Transformation of shock-compressed graphite to hexagonal diamond in nanoseconds

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The graphite-to-diamond transformation under shock compression has been of broad scientific interest since 1961. The formation of hexagonal diamond (HD) is of particular interest because it is expected to be harder than cubic diamond and due to its use in terrestrial sciences as a marker at meteorite impact sites. However, the formation of diamond having a fully hexagonal structure continues to be questioned and remains unresolved. Using real-time (nanosecond), in situ x-ray diffraction measurements, we show unequivocally that highly oriented pyrolytic graphite, shock-compressed along the c axis to 50 GPa, transforms to highly oriented elastically strained HD with the (100) HD plane parallel to the graphite basal plane. These findings contradict recent molecular dynamics simulation results for the shock-induced graphite-to-diamond transformation and provide a benchmark for future theoretical simulations. Additionally, our results show that an earlier report of HD forming only above 170 GPa for shocked pyrolytic graphite may lead to incorrect interpretations of meteorite impact events.

INTRODUCTION

Diamond formation through the compression of graphite under diverse thermodynamic conditions has been a subject of intense research activity for more than six decades (1–6). Under static pressure, both cubic and hexagonal structures have been reported, with many comparable physical properties (4), except that hexagonal diamond (HD) is predicted to be significantly harder (58%) than cubic diamond (CD) (7, 8). In nature, HD is found mostly at meteorite impact sites (9). Therefore, HD (also called lonsdaleite) is viewed as a signature of major meteorite impact events and related catastrophic consequences, such as mass extinctions (5, 6, 10–14).

Although the earliest observation of catalysis-free formation of diamond from graphite was in samples recovered after shock loading (2), the formation of high-pressure polymorphs in statically compressed graphite has received the most attention (1, 3, 4, 15–23). Theoretical investigations indicate a higher activation barrier for HD than for CD (21, 22). First-principles calculations and/or experiments have also suggested several other precursors or competing super hard forms of carbon with sp3 bonding such as monoclinic (24, 25), orthorhombic (26), body-centered tetragonal (bct) (27), and n-diamond (28, 29). In addition, despite the observation of micrometer-size natural HD monocrystals in regionally metamorphosed rocks in Russia (9), the existence of pure HD has recently been questioned (30–32).

Early shock compression recovery experiments (2) and the observation of both CD and HD at meteoritic sites (5, 6, 10, 12–14) suggest a fast mechanism for the graphite-to-diamond transformation under shock compression. In the early 1990s, wave profile measurements in planar shock experiments showed that highly oriented pyrolytic graphite (HOPG) shocked beyond ~20 GPa transforms rapidly (~10 ns) to a phase with a density somewhat less than that expected for hydrodynamically compressed CD (33, 34). However, the absence of in situ structural measurements left much to speculation, and various high pressure structures were suggested: CD (33), disordered HD, or n-diamond (34). A recent publication, using in situ x-ray diffraction (XRD) on laser-shocked graphite (35), reported that pyrolytic graphite transforms to CD above 55 GPa and to HD at a much higher stress (~170 GPa). Molecular dynamics (MD) simulations on graphite under shock compression have predicted that it transforms either to CD through a metastable layered structure (36) or predominantly to HD (37).

The disparate and contradictory results from numerous previous investigations show that the high-pressure structure and the transformation mechanism of the graphite-to-diamond transition under shock compression constitute important and unresolved scientific questions. Here, we report real-time (nanosecond), in situ synchrotron XRD measurements in well-controlled, planar impact experiments on HOPG to directly determine the structure and orientation of the high-pressure phase.

RESULTS

Figure 1 shows the overall configuration used for three shock compression experiments on ZYB-grade HOPG (38). A LiF(100) disk, accelerated to ~5.1 km/s using the two-stage gas gun at the Dynamic Compression Sector (DCS) at the Advanced Photon Source (APS), impacted the HOPG (ZYB grade) sample, resulting in a planar shock wave (~50-GPa amplitude) propagating along the c axis of the HOPG. Although the transformation onset stress is ~20 GPa (33, 34), 50-GPa peak stress was chosen for these experiments to avoid multistage profiles that occur at lower peak stresses (33, 34) and, in turn, would complicate the XRD analysis. For an overdriven shock at 50 GPa (33, 34), the XRD data obtained during shock wave propagation through the HOPG consists of diffraction from ambient HOPG and from the 50-GPa shocked state. Wave profiles measured at the HOPG rear surface, using a laser interferometer, confirmed ~10-ns rise times to the 50-GPa peak state. In each of the three ~50-GPa XRD experiments conducted, two XRD patterns were recorded after impact, but before the shock wave had reached the sample rear surface. These XRD data were analyzed in detail (38) to determine the high-pressure structure and its orientation.

