High-Pressure Synthesis of sp^2-Bonded Carbon Nitrides

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We have synthesized amorphous sp^2-bonded carbon nitrides at high pressure. A precursor composed of carbon and nitrogen, tetracyanoethylene, was compressed in a diamond anvil cell and laser heated to approximately 2000 °C. Transmission electron microscopy, electron diffraction, electron energy loss spectroscopy, and energy-dispersive X-ray analysis have been used to characterize the structure, bonding, and composition of the carbon nitrides. The amount of nitrogen incorporated into the network increases with pressure, ranging from 24% (C_3N) at 18 GPa to 38% at 42 GPa ($C_3N_{1.9}$), which represents the most nitrogen-rich carbon nitride yet prepared under pressure. A crystalline carbon phase is also found.

Introduction

The synthesis of covalently bonded, extended networks composed of carbon and nitrogen is an area of intense research. It has been predicted that carbon nitrides that have tetrahedral sp^3 carbon could exhibit bulk moduli and hardnesses comparable to or even exceeding that of diamond.[1−3] We note that though much attention has been focused on carbon nitrides with the β-Si_3N_4 structure,[1,2] many different crystalline and amorphous carbon nitride structures can be envisioned.[3,4] Techniques such as thermal decomposition of molecular precursors containing carbon and nitrogen, deposition with atomic beams, and high-pressure shock wave synthesis have been used in attempts to synthesize carbon nitrides.[5−11] With thermal decomposition techniques amorphous sp^2-bonded carbon nitrides ranging in composition from C_5N to C_3N_4 have been prepared.[5,7] Materials prepared by beam deposition and laser-ablation techniques are reported to be mixtures of amorphous sp^2 phases and crystalline phases that have some diffraction lines matching the pattern expected for either β-C_3N_4 or α-C_3N_4.[12,13] However, no information about the bonding (sp^2 vs sp^3) in the crystalline regions or their composition, which can be determined from electron energy loss (EELS) spectra,[14] has been reported.[8,12,13]

We believe that high-pressure techniques offer the most promising route for the first synthesis of crystalline carbon nitrides that contain sp^3 carbon. Diamond, for example, was first synthesized by high-pressure techniques.[15] Following synthesis at high pressure, a substantial effort was required to determine the appropriate conditions for synthesis of diamond by deposition techniques.[16] Two different routes can be envisioned for the synthesis at high pressure of carbon nitrides containing tetrahedral carbon. If appropriate precursors and reaction conditions can be found, compression at room temperature could lead to polymerization, potentially topochemically, into an extended crystalline or amorphous carbon−nitrogen network. Virtually any compound containing unsaturated bonds can be polymerized under pressure.[17−21] Alternatively, pressure can be used to alter the thermodynamics of the reaction to form carbon nitrides.[22] The thermodynamic driving force for the formation of carbon nitrides under pressure is the large volume of molecular nitrogen relative to three-dimensionally bonded carbon nitrides.[18,22] In these syntheses, heating is required to effect a reconstructive transformation to a carbon nitride that is thermodynamically stable at high pressure. Because the carbon−nitrogen and carbon−carbon bonds in candidate carbon nitride structures are very strong, it is reasonable to expect that crystalline carbon nitrides will be quenchable in metastable form to ambient pressure.[1,2,18,22]

Here we report the synthesis at high pressure of sp^2-bonded carbon nitrides using a laser-heated diamond anvil cell. Tetracyanoethylene (TCNE), composition C_6N_4, was used as a precursor for the synthesis of carbon nitrides. This compound provides a source of nitrogen and carbon that are mixed on an atomic scale and contains no other elements. The use of a precursor such as TCNE does not preclude the formation of carbon nitrides containing more nitrogen (e.g., C_4N_3,[4] C_3N_4)

