



Shock-compression of C–N precursors for possible synthesis of β -C₃N₄

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Received 28 October 1999; accepted 25 August 2000

Abstract

We report on the possible synthesis of the theoretically predicted β -phase of carbon nitride (C₃N₄) by shock compression of sodium dicyanamide mixed with sodium azide and carbon tetra-iodide. Shock-compression experiments were performed on starting precursor blended with ~95 wt.% Cu powder, statically pressed in steel capsules. The capsules were impacted under conditions of constant shock amplitude, but varying shock-pulse duration. TEM analysis of the recovered shock-compressed residue showed crystallites of a cubic C–N compound dispersed in an amorphous matrix, with overall yield of the crystalline phase being a function of the shock-pulse duration. Parallel-detection electron energy loss spectroscopy of the nitrogen-containing crystallites revealed diamond-like sp³ bonding. Infra-red spectroscopy indicated absorption lines in regions calculated to be appropriate for β -C₃N₄. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: C. Transmission electron microscopy; Electron energy loss spectroscopy; Infrared spectroscopy

1. Introduction

Various types of pressure-less [1,2] as well as static and dynamic high-pressure techniques [3,4], have been successfully employed for synthesizing the two hardest known materials — diamond with sp³ type carbon bonding and the cubic-phase of boron nitride. Synthesis of these super-hard materials has been accomplished not only via transformation of graphitic or amorphous precursors into the cubic phase, but also via chemical reaction of the decomposing carbonaceous precursors with other reactants [3]. The high-pressure shock-compression loading technique has proven to be an important method, not only for fundamental studies of structural and chemical changes, but also for the post-mortem characterization and property evaluation of the recovered high-pressure phases and metastable compounds [5,6].

The metastable tetrahedral phase of carbon nitride (β -C₃N₄) has been predicted by Cohen [7–9] using both a

semi-empirical scaling relationship and a pseudo-potential total energy calculation, to have bulk modulus approaching that of diamond and exceeding that of cubic boron nitride. The semi-empirical model [7–9] expresses the bulk modulus, B , in GPa, as: $B = N_c/4\{(1971 - 220 \times I)/d^{3.5}\}$, where N_c is coordination number, d is bond length in Å, and I is a measure of the ionicity of the compound. The form of the equation shows a strong dependence on bond length and a weak dependence on the degree of ionicity. Thus, for diamond, assuming $I = 0$, $N_c = 4$, and $d = 1.54$ Å, one obtains $B = 435$ GPa, which is in good agreement with an experimental value of bulk modulus equal to 443 GPa. Similarly, predictions for c-BN reveal bulk modulus exactly the same as the experimental value of 369 GPa, and for β -Si₃N₄ a predicted value of 230 GPa compared to the experimental value of 250 GPa. Based on a crystal structure of β -phase C₃N₄, with a coordination number equal to 3.43 and bond length of 1.43 Å, the bulk modulus of this compound is calculated to be 414 GPa. Likewise pseudopotential calculations predict the bulk modulus of β -C₃N₄ to be equal to 427 GPa [7–9].

Synthesis of the theoretically predicted β -C₃N₄ super-hard material is complicated because, unlike diamond, it involves two chemical components: sp³-bonded carbon

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and sp^2 -bonded nitrogen. Several attempts have been made to synthesize carbon nitride using a variety of techniques [10–19]. Most of the approaches, in general, have resulted in the formation of hydrogenated or partially crystalline compounds, or non-stoichiometric (nitrogen deficient) compounds. Haller et al. [10] patented the synthesis of β - C_3N_4 and α - C_3N_4 compounds by sputter deposition. Their synthesized films had a nominal composition of C_3N_2 (40 at.% N) with ~ 12 at.% oxygen. Chen et al. [11] also attempted the synthesis of carbon–nitride compounds by sputter deposition. They obtained mixtures of amorphous and crystalline forms which were nitrogen deficient (29 at.% N) on average, and contained about 3 at.% oxygen. Niu et al. [12] reported the synthesis of β - C_3N_4 by pulsed laser ablation of graphite targets combined with an intense atomic nitrogen source with kinetic energies exceeding 1 eV. Up to 40 at.% N was incorporated on average, and photoelectron spectroscopy confirmed C–N covalent bonds.