Figure 2A shows a single-pulse XRD pattern for a ZYB-grade HOPG sample under ambient conditions. The ZYB-grade HOPG has a nominal 0.8° ± 0.2° full width at half maximum mosaic spread of the graphite c axis relative to the loading direction; the transverse orientations of the graphite grains are distributed randomly around the c axis (fiber texture). Thus, the ambient XRD spots are localized, as expected, because of the low mosaic spread. Figure 2 (B and C) shows XRD patterns obtained after impact, but before the shock wave reached the HOPG free...
Surface; a number of new diffraction spots are apparent, together with spots from ambient HOPG. As shown below, the new spots can be ascribed to HD with the (100) HD plane oriented normal to the shock propagation direction (graphite c axis). The HD spots were also observed in the XRD pattern obtained after the shock had reached the HOPG free surface; the HD spots are indexed in Fig. 2D.

Typical measured XRD patterns reported for polycrystalline HD have a trident of diffraction peaks—{100} HD, {002} HD, and {101} HD—all located near the scattering angle expected for the CD {111} CD peak, making it difficult to conclusively ascribe the observed diffraction peaks to either CD or HD structures (4, 18, 30–32). In contrast, our in situ XRD data on HD do not suffer from this difficulty because the HD formed by shock-compressing ZYB-HOPG along the graphite c axis is highly oriented (about ±2° mosaic spread based on azimuthal widths of the diffraction spots), and some {100} HD, {002} HD, and {101} HD XRD peaks are present in the detector data without overlap from other peaks with similar scattering angles (38). Thus, we are able to determine the lattice plane d spacings from individual spots with each spot corresponding to a particular HD (hkl) plane, with the plane normal making an angle γ with the shock propagation direction; the angle γ is determined directly from the spot location on the detector and the experimental geometry using the Laue condition. Average d-spacing results and nominal γ angles for the XRD spots from equivalent lattice planes for each experiment are listed in Table S5.

Diffraction spots 5 and 6 are from (002) HD planes, which are parallel to the shock loading direction (γ = 90°), and their measured d spacing directly provides the a-axis lattice constant transverse to the loading direction a_{HD,T} = 2d_{002,HD}. Because (002) HD and (120) HD planes are parallel to the loading axis, (100) HD planes are perpendicular to the loading direction (graphite c axis).

The measured d spacings for lattice planes not parallel to the loading direction (γ < 90°) are somewhat smaller than expected for a hexagonal lattice with lattice parameters a_{HD,T} and c_{HD}, indicating that the HD lattice undergoes additional compression along the loading direction. The average additional compression of the HD basal plane along the loading direction, determined by analyzing diffraction spots from planes not normal to the loading direction, was 1.5(5)%.

In Fig. 2F, simulated XRD spots are superimposed (yellow lines) over the measured diffraction pattern obtained 297 ns after impact. The simulations used the transverse HD lattice parameters given in Fig. 2E and the additional lattice compression (1.5%) along the loading direction. The simulations also assumed a 2° maximum misorientation of the (100) HD plane normal relative to the loading direction, with random transverse HD grain orientation about the loading axis (fiber texture). The good match between the simulated and measured diffraction patterns confirms that the high-pressure structure of ZYB-HOPG shocked to 50 GPa is HD with (100) HD planes normal to the loading direction. Similar simulations provided a good match to the measured diffraction spots for the other two experiments as well, as shown in Fig. S8 (38).

Other XRD simulations with a (001) HD or (110) HD plane parallel to the (002) graphite plane differed significantly from measured diffraction patterns ruling out these other HD orientations. Other proposed high-pressure phases (24–29) of sp2-bonded carbon are also inconsistent with our experimentally observed diffraction patterns. Diffraction patterns for CD only have a single diffraction peak (111) CD with lattice spacing between 0.18 and 0.22 nm, whereas we observed three distinct diffraction peaks (characteristic of HD) over this range. We can also rule out bct carbon (27) and n-diamond (29) because they also have only a single diffraction peak with lattice spacing between 0.18 and 0.22 nm. Monoclinic carbon and orthorhombic carbon structures are ruled out because they have more than 10 diffraction peaks with a lattice spacing greater than 0.12 nm (24, 26), and we only observed four diffraction peaks over this range.