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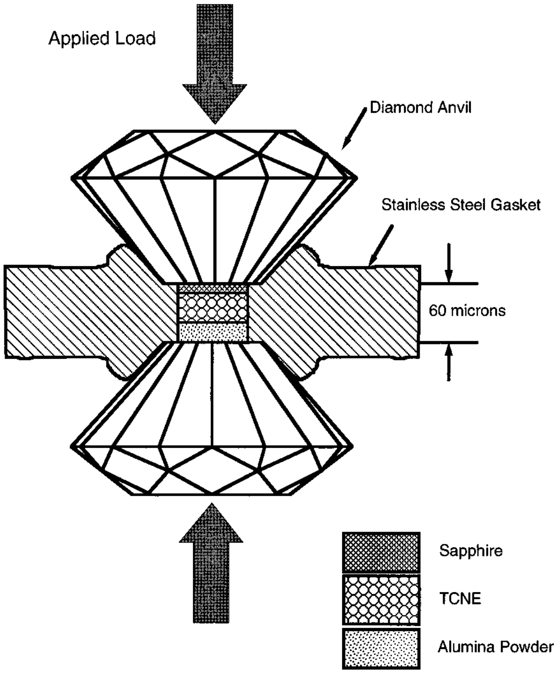

Figure 1. Schematic of the configuration of the diamond anvil sample chamber. The sample is sandwiched between a layer of fine alumina powder and a thin plate of sapphire. Laser heating is performed through the transparent sapphire plate.

since phase separation into diamond and carbon nitride should occur if the carbon nitride is thermodynamically stable at the reaction pressure. The precursor was compressed to pressures of up to 42 GPa (1 GPa ≈ 10 000 atm) and laser heated to approximately 2000 °C. A two-phase product, containing amorphous sp^2-bonded carbon nitride and crystalline carbon, was formed; the relative proportions of the two phases depends upon the duration of laser heating. The amount of nitrogen incorporated into the network increases with pressure, ranging from 24% (C_3N) at 18 GPa to 38% at 42 GPa ($C_3N_{1.9}$). These materials represent the most nitrogen-rich carbon nitrides yet prepared under pressure. Infrared spectra suggest that they exhibit significant structural differences from sp^2-bonded carbon nitrides prepared by deposition techniques.

Experimental Procedure

Purification of Precursors. TCNE was purchased from Aldrich Chemicals (98% purity) and was purified by vacuum sublimation at 100 °C immediately before use. The resulting white crystals had a sharp melting point of 198 °C. The infrared spectrum of these crystals contained no lines due to impurities.

Syntheses. A Mao-Bell diamond anvil cell[23,24] was used for the high-pressure syntheses. TCNE was ground to a fine powder in an agate mortar and pestle, loaded into a 150 μm diameter hole in a stainless steel gasket that was partially filled with a fine alumina powder on the bottom, and covered with a ~12 μm thick sapphire plate (Figure 1). Both the alumina powder and the sapphire plate thermally insulate the sample from the diamonds during laser heating,[25] protecting the diamond faces from damage and also allowing more even heating of the sample. Pressure was measured by means of ruby fluorescence collected with a Dilor *XY* triple spectrometer equipped with a Princeton Instruments liquid nitrogen cooled TKB1024 CCD detector.[24,26] The 514.5 nm line of a Spectra-Physics Model 164 argon ion laser at 35° incidence was used to excite the ruby fluorescence. The sample was heated with a focused beam from a Quantronix 4216D Nd:YLF infrared laser producing 32 W TEM$_{00}$ in continuous-wave (cw) mode at 1053 nm. The temperature of the laser heated spot can be controlled by varying the laser power. We did not directly measure temperatures[27] but instead estimated relative temperatures from the color and brightness of the laser spot.

Analyses. Analysis of the samples was carried out using electron microscopy techniques. Techniques such as Rutherford backscattering (RBS), X-ray photoelectron spectroscopy (XPS), and other surface techniques can give only the composition of the bulk.[11,28] For multiphase samples, such as those typically produced in syntheses of carbon nitrides,[7,12,13] it is crucial to obtain compositional, bonding, and structural information on each of the individual phases in a sample.[8,22] Transmission electron microscopy (TEM/STEM), selected area electron diffraction (SAED), windowless energy-dispersive X-ray analysis (WEDX), and electron energy loss spectroscopy (EELS) were used to characterize each of the phases in the quenched samples. After the samples were crushed between sapphire disks and dispersed on holey carbon film grids, each of these techniques was used to probe individual particles.

