Articles

Quenchable Transparent Phase of Carbon

E. D. Miller, D. C. Nesting, and J. V. Badding*

Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802

Received May 20, 1996. Revised Manuscript Received July 29, 1996[⊗]

The sp^3-bonded “transparent phase” of carbon, formed by compression of single-crystal graphite to 18 GPa, has been found to be quenchable to atmospheric pressure at low temperatures (<100 K). The quenched transparent phase reverts to graphite upon warming to room temperature, indicating that there is a surprisingly small activation barrier for a transformation that must involve carbon−carbon bond breakage. Visual observations and Raman spectroscopy are used to document the novel ambient pressure transformation.

Introduction

Carbon exhibits a very rich structural chemistry because it can bond in linear (sp), trigonal (sp^2), and tetrahedral (sp^3) coordination. In the elemental state, many crystalline forms are known such as chemical vapor deposited (CVD) diamond, diamond-like carbon, fullerenes, polymeric fullerenes, nanotubes, cubic diamond, Lonsdaleite (hexagonal diamond), carbynes, linear (sp) carbon, and graphite.[1−5] Amorphous carbon can exhibit both sp^2 and sp^3 bonding in proportions ranging from primarily sp^3 (tetrahedral amorphous carbon) to primarily sp^2 (a-carbon).[6] Recent successes in the synthesis of new forms of carbon[4,5] have stimulated considerable theoretical and experimental interest in the synthesis of other new allotropes.[1,7−10] Though only graphite is thermodynamically stable under ambient conditions, the other thermodynamically metastable forms can exist because strong carbon bonds must be broken and a substantial activation barrier (typically >0.8 eV) must be overcome in the transformation to graphite. Because of this activation barrier, high temperatures and or pressures are generally required for the formation of new phases of carbon. The processes by which these transformations are initiated and proceed are only beginning to be understood yet are of great scientific and technological importance.[11,12] The tranformation of graphite to diamond at high pressures and high temperatures, for example, is of considerable industrial importance.[13]

Here we report the preparation of a form of carbon that exhibits an unprecedented transformation: an optically transparent form with at least partial sp^3 bonding that gradually transforms to graphite upon warming from temperatures below 80 K to room temperature. It is prepared by quenching at low temperatures the “transparent phase” of carbon, which forms when hexagonal graphite is compressed at pressures in excess of 18 GPa.[14,15] At room temperature, the transparent phase cannot be quenched and reverts to graphite upon release of pressure. It is referred to as the transparent phase to distinguish it from cubic or hexagonal diamond, which exist in metastable form under ambient conditions. The observations reported here show that though thermally activated processes must be important, the activation barrier for the transformation of the transparent phase to graphite is surprisingly low. Other known forms of carbon require substantially higher temperatures to induce any type of transformation. The quenched transparent phase may represent a new form of carbon, possibly an intermediate form that exhibits both sp^2 and sp^3 bonding.

Powder diffraction experiments performed on graphite under high pressure in a Drickamer-type high pressure press are suggestive of a phase with a structure related to that of hexagonal diamond (lonsdaleite).[16] High pressure diffraction measurements in a

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* To whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1996.

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S0897-4756(96)00288-8 CCC: $14.00

diamond anvil cell indicated a polytype structure different from that of cubic or hexagonal diamond.[17] Many other investigations of the transparent phase have been performed,[14–16,18] but the differences between the transparent phase and diamond and the reasons it is not quenchable at room temperature remain uncertain.

Experimental Section

High-quality graphite single crystals that precipitated from natural marble were utilized in these studies. The graphite can be separated by dissolving the marble in dilute hydrochloric acid.[19] Using scotch tape, the crystals were cleaved to a thickness estimated to be 1−5 μm based upon optical observations with a microscope, much thicker than the samples of ref 14, which were partially transparent at ambient pressure. Because the penetration depth of light into graphite is only 0.03 μm, these crystals must have been less than 0.1 μm thick. Subsequently the crystals were removed from the adhesive and cleaned with acetone. Individual crystals were then selected from solution using a metal probe, loaded with a potassium bromide medium into a modified Merrill-Bassett diamond anvil cell[20] and compressed at room temperature. The *a* axis, which contains the graphitic planes, was oriented normal to the applied load of the diamond anvil cell. The crystals were maintained at a pressure of 35 GPa for several days.