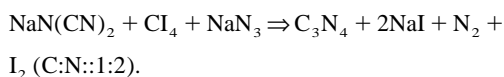
Shock compression of C–N–H-containing precursors has been studied by Wixom [17] to prepare β - C_3N_4 . While no carbon–nitride compounds were formed, their results were very encouraging. Products of decomposition of the precursor materials, containing well-ordered diamond were recovered. Later, the results of Ricci et al. [18] and Sekine [19] using plasma enhanced chemical vapor deposition and shock synthesis, respectively, indicated that the presence of hydrogen in the precursor was severely detrimental to the synthesis process. The results obtained by Wixom [17] and Sekine [19] demonstrated that decomposition of organic precursors and subsequent chemical reactions do occur during shock-compression. Their results also affirmed that metastable reaction products, such as the ordered diamond phase, can be kinetically captured if just enough shock energy is used to decompose the reactants and quench the accompanying thermal energy.

In the present work, synthesis of possible metastable β -phase C_3N_4 was studied by a method employing shock-induced decomposition and chemical reaction in precursors of a compound containing C–N seed molecules and excess carbon and nitrogen, but no hydrogen. Recent theoretical studies as well as experimental investigations of time-resolved measurements have revealed that chemical reactions resulting in the formation of compounds (in highly activated state) can indeed occur during the micro-second duration of the high-pressure shock-compression state [20–23]. The influence of shock-pressure pulse-duration on the yield of the recovered compound was also studied by performing impact experiments using projectiles of two different flyer-plate thicknesses.

2. Experimental procedure

The precursor selected in the present work was hydrogen-free, and it contained constituents (other than carbon

and nitrogen) that would form either stable diatomic gases or ionic salts. Hence, sodium dicyanamide [$NaN(CN)_2$] was selected as the main precursor which would also provide a seed for heterogeneous nucleation of the CN compound, and carbon tetra-iodide (CI_4) and sodium azide (NaN_3) were included as additional sources of carbon and nitrogen, respectively. Compounds of commercial purity were purchased from Aldrich and mixed to produce appropriate atomic ratios of carbon and nitrogen. The expected reaction, stated below, was based on the assumptions that the azide group would lose a nitrogen molecule, sodium and iodine would form an ionic salt, and excess nitrogen would form a diatomic gas



The precursor mixture was then blended with 95 wt.% copper powder (added to quench the heat generated during shock-compression and exothermic chemical reaction) and packed in steel capsules at $\sim 85\%$ theoretical maximum density (TMD) for shock synthesis experiments.

Shock-compression experiments performed in a previous study by Wixom [17] used extreme pressures (~ 100 GPa), typical of those appropriate for diamond synthesis via phase transformation of graphite. The present work was based on chemical reactions between products of decomposing organic precursors, which are expected to occur at much lower shock pressures. Hence, the experiments were performed using a three-capsule gas-gun impact fixture (shown schematically in Fig. 1) at an impact velocity of ~ 700 m/s, using projectiles with flyer plates of two thicknesses (4.75 mm and 9.5 mm) to yield different pulse durations. The incident one-dimensional shock pressure for the gas-gun impact experiments at 700 m/s impact velocity, was calculated to be ~ 2 GPa, and the maximum peak pressure generated due to two-dimensional radial wave focusing effects was determined to be 20–25 GPa. The corresponding shock pulse durations for the two gas gun experiments were calculated to be ~ 1.8 μ s with the 4.75-mm flyer thickness and 3.6 μ s with the 9.5-mm thickness flyer plate. It should be noted that these estimated shock conditions are those for pressed copper powder (95 wt.% of total mass). The small fraction of organic precursor used and lack of their available Hugoniot characteristics precluded determination of the shock conditions in the precursors. Hence, the differences in shock conditions are only for qualitative comparison.