We expect that the error in the WEDX measurement is approximately 5% due to the lack of suitable standards for the determination of k factors.[29] Quantification of electron energy loss spectra is better understood for the analysis of light elements. Computer programs for determining the hydrogenic k-shell cross sections are widely available.[30] We estimate that the compositions determined by the EELS method are accurate to approximately 3%.

Imaging and diffraction data were collected on either a JEOL 1200 EXII electron microscope operated at 120 keV or a JEOL 4000 EX operated at 400 keV. Further analyses, EDX and EELS, were performed using a Vacuum Generators HB501A field emission scanning transmission electron microscope (STEM) operated at 100 keV. The STEM is equipped with both a serial and parallel EELS detector and a Link Systems LZ-5 windowless energy-dispersive X-ray spectrometer (WEDX). The grids were loaded into beryllium holders and were baked at 170 °C in the STEM antechamber to remove any volatile contaminants.

Infrared spectroscopic analysis was performed at line U-2B of the National Synchrotron Light Source of Brookhaven National Laboratory using a Spectra Tech “IR μs” integrated rapid-scan FTIR with an infrared microscope.[31,32] The samples were embedded in potassium bromide and were approximately 30 μm thick. Several spectra from different points within the sample were collected. Background spectra from sample regions containing only KBr were also collected. Raman spectra were collected using the same experimental conditions used for ruby fluorescence.

Results and Discussion

At pressures between 4 and 6 GPa, the molecular precursor TCNE develops a transparent red appearance. The transition from colorless to red is due to closure of

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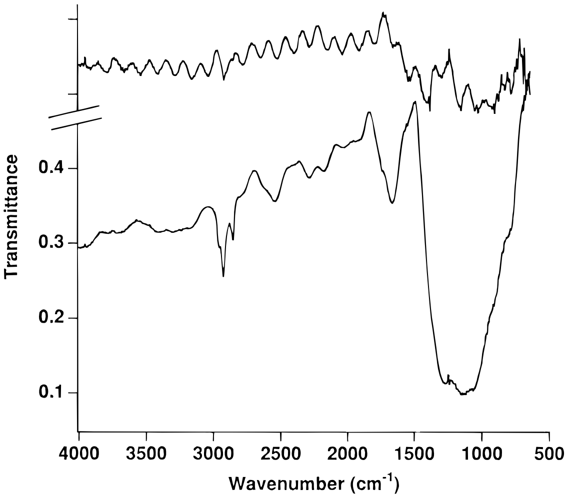

Figure 2. Infrared absorption spectrum of the sample laser heated at 42 GPa collected after removal from the diamond anvil cell (bottom). Background spectra were collected on pure KBr (top).

Table 1. Comparison of Sample Crystallinity, Appearance, and Composition as a Function of Pressure and Heating Duration

run no.	run pressure (GPa)	heating time	sample appearance	phase no.	crystallinity of phase	nitrogen composition (%)
1	18	short	deep orange	1	amorphous	24
				2	crystalline	0
2	42	short	deep orange	1	amorphous	38
				2	crystalline	0
3	42	long	light orange	1	crystalline	0

the energy gap for the $\pi-\pi^*$ transition under pressure as a result of enhanced intermolecular interactions.[33] Upon compression to pressures above 14 GPa, TCNE begins to polymerize through the nitrile groups and becomes opaque.[18,34] The opacity is associated with the development of graphitic structures during polymerization.[18] Several heating and pressure regimes were investigated as discussed below. The results are tabulated in Table 1.