**DISCUSSION**

Within experimental uncertainties, the HD specific volumes determined from the in situ, XRD measurements (38) match the specific volumes determined from continuum measurements (see Fig. 3), showing near full transformation to HD at 50 GPa. HD densities determined from our XRD measurements and continuum measurements (34, 38) agree well with the elastic response of HD compressed uniaxially, normal to the (100) HD plane (see Fig. 3). By analyzing measured wave profiles (34) using a continuum model, a previous study (39) inferred an elastic diamond response for the transformed phase. Although this continuum model (39) assumed a CD structure, the continuum results (Fig. 3) are equally consistent with an HD structure because the HD and CD continuum elastic responses under shock compression are almost identical (38).

Our in situ XRD results demonstrate unambiguously that shock-compressed HOPG is transformed to the HD structure at 50 GPa. Additionally, wave profiles at the HOPG rear surface show that the transformation occurs within several nanoseconds (38), and previous
Fig. 2. Shocked HOPG XRD results. (A) Single-pulse XRD pattern for ambient HOPG (red spots are from diffraction simulations). Because the x-rays are in the horizontal plane and the HOPG has a fiber texture, the diffraction patterns from the ambient and shocked HOPG all have mirror symmetry about the horizontal blue dashed line containing the direct x-ray beam/detector intersection. The indexed spots refer to families of (hkl) graphite planes. (B to D) Single-pulse XRD patterns obtained after impact; time after impact is listed in the images. In (B) and (C), the shock wave has propagated through 47 and 98% of the HOPG, respectively. In (D), the shock wave has released from the HOPG rear surface. The same HD diffraction spots are observed in all three XRD frames obtained after impact. Bright XRD spots from the LiF(100) impactor are easily recognized because they do not have mirror symmetry about the horizontal line. For reference, the HD spots are labeled with yellow numbers in (C) and indexed in (D). Not all 16 spots are labeled because some spots are masked by LiF diffraction spots and some are not in the detector field of view for this experiment; spots 4, 10, 13, and 15 are mirror images about the horizontal blue dashed line of spots 2, 8, 14, and 16, respectively (38). (E) HD orientation and average lattice parameters/distortions at ~50 GPa. (F) Diffraction pattern for HD formed by shock compression of HOPG to 50 GPa; the image was obtained from (C) by subtracting a fraction of the ambient HOPG XRD pattern (A). The yellow lines are XRD simulations of HD using the lattice parameters/distortions shown in (E).

wave profile measurements at lower stresses (33, 34) show that the transformation is initiated at ~20 GPa. These findings are in marked contrast to those of Kraus et al. (35), who reported CD observation for pyrolytic graphite shocked to stresses above 55 GPa; HD was reported only for stresses above ~170 GPa. Because these previous conclusions were drawn from fairly limited diffraction data (one peak for CD and only two peaks for HD, with all three peaks located at similar scattering angles), those experiments (35) should be revisited. Our results also show that HD observation at meteoritic sites does not necessarily imply impact stresses beyond ~170 GPa.

We note that the peak stress durations were considerably different in the laser shock experiments on pyrolytic graphite (35) and our gas gun experiments on HOPG; peak stress duration was ~10 ns in the previous laser shock XRD experiments (35) compared to a few hundred nanoseconds in our in situ XRD impact experiments. However, the transformation times are several nanoseconds or less for both the laser shock experiments (35) and plate impact experiments (34, 38).

HD has been recovered previously from shock-loaded HOPG or CD samples (40, 41). However, HD was also observed in phase transition reversal from diamond to graphite (42). Therefore, it is difficult to determine from earlier studies whether HD formation occurred during shock compression or during the complex post–shock loading/unloading processes encountered in recovery experiments (40, 41) and meteorite impacts (32). Complex loading/unloading history effects may also explain the limited hexagonality observed in diamonds found at meteorite impact sites (31, 32). Furthermore, first-principles calculations (32) were used to suggest that HD formation is energetically unfavorable during compression, but HD could be formed during stress release. In contrast, the present results clearly demonstrate that HD is formed during shock compression of HOPG along the c axis and that HD can persist upon initial stress release for at least tens to hundreds of nanoseconds; the same HD peaks observed in the shocked state (Fig. 2C) are seen in the XRD pattern recorded 147 ns after the shock released from the HOPG free surface (Fig. 2D).

On the basis of the present results, it seems likely that even in graphite samples with less controlled microstructure, such as pyrolytic graphite, some regions having hexagonal graphite would transform to HD at comparable pressures. However, additional in situ XRD investigations on graphite, with different initial microstructures, in both the shocked and released states are needed to provide a broader understanding of the graphite-to-diamond transformation including phenomena occurring in natural impact events.