Following shock-compression, the compacts were recovered by machining the steel capsules. Boiling concentrated nitric acid was used to dissolve the copper and product salts from the recovered shock-compressed material. Typical yields of residue recovered were ~ 50 – 100 mg of fine black powder, collected by filtration on a fine glass frit. Implicit in this sample recovery procedure is the expected assumption that carbon nitride is insoluble in

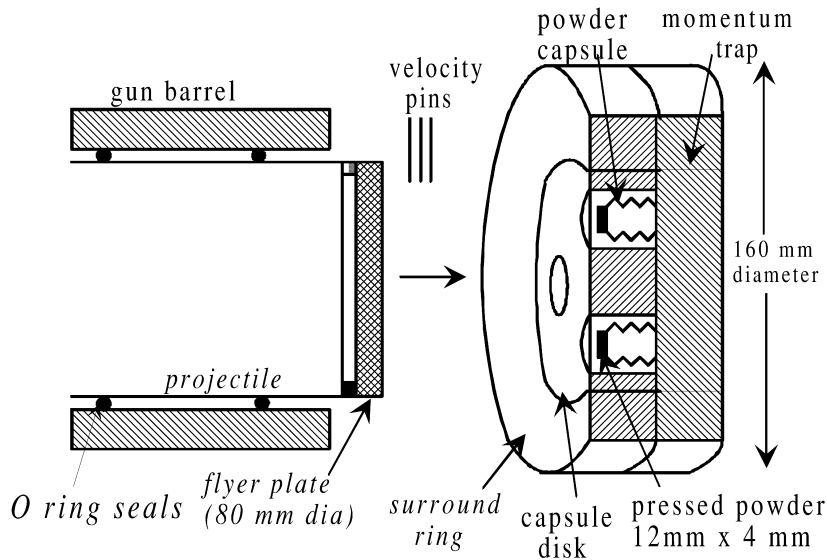


Fig. 1. Schematic showing the loading configuration employed using the three-capsule gas-gun shock-compression recovery fixture.

boiling concentrated nitric acid. The residue recovered from the shock-compressed samples after dissolving the copper and salts with acid treatment, was examined by transmission electron microscopy (TEM), energy dispersive spectroscopic (EDS) analysis, parallel-detection electron energy loss spectroscopy (PEELS), and infra-red (IR) spectroscopy.

3. Results and discussion

Table 1 summarizes the gas-gun shock-compression experimental conditions and results of microstructural observations of the two recovered samples which will be discussed below.

TEM characterization, coupled with EDS and PEELS analysis, was used to identify phases formed in sample no. 5-2. The recovered powder residue was suspended on a carbon-coated Cu grid. Dark field imaging showed the presence of isolated bright-contrast diffracting particulates

(of ~ 40 nm) dispersed in an amorphous matrix, as shown in Fig. 2a. The crystallinity of the dispersed phases was confirmed by the SAED pattern which revealed diffraction spots of cubic symmetry (Fig. 2b). The particles were unstable under the electron beam, thus, making the diffraction pattern highly transitory in character. However, the most significant result was exhibited by TEM/PEELS analysis of the diffracting crystallites observed in Fig. 2a. As shown in Fig. 2c, the K-edge absorptions of carbon at 292 eV and nitrogen at 401 eV, reveals an sp^3 type atomic bonding, characteristic of diamond-like [24] material with high hardness and bulk modulus. Considering the ionization cross-section ratio for C:N to be 2.5:2.0, it appears that the region with crystallites embedded in a carbon matrix contains ~ 8 –13 at.% N, indicating that the material is nitrogen-containing sp^3 bonded carbon phase.