After laser heating for several minutes at pressures ranging from 18 to 42 GPa and temperatures of ~2000 °C, the pressure dropped several GPa and the samples became deep orange and transparent. Since graphitic carbon nitrides, like graphite itself, should have a very small bandgap and a shallow penetration depth for visible light (~300 Å in graphite), the optical transparency indicates the presence of at least partial sp^3 bonding.[35,36] Immediately after quenching to ambient pressure the samples remained transparent. However, some of the samples slowly became opaque with time, suggesting unstable sp^3-bonded material may be undergoing spontaneous transformation to sp^2 bonding.[35,36]

Infrared spectra (Figure 2) of the 42 GPa sample contain several peaks superimposed on a background containing interference fringes that arise because of the sample geometry. The spectra do not contain peaks characteristic of nitriles, which are typically present near 2200 cm^{-1}. A small feature at 2173 cm^{-1} that might be attributed to a nitrile stretch was also found in all of the background spectra, indicating that it is due to an interference fringe. Because terminal nitrile absorptions can be weak, it is not possible to rule out the presence of some sp-hybridized nitrile groups from the infrared spectra alone. Raman spectra collected on the 42 GPa sample exhibited background fluorescence but no peaks in the 2200 cm^{-1} region. Since the intensities of Raman peaks due to nitriles tend to be strong, this also suggests that the number of unreacted nitriles remaining in the sample is small. As mentioned previously, nitriles and other unsaturated groups react to form more extended structures upon compression to high pressure.[21] Heating of carbon nitrides produced by laser ablation significantly reduces the number of nitrile groups present.[8] In view of the extreme pressures and temperatures the 42 GPa sample has been subjected to and the absence of nitrile peaks in the Raman and infrared spectra, we conclude that the number of nitriles in this sample must be quite small.

The features at 2929 and 2856 cm^{-1} in the infrared spectrum, which have shoulders at 2953 and 2868 cm^{-1}, are characteristic of hydrogen bonded to sp^3 carbon. Similar features are found in the infrared spectra of chemical vapor deposited (CVD) diamond films that contain small amounts of hydrogen.[37] The intensity of the absorption varies monotonically with hydrogen content. In diamond films containing 3 atom % hydrogen, the absorption coefficient for the strongest C−H absorption is approximately 100 cm^{-1}.[38] In the 30 μm thick 42 GPa sample, an absorption with this intensity would lead to a change in transmittance of approximately 24%, considerably larger than observed for the C−H stretch in Figure 2. We conclude that the amount of hydrogen impurity incorporated into the sample must be on the order of a few percent or less. Contamination of sample or the KBr it was embedded in from atmospheric water vapor is the most likely source of this impurity.

The weak two-phonon bands found in the infrared spectrum of diamond near 2200 cm^{-1} were not observed.[39] The broad bands centered near 1659 and 1138 cm^{-1} can be attributed to carbon−carbon and/or carbon−nitrogen double bond and carbon−nitrogen single-bond stretching modes, respectively. The presence of these bands and the absence of nitriles indicates incorporation of nitrogen into a carbon−nitride network.

Two phases, one crystalline and one amorphous, were found by analysis of SAED patterns collected on the samples compressed to 18 and 42 GPa and laser heated for several minutes (Table 1). By EELS and WEDX analysis the crystalline phase was found to be pure carbon. The carbon K edge in the EELS spectrum contains a strong π^* feature, indicating primarily sp^2 bonding[14,40] and suggesting that the crystalline carbon phase could be graphite. However, SAED patterns collected on this phase exhibit single-crystal spot patterns that contain interplanar spacings that cannot be