The entire cell assembly was then cooled to temperatures between 15 and 30 K, the pressure was released, and the upper diamond anvil was removed. The temperature was controlled by a specially designed vertical helium flow cryostat (type SP152-9, Cryo Industries of America, Inc.; Atkinson, NH). A gearbox that engaged a set of four screws in the diamond cell, two right-handed and two left-handed, each with Belleville type washers, was used to release the pressure. The cell was seated in a mount which held the lower half of the diamond cell while allowing removal of the upper half, which contains the upper diamond. Because manipulation of the gearbox and removal of the upper half of the cell must be performed with control rods that extend from the top of the cryostat, after release of pressure it was necessary to rotate the bottom half of the cell containing the sample 90° to allow for access through the horizontal optical axis. Raman spectra were collected by means of a Dilor *XY* spectrometer in conjunction with a Princeton Instrument CCD camera and 514.5 nm excitation. Removal of the upper diamond allowed Raman spectra of the sample to be collected free from interference from the Raman spectrum or the fluorescence of the diamond anvil.

Results and Discussion

Upon increasing the pressure, at 18 GPa the graphite became transparent (Figure 1A), as seen by previous workers.[14,15] After releasing the pressure at low temperature, the center of the samples remained very transparent (Figure 1B), indicating that the transparent phase is quenchable to ambient pressure. The areas surrounding the center became darker but were still transparent. These areas were not compressed to as high a pressure as the center because of radial pressure gradients that are present when a potassium bromide medium is used. The greater transparency of the center of the sample, both at high pressure and after quenching, is likely due to conversion of a greater fraction of this area to the transparent phase by the higher pressure.[15] With increasing temperature the transparency of the sample slowly decreased, darkening at temperatures of 130−170 K, and becoming completely opaque at 260 K (Figure 1C).

Table 1. Line Widths of the Raman Peak Centered near 1581 cm^{-1} and Estimated sp^2 Carbon Domain Sizes at Different Temperatures[a]

T/K	L_a/Å	$\Delta\nu_{1/2}$
<30	≤90	60−80
240	~140	~40
298	≥350	~23

[a] The domain sizes are estimated from the ratios of the intensities of the 1581 cm^{-1} to the 1355 cm^{-1} Raman lines.[22] At the lowest temperatures, the width of the 1581 cm^{-1} line is larger than expected for microcrystalline graphite with a domain size of 90 Å (see text).

To investigate the bonding in the quenched transparent phase, we collected Raman spectra at temperatures below 40 K of transparent sections of the sample (Figure 2A). These spectra exhibit a broad peak ($\Delta\nu_{1/2} \sim$ 60−80 cm^{-1}) centered at 1581 cm^{-1} and another, weaker, broad peak near 1355 cm^{-1} that are characteristic of sp^2 carbon with a very small domain size. In situ Raman spectra of the transparent phase compressed with both helium and xenon quasi-hydrostatic media at high pressure also exhibit a broad peaks near 1581 and 1355 cm^{-1}, but with the peak positions shifted by the application of pressure.[15] The similarity in the Raman spectra strongly suggests that the transparent phase has been quenched at low temperature.

In graphite, the domain size can be estimated from the ratio of the intensities of the E$_{2g}$ first-order mode, centered at 1581 cm^{-1}, to that of the disorder-induced peak centered at 1355 cm^{-1}.[21,22] We assume a similar relationship for the sp^2 carbon of the transparent phase to estimate the domain size. By this analysis the domain size of the sp^2 carbon is ~90 Å (Table 1).

However, the width of the 1581 cm^{-1} Raman peak observed for the quenched transparent phase (60−80 cm^{-1}) is much larger than observed for microcrystalline graphite samples with an average domain size of 90 Å.[22] In microcrystalline graphite samples with very small domain sizes, a peak located at 1620 cm^{-1} next to the E$_{2g}$ mode is present that increases in intensity with decreasing domain size. It has been proposed that the appearance of the 1620 cm^{-1} peak is a result of the breakdown of wave-vector conservation as the domain size decreases.[22] At a domain size of 25 Å, the 1620 cm^{-1} line is observed as a shoulder on the E$_{2g}$ mode. In glassy carbon, which has a domain size less than 25 Å, the two lines merge to form a broad peak with a width of approximately 60 cm^{-1}.[22] The appearance of the peak near 1581 cm^{-1} in the quenched transparent phase, a single broad peak with a width comparable to that observed for glassy carbon, is consistent with a domain size comparable to that of glassy carbon (≤25 Å). However, glassy carbon exhibits a much more intense 1355 cm^{-1} feature than is found for the quenched transparent phase.[22] Therefore, we conclude that though Raman scattering from sp^2 carbon is present in the quenched transparent phase, the Raman spectrum is not that of graphite or glassy carbon. Because the Raman spectra and the optical properties of the quenched transparent phase are not characteristic of graphite or