Infra-red (IR) spectroscopy was also employed in an attempt to characterize the bulk composition and bond structure. Samples of the shock-compressed organic residue were examined by pressing it with KBr to form

Table 1
Experimental conditions and results of observations of recovered samples

Sample no.	Packing density	Impact velocity (pulse duration)	Critical results and key observations
4-2	$\sim 92\%$	700 m/s (1.8 μ s)	C and N-containing amorphous product observed by TEM/EDX, and IR signal showed β -phase
5-2	$\sim 88\%$	700 m/s, (3.6 μ s)	C and N-containing nano-crystallites in amorphous matrix observed by TEM, EDX, and EELS analysis, IR signal showed β -phase

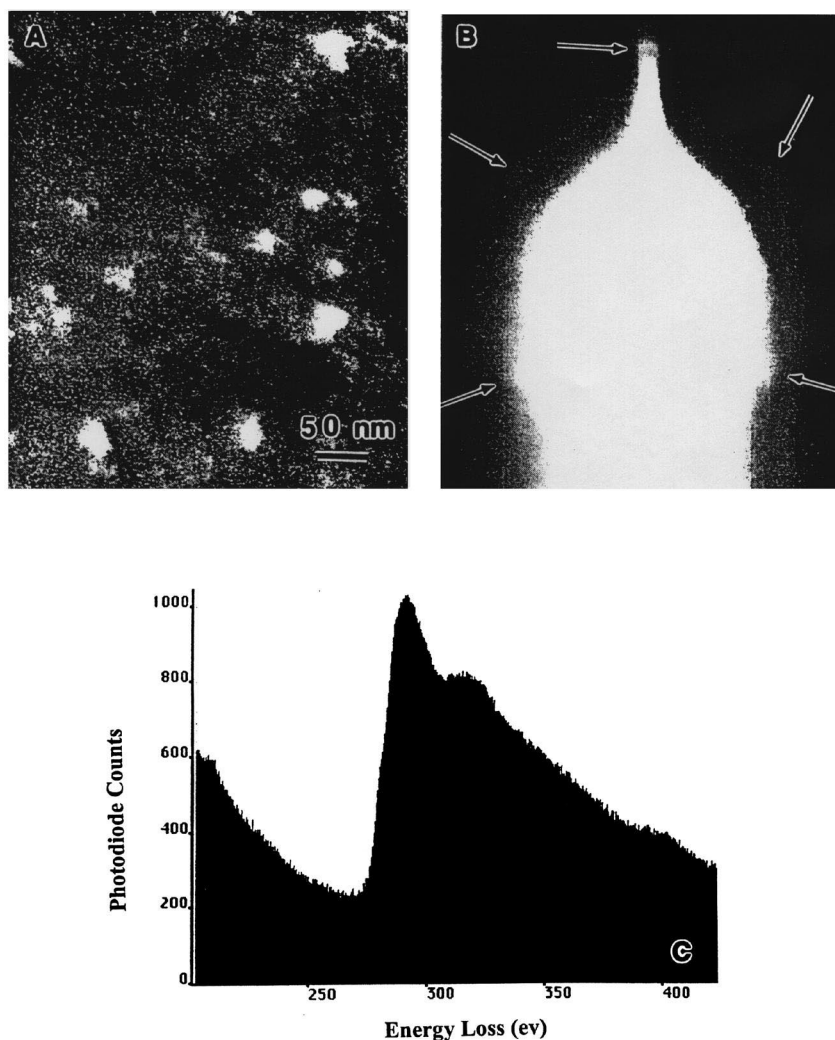


Fig. 2. (a) Dark field image showing diffraction of nitrogen-containing particles in shock-synthesized residue of sample no. 5-2, along with corresponding (b) diffraction pattern and (c) PEELS spectrum of carbon- and nitrogen-containing crystallite, showing characteristic K-edges, indicating diamond-like sp^3 bonding.