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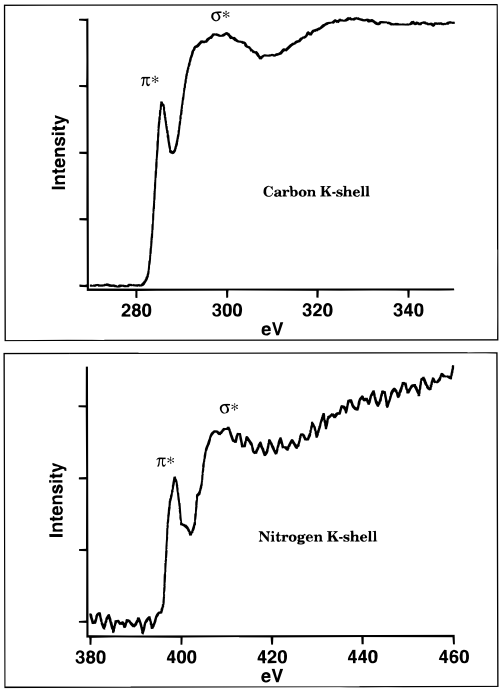

Figure 3. Parallel EELS spectrum of the nitrogen and carbon K edges for the sample laser heated at 42 GPa . The pre-edge peaks at 285.5 eV (C) and 398.5 eV (N) are due to transitions from 1s to π^* states. The peaks at 292 eV (C) and 407.5 eV (N) are due to transitions from 1s to σ^* states. The presence of a strong π^* peak is indicative of sp^2 bonding.

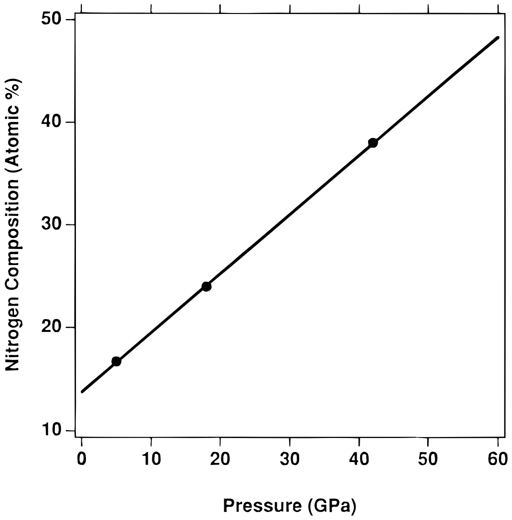

Figure 4. Nitrogen composition vs pressure for sp^2-bonded carbon nitride. Data at 5 GPa are from ref 6. The line drawn through the data points is a guide to the eye. The material synthesized at 42 GPa represents the most nitrogen-rich carbon nitride yet prepared under pressure. The relationship between pressure and nitrogen content suggests that more nitrogen-rich carbon nitrides may be preparable at higher pressures.

attributed to graphite, diamond, or londsdaleite (hexagonal diamond). The transparency of the samples and the position of the C−H stretching modes in the infrared spectra are suggestive of the presence of sp^3 bonding. Therefore, it is surprising that this phase is sp^2 bonded. Further characterization of this crystalline phase will be reported in the future.

The amorphous phase is a sp^2-bonded carbon nitride. The nitrogen composition determined by WEDX analysis is 21% for the 18 GPa sample and 34% for the 42 GPa sample. The nitrogen content derived from EELS analysis is 24% for the 18 GPa sample and 38% for the 42 GPa sample, in good agreement with the compositions determined by WEDX (Table 1). As described in the Experimental section, we expect the compositional analysis derived from the EELS spectra to be more accurate. Both the nitrogen and carbon edges observed in the EELS spectra contained strong π^* features, indicating primarily sp^2 bonding (Figure 3). The similarity in the shapes of the nitrogen and carbon edges indicates that both nitrogen and carbon must be part of the network.[41] The postedge fine structure of the EELS spectrum is weak and broad, which is consistent with a material having an amorphous structure.[40,42,43]

The deep orange color of the samples is due to the of the sp^2-bonded amorphous carbon nitride. The transparency of the samples does not preclude the presence of substantial amounts of sp^2-bonded material. If sp^2 and sp^3 carbon are mixed on a scale smaller than the wavelength of visible light, a mixture containing substantial amounts of sp^2-bonded material can still be partially transparent.[44]