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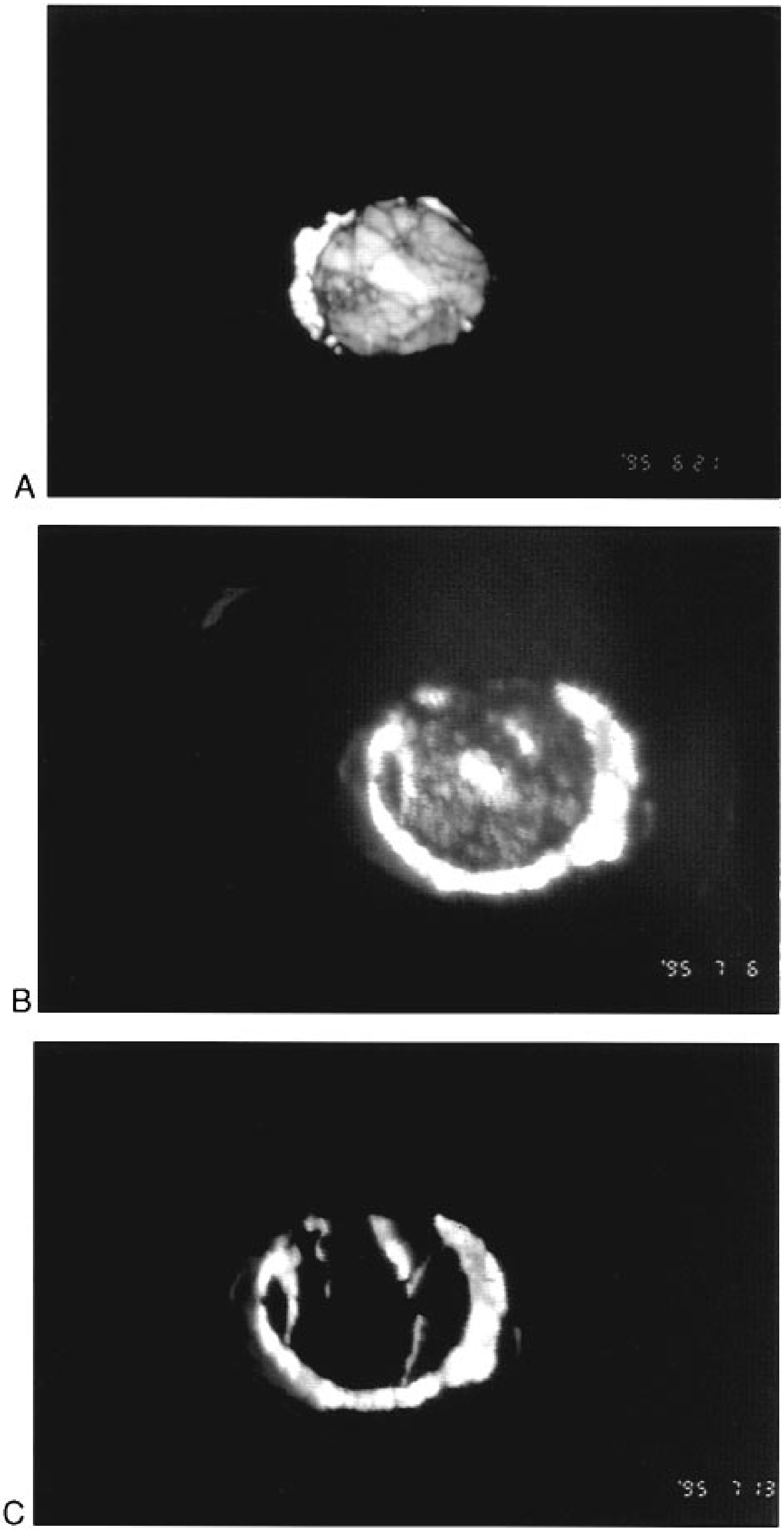

Figure 1. (A) Transparent phase at 25 GPa, 300 K. (B) Quenched transparent phase after release of pressure to 0.1 MPa at a temperature less than 30 K. The sample remains transparent, particularly in the center. (C) Sample after warming to 300 K. Areas that were formerly transparent have become opaque. During warming to room temperature, the sample cracked in several places, suggesting an expansion as a result of the transformation to graphite.