pellets. A typical IR spectrum of sample no. 4-2 is shown in Fig. 3. The envelope of lines between 300 and 400 cm^{-1} and also between 470 and 710 cm^{-1} can be assigned to the SnO_2 impurity, which came from the Sn-impurity present in the commercially acquired Cu powder. No SnO_2 lines above 800 cm^{-1} are expected [25]. The broad envelope of lines between 900 and 1300 cm^{-1} can be assigned to a $\beta\text{-C}_3\text{N}_4$ structure, based on comparing the envelope with that of the published IR spectra of $\beta\text{-Si}_3\text{N}_4$ [26,27]. Three lines at 910 , 985 , and 1040 cm^{-1} are observed in this region of the spectrum of $\beta\text{-Si}_3\text{N}_4$, as shown in the insert in Fig. 3. Assuming that these lines are associated primarily with Si–N stretching motions, we can predict the shift of these lines for $\beta\text{-C}_3\text{N}_4$, replacing Si

with C. Thus, considering the scaling factor to be the ratio of stretching frequencies (ω) related to reduced-mass (μ) ratios for $\beta\text{-Si}_3\text{N}_4$ and $\beta\text{-C}_3\text{N}_4$, we have:

$$\left(\frac{\omega_{\text{Si-N}}}{\omega_{\text{C-N}}}\right) = \left(\frac{\mu_{\text{C-N}}}{\mu_{\text{Si-N}}}\right)^{1/2}.$$

This calculation gives a scaling factor of 0.8322, with which we find the corresponding positions for carbon nitride to be 1093 , 1183 and 1249 cm^{-1} . Three spectral features are indeed observed in this range at 1040 , 1100 , and 1150 cm^{-1} in the IR spectrum of sample no. 4-2, as shown in Fig. 3. The agreement with the calculated frequencies is fairly good considering that the shock synthesized product most probably does not have an ideal

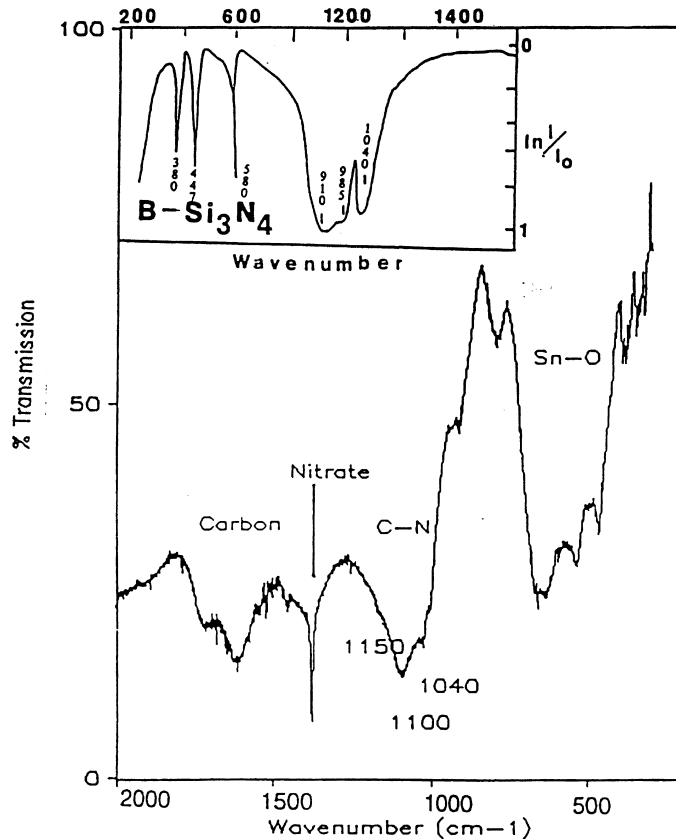


Fig. 3. Typical IR spectrum for sample no. 4-2 showing C–N bond structure analogous to that of β -phase Si_3N_4 , inferred from published IR pattern of β - Si_3N_4 shown in the insert [24,25].