The present results can guide improvements to theoretical approaches for understanding the shock-induced graphite-to-diamond transformation. Although MD simulations by Pineau (37) find that shock-compressed HOPG transforms to HD, their suggested mechanism has (001)_{HD} planes normal to the graphite c axis and is inconsistent with our experimental findings. MD simulations by Xie et al. (23) do not match our observations because their calculations predict that HD formation requires large anisotropic stresses in the graphite basal plane in addition to large compression along the graphite c axis. Using a stochastic approach, Xie et al. (43) found that HD formation from graphite is kinetically favored over CD
because of low-energy coherent graphite/HD interfaces having the same orientation relation between graphite and HD, as observed in our experiments. However, additional work is needed to understand how their approach would apply to the transformation under shock compression, which occurs in nanoseconds.

The coupling of planar impact experiments and synchrotron XRD measurements has provided real-time, in situ structural information on the shock-induced graphite-to-diamond transformation. Shock-compressed pyrolytic graphite transforms to HD at a much lower stress than previously reported (35) and without CD formation. In addition to graphite, other shock-compressed minerals (for example, quartz) that transform to high-pressure structures are also used as markers for meteorite impacts (44). Thus, experimental results—similar to those presented here for the graphite-to-diamond transformation—can greatly benefit studies of shock metamorphism in other minerals.

MATERIALS AND METHODS

Experimental design

The ZYB-grade HOPG samples used in the XRD impact experiments were obtained from Momentive Performance Materials. The HOPG samples were cylindrical plates with the graphite c axis nominally oriented along the normal to the plates. The mosaic spread of the c axis reported by the manufacturer was $0.8^\circ \pm 0.2^\circ$. HOPG densities were determined from the measured mass, thickness, and diameter. The dimensions and densities for the HOPG samples are given in table S1. The rear surfaces of the HOPG samples were coated with thin vapor-deposited Al mirrors for velocity interferometry measurements for experiments 2 and 3. For experiment 1, an Al mirror was vapor-deposited onto a polycarbonate window, which was epoxy-bonded to the rear surface of the HOPG. A velocity interferometer system for any reflector (VISAR) (45) was used to record the shock wave arrival at the center of the HOPG rear surface, and several surrounding photon Doppler velocimetry (46) probes were used to determine the impact tilt and shock arrival time at the rear surface of the HOPG.

The x-rays used for the in situ diffraction experiments were generated using the 2.7-cm period undulator (11.556-mm gap) at the 35-ID beamline at the DCS at the APS (Argonne, IL). Four Kirkpatrick-Baez (KB) mirrors (two horizontal and two vertical) were used to focus and filter the incident x-rays, resulting in an x-ray beam height of ~800 μm at the target; the x-ray beam width at the target was ~300 μm for experiment 1 and ~150 μm for experiments 2 and 3. The x-ray beam was centered on the HOPG sample vertically and offset somewhat horizontally from the center of the sample on the impact surface, so that the x-ray beam probed the material closer to the sample center for the XRD frames after impact. The horizontal offset was toward the x-ray beam source side (away from the detector). The horizontal offsets were 2.25, 1.47, and 1.45 mm for experiments 1, 2 and 3, respectively.

The two A-station KB mirrors and two E-station KB mirrors had Rh coatings, and the A-station (E-station) mirrors had pitches of ~2.1 mrad (~2.7 mrad). In addition to focusing the x-rays, the mirrors filtered out x-rays from the fourth and higher harmonics. X-rays from the first and second harmonics were filtered out by placing 250-μm Al and 25-μm Ag filters in the incident beam. The x-ray flux spectrum of the third harmonic was measured using a channel-cut Si monochromator and a PIN diode. A representative flux spectrum is shown in fig. S1.

The in situ XRD experiments on HOPG were performed using the APS 24-bunch mode: X-ray pulses are 153.4 ns apart and have 100-ps duration. A millisecond shutter was used such that the pulsed x-rays were incident on the target starting several milliseconds before impact and ending several milliseconds after impact. During the impact event, the pulsed x-rays passed through the polycarbonate projectile/LiF(100) impactor and the HOPG target in the horizontal plane at an angle of 27.6° relative to the impact surface, as shown in Fig. 1. A four-frame, 150-mm-diameter pixelated x-ray detector was oriented such that the detector plane is perpendicular to the direct x-ray beam. The effective detector pixel size is 86.96 μm. The times at which XRD frames were obtained in the three impact experiments are given in table S2.