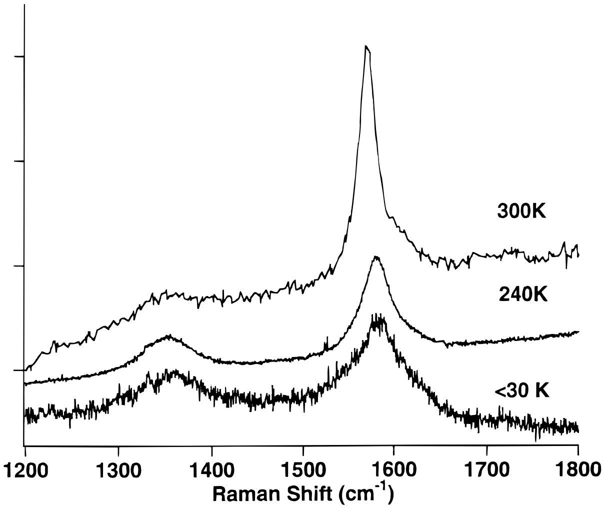

Figure 2. Raman spectra of quenched transparent phase (A) at 30 K. Broad Raman peaks at 1581 cm^{-1} and 1355 cm^{-1} indicative of the presence of sp^2 carbon are present. (B) At 240 K the 1581 cm^{-1} line has become narrower and stronger. (C) By 300 K the Raman spectrum is characteristic of graphite. The background level for the 300 K spectrum was considerably lower than at the other two temperatures. This is not apparent from the figure because the background levels are not to scale.

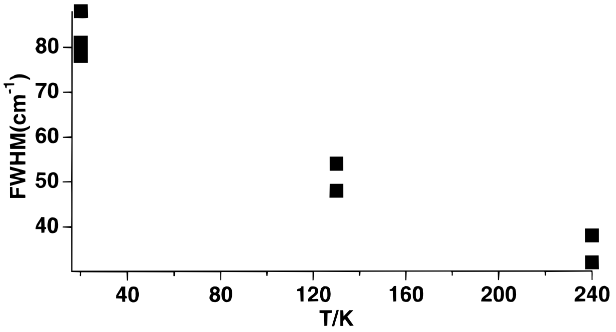

Figure 3. Line widths of the Raman peak centered near 1581 cm^{-1} as a function of temperature. Each data point represents a linewidth measured at a different location on the sample. The transformation to graphite is associated with narrowing of the line widths, consistent with an increase in the size of the sp^2 carbon domains.

glassy carbon, the domain sizes estimated here should be compared with those obtained by diffraction techniques.

Raman spectra collected upon warming to room temperature provide evidence that the domain size of the sp^2 carbon increases with temperature. With increasing temperature, the width of the 1581 cm^{-1} Raman peak narrows (Figures 2B,C and 3), approaching a value at 298 K of approximately 20 cm^{-1}, characteristic of graphite; the decrease in the width of this peak is paralleled by the decrease in the transparency of the sample. The 1581 cm^{-1} peak also became much more intense relative to the 1355 cm^{-1} peak, which is also consistent with an increase in domain size. Analysis of the relative intensities shows that by 298 K the sample has transformed to microcrystalline graphite with a domain size of at least 350 Å (Table 1).

