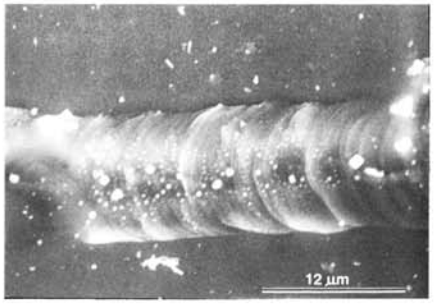


Fig. 5 (left). Scanning electron microscope image of the damaged area. A backscattered electron imaging mode was used to enhance topography. Shading lighter than that of the surrounding flat anvil area indicates a slope to the right and darker shading indicates a slope to the left. The portion of the damaged area that was at higher pressure is best described as a furrow. Scale bar, 30 µm. Fig. 6 (right). Secondary electron image of the furrow. The round bright objects in the furrow are spherules of KBr. Many of these spherules remained after the anvil was soaked in water, indicating that they are completely encapsulated in the carbon. Scale bar, 12 µm.

References and Notes

1. J. A. Van Vechten, *Phys. Rev. B* **7**, 1479 (1973).
2. M. Ross, *Nature (London)* **292**, 435 (1981).
3. N. V. Sobolev, E. S. Efimova, L. N. Pospelova, *Geol. Geofiz.* **12**, 25 (1981).
4. J. S. Dickey, W. A. Bassett, J. M. Bird, M. S. Weathers, *Geology* **11**, 219 (1983).
5. F. P. Bundy, *J. Geophys. Res.* **85**, 6930 (1980).
6. A. Ferraz and N. H. March, *Phys. Chem. Liq.* **8**, 289 (1979).
7. R. Grover, *J. Chem. Phys.* **71**, 3824 (1979).
8. A. G. Whittaker, *Science* **200**, 763 (1978).
9. F. P. Bundy, *J. Chem Phys.* **38**, 631 (1963).
10. W. A. Bassett, M. S. Weathers, J. S. Gold, J. M. Bird, *Eos* **64**, 847 (1983).
11. W. A. Bassett, *Annu. Rev. Earth Planet. Sci.* **7**, 357 (1979).
12. L. Ming and W. A. Bassett, *Rev. Sci. Instrum.* **45**, 1115 (1974).
13. T. R. Lettieri, E. M. Brody, W. A. Bassett, *Solid State Commun.* **26**, 235 (1978).
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