The ambient sample-to-detector distances were determined before each experiment by recording a diffraction pattern from a thin polycrystalline Si calibration target. Diffraction simulations for the polycrystalline Si were then performed using the measured flux spectrum (see fig. S1) and varying the sample-to-detector distance in 100-μm increments. The polycrystalline Si calibration target-to-detector distance was determined from the diffraction simulation that best matched the measured Si diffraction peaks. The ambient HOPG sample-to-detector distance (defined as the distance from the intersection of the direct x-ray beam with the center of the HOPG thickness along the direct x-ray beam path) was then calculated by accounting for the different sample and target plate thicknesses for the Si calibration target and the HOPG target. Ambient HOPG sample-to-detector distances are given in table S2. The effective sample-to-detector distance after impact (defined as the distance from the intersection of the direct x-ray beam with the center of the shocked portion of the HOPG thickness along the direct x-ray beam path) differed for each XRD frame. The thickness of the shocked portion of the HOPG also varied between frames. Effective sample-to-detector distances and shocked sample thicknesses are given in table S2 for the second and third XRD frames obtained after impact; the second and third XRD

**Fig. 3. Stress-volume states of shock-compressed ZYB-grade HOPG.** Results shown are for HOPG below the phase-change threshold (47), at the phase-change threshold (34, 38), and above the phase-change threshold (34, 38). XRD results (red squares) and laser interferometry measurements on shocked ZYB-grade HOPG from the present work (blue circles) (38) and from a previous study (open black circles) (34) are shown. The continuum results have comparable uncertainties. The gray band is the elastic HD stress-volume curve for uniaxial strain normal to the (100) HD plane calculated using published second-order elastic constants (38). The band represents ±1% uncertainty in the HD density.
frames were recorded before the shock wave reached the HOPG rear surface. The estimated uncertainty in the effective sample-to-detector distance for each frame is ±300 μm.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi-content/full/3/10/eaao3561/DC1

section S1. In situ HOPG XRD impact experiment details
section S2. Detailed XRDR results
section S3. Detailed XRDR analysis
section S4. XRD simulations
section S5. Graphite and HD structures and HD specific volume
section S6. HOPG continuum response

fig. S1. Representative x-ray flux spectrum for in situ XRD experiments on HOPG.
fig. S2. Diffraction patterns for experiment 1.
fig. S3. Diffraction patterns for experiment 2.
fig. S5. Diffraction patterns for shocked HOPG after subtraction of ambient graphite peaks.
fig. S6. Representative diffraction peaks for several diffraction spots from the third XRD frame from experiment 1.
fig. S7. Average d spacings for several lattice planes from all three 50-GPa HOPG shock compression experiments.
fig. S8. Diffraction patterns and simulations.
fig. S9. Graphite basal plane as viewed along the c axis.
fig. S10. HD basal plane as viewed along the c axis.
fig. S11. Configuration for VISAR experiments (experiments 4 and 5) on ZYB-grade HOPG.
fig. S12. Transmitted particle velocity history measured at ZYB-HOPG/LIF interface for experiment 4.

Fig. S1. Graphite and HD structures and HD specific volume

Table S1. Graphite and HD structures and HD specific volume

Table S2. Experimental parameters for in situ XRD measurements on shock-compressed ZYB-grade HOPG.

Table S3. Diffraction patterns for experiment 2.
Table S4. Diffraction patterns for experiment 3.
Table S5. Diffraction patterns for shocked HOPG after subtraction of ambient graphite peaks.
Table S6. Representative diffraction peaks for several diffraction spots from the third XRD frame from experiment 1.

Table S7. Average d spacings for several lattice planes from all three 50-GPa HOPG shock compression experiments.
Table S8. Results for VISAR transmission experiments on ZYB-grade HOPG.

REFERENCES AND NOTES

26. Complete XRD data and additional Materials and Methods are available as Supplementary Materials.

**Acknowledgments:** Y. Toyoda, P. Rigg, and the DCS staff are thanked for their assistance with the in situ XRD impact experiments. **Funding:** This publication is based on work supported by the U.S. Department of Energy (DOE)/National Nuclear Security Administration (NNSA) under award no. DE-NA0002007. This publication is also based on work performed at the DCS, which is operated by Washington State University under the DOE/NNSA award no. DE-NA0002442. This research used resources of the APS, a DOE Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under contract no. DE-AC02-06CH11357. **Author contributions:** S.J.T., T.J.V., J.M.W., and Y.M.G. designed the study. T.J.V. built and characterized the HOPG targets. S.J.T. and T.J.V. performed the in situ XRD experiments. S.J.T. and S.M.S. analyzed the XRD data. J.M.W. and Y.M.G. did the continuum modeling and simulations. All authors contributed to the writing of the manuscript. **Competing interests:** The authors declare that they have no competing interests. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 11 July 2017
Accepted 27 September 2017
Published 27 October 2017
10.1126/sciadv.aao3561

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Sci Adv 3 (10), eaao3561.
DOI: 10.1126/sciadv.aao3561