The transparency of the samples at high pressure and after quenching implies that substantial amounts of sp^3 carbon must be present. Supporting this conclusion, optical reflectivity measurements show that the high-pressure phase has an index of refraction approaching that of diamond.[23] Considerable background fluorescence, which is often found in sp^3 phases of carbon, was present in the Raman spectrum of the quenched phase. After warming to room temperature, the background level decreased greatly. Further evidence for sp^3 bonding comes from experiments in which the transparent phase induced ring cracks in diamond anvils upon compression to 50 GPa, demonstrating that it is as hard as diamond.[17] Molecular dynamics simulations indicate that compression perpendicular to the *c* axis of graphite induces shifting, buckling, and bonding of the graphitic planes in a concerted process to form sp^3 phases.[12]

Though we could observe the Raman spectrum of the quenched transparent phase without interference from the Raman spectrum of the diamond anvils, no Raman scattering from sp^3 carbon could be detected. This implies that the sp^2 and sp^3 domains must be mixed on a small length scale (less than 0.5 μm). The Raman spectra of mixtures of sp^2 carbon and sp^3 carbon phases for which the domain size is large are dominated by scattering from the sp^3 phase, which has a larger penetration depth and therefore a larger scattering volume. As the domain size decreases, the penetration depth of the sample decreases and the scattering from sp^2 carbon, which is inherently approximately 50 times stronger than that of sp^3 carbon, begins to dominate.[24] Graphitic Raman peaks are also observed in diamond-like films prepared by chemical vapor deposition (CVD) techniques.[25] These films have a Raman spectrum dominated by graphitic features but still have substantial amounts of sp^3 carbon, as documented by electron energy loss spectroscopy (EELS), which can give direct information about the bonding state of carbon.

It is surprising that the quenched transparent phase, which exhibits properties characteristic of carbon in a bonding environment with four strong bonds (typical C$-$C bond enthalpies are 345 kJ/mol[26]), transforms to graphite so readily upon warming, a process that requires breakage of the C$-$C bonds. The formation of sp^3 bonded carbon from graphite upon static compression to 18 GPa can proceed even if the activation barrier is quite high. This is because the volume of activation for the transformation is negative, allowing a large activation barrier to be overcome primarily by pressure alone. In the reverse process, after release of pressure, there is no means to overcome a large activation barrier because both the pressures and temperatures are low. Therefore, we conclude that the activation energy required to initiate transformation must be small compared with typical activation energies required to break C$-$C bonds.

The observed kinetics and the increase in the sp^2 carbon domain size upon warming suggest that the transition involves a concerted process in which the sp^2 and sp^3 bonded domains maintain a specific, topochemical relationship. This implies that many of the sp^2 and sp^3 carbon domains must be bonded together and are not divided by grain boundaries. Because nanocrystalline diamond and nanocrystalline graphite are both

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kinetically stable, the carbon in the quenched transparent phase must be organized differently from mixtures of these two phases, which would not exhibit the behavior reported here. Our analysis of the Raman spectra of the quenched transparent phase suggests that the sp^2 carbon domain size could be as small as 15−20 Å. Theoretical calculations show that microcrystalline graphite domains with sizes of less than 25 Å have an electronic structure different from bulk graphite.[27] If the sp^2 domains are smaller than 25 Å, the quenched transparent phase must represent a new intermediate sp^2/sp^3 form of carbon that is metastable only below 100 K. Further investigation should be performed on the quenched transparent phase by techniques such as low-temperature transmission electron microscopy (TEM) and EELS,[27] a challenging but not impossible experiment in view of the necessity of loading the quenched transparent phase at low temperatures into the electron microscope.

The kinetic stability of sp^3 carbon relative to sp^2 carbon is crucial to the technological application of diamond. Our results demonstrate that it is possible for sp^3 carbon that is kinetically stable at ambient pressure to transform to sp^2 carbon at temperatures much lower than previously thought. As new forms of carbon are synthesized or existing forms are prepared using novel techniques, the potential for facile transformation of sp^3 to sp^2 carbon must be considered. In efforts to synthesize carbon nitride compounds by laser heating appropriate precursors at pressures of 35−40 GPa, we have prepared samples that are transparent after release of pressure at room temperature, but then slowly become opaque, suggesting spontaneous transformation of sp^3 carbon to sp^2 carbon. Examination of these samples by TEM and EELS reveals crystalline sp^2 carbon.[28] Similar transformations may be possible in diamond or diamond-like carbon prepared by chemical vapor deposition (CVD), which can contain varying proportions of sp^2 and sp^3 carbon and may exhibit other structural features not found in pure diamond.[3]

Acknowledgment. We thank Giacinto Scoles of Princeton University for providing the graphite crystals used in these experiments. This work was supported by the National Science Foundation under Grant DMR-9314020 and a NYI award to J.V.B. and by a David and Lucile Packard Foundation Fellowship to J.V.B.

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