The most notable feature in Table 1 is that the nitrogen content increases with increasing pressure. By 42 GPa, the nitrogen content (38%), determined from the EELS spectra, is nearly as high as the precursor tetracyanoethylene (40%). This demonstrates that under appropriate synthesis conditions carbon nitrides containing substantial amounts of nitrogen can be prepared under pressure. This phase is the most nitrogen rich carbon nitride yet prepared with high-pressure techniques (Figure 4). As mentioned previously, physical deposition techniques can produce amorphous carbon nitrides with nitrogen composition as high as 50%, but infrared spectroscopy shows that as the nitrogen content increases in these materials, the nitrogen is incorporated as terminal nitrile groups.[8] Thermal decomposition of appropriate precursors can form an amorphous structure with the stoichiometry C_3N_4 that contains only small numbers of terminal nitrile groups.[5]

The infrared spectra of the material compressed to 42 GPa differs from the infrared spectra of carbon nitrides prepared by other techniques. Carbon nitrides prepared by thermal decomposition or physical deposition exhibit very broad peaks in the range 1650−1150 cm^{-1},[5,8] encompassing the carbon−nitrogen and carbon−carbon bond stretch regions. In contrast, two discrete peaks are observed in same region in the infrared spectrum of the 42 GPa sample that are centered near 1659 and 1138 cm^{-1}. Some of the infrared absorption in this material may be coming from the sp^3-bonded phase; a broad feature from below 900 to about 1350 cm^{-1} is found in diamond that has incorporated small amounts (<0.3%) of nitrogen.[39] However, it is likely that a significant portion of the absorption is due to the sp^2-bonded amorphous phase because the transparency of the 30 μm thick sample in the visible and IR

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(maximum transmission 50%) is less than would be expected for pure sp^3-bonded carbon, even if nitrogen were incorporated.[39] The differences in the infrared spectra between the carbon nitride prepared under high pressure and the carbon nitrides prepared by thermal or physical decomposition suggest that these materials may exhibit significant structural differences, which should be characterizable by further analysis with electron microscopy techniques.

We compressed another tetracyanoethylene sample to 41 GPa and heated for a longer period of time (1 h). After heating, the pressure dropped to 35 GPa. Compared to samples prepared with shorter heating times, this sample was a lighter orange and more transparent, suggesting transformation of more of the sample to sp^3 bonding (Table 1). In situ Raman spectra collected at 31 GPa on this sample exhibited peaks located at 2378 and 2404 cm^{-1} characteristic of the molecular vibron of nitrogen in the solid state.[23] EELS spectra exhibit only a very weak π* feature, indicating that a large fraction of this sample is sp^3-bonded. No evidence of incorporation of nitrogen was found. We conclude that at pressures below 42 GPa, extended heating to temperatures of ~2000 °C induces loss of nitrogen, which is retained within the sample chamber of the diamond anvil cell.

LDA calculations predict that sp^3-bonded carbon nitrides are only about 20 kJ/mol less stable than sp^2-bonded carbon nitrides.[3] The experiments reported here show that laser heating of tetracyanoethylene at a pressure 42 GPa can produce amorphous sp^2-bonded carbon nitride. By analogy with the graphite-to-diamond transition, further compression and heating of this material should induce a transition to a denser, sp^3-bonded, crystalline carbon nitride. Since we have observed that nitrogen is lost upon more extended laser heating at 42 GPa, it is evident that higher pressures will be required for the equilibrium synthesis of a crystalline sp^3-bonded carbon nitride. By estimating cohesive energies of carbon nitrides from bond strengths and integration of the equations of states of products and reactants to obtain the changes in the free energy of formation reactions such as

$$3C + 2N_2 = C_3N_4 \tag{1}$$

under pressure, we have determined that pressures in the range 50−150 GPa will likely be necessary for the formation of crystalline carbon nitrides,[22] in agreement with the present experimental observations. Pressures in excess of 200 GPa are within the experimental capabilities of current diamond cell technology.[23] Experiments at higher pressures are in progress.

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