β - C_3N_4 structure and that the absolute values of the force constants for C_3N_4 may be somewhat different from those of Si_3N_4 .

IR spectroscopy of these shock-compressed samples also showed the dependence of the yield of β -phase C_3N_4 on the duration of the shock-pressure pulse. The IR spectra of the short duration sample no. 4-2, and the long duration sample no. 5-2, shown in Fig. 4a and b, respectively, reveal clear indication of IR structure analogous to that of β -phase Si_3N_4 , described above. The peaks in the 1960 to 2140 cm^{-1} region of the spectrum arise due to C=N stretching vibrations from perhaps unreacted sodium dicyanamide precursor. The sharp line at 1380 cm^{-1} can be assigned to un-extracted copper nitrate. The broad absorption around 1080 cm^{-1} , as well as the three sharp absorption lines at 470, 500, and 590 cm^{-1} , are attributed to β -phase C_3N_4 bonded similarly to β - Si_3N_4 .

Comparison of the IR traces from samples of the two gas gun experiments shows that there is a larger volume fraction of the crystalline β - C_3N_4 phase in the recovered product obtained from the longer duration experiment. This is indicated by the increased intensity of absorption in

the longer duration sample. The increased crystallinity in the longer duration sample suggests the influence of an imposed kinetic constraint on the formation (or retention) of crystalline β -phase carbon nitride during shock-compression.

4. Summary and conclusions

Organic precursors containing sodium dicyanamide, sodium azide, and carbon tetra-iodide, mixed with 95 wt.% Cu powder, were shock-compressed under different pressure-pulse duration, and shown to result in the possible formation of β -phase carbon nitride. TEM characterization showed presence of crystallites dispersed in an amorphous matrix, with PEELS analysis of the nitrogen-containing crystallites showing diamond-like sp^3 bonding, with N-content of ~ 8 –13 at.%. Infrared spectroscopy indicated absorption in the regions calculated to be appropriate to the β -phase C_3N_4 . The synthesis of this possibly β -phase C_3N_4 compound was observed to show increasing yield (based on increasing IR-peak intensity) in samples ob-

IR SPECTRA OF MIX II - $\text{NaN}(\text{CN})_2 + \text{Cl}_4 + \text{NaN}_3$

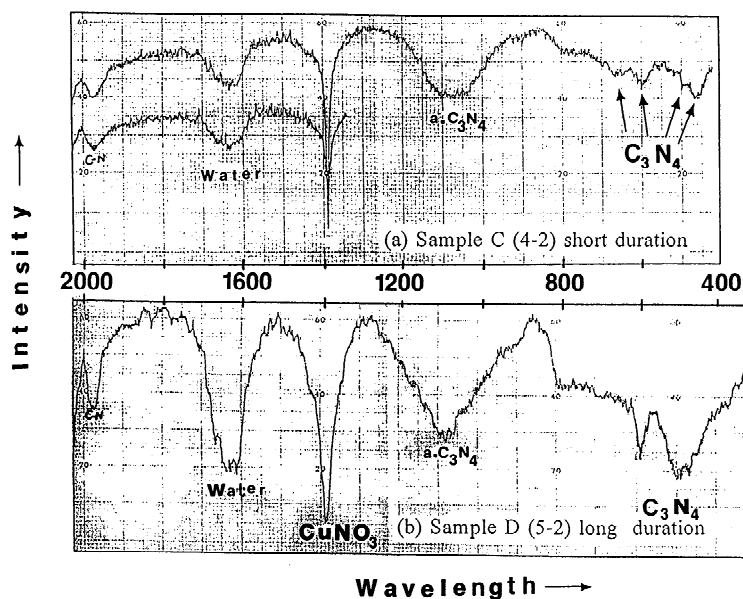


Fig. 4. IR spectra of (a) sample no. 4-2 (short duration) and (b) sample no. 5-2 (long duration), showing higher intensity β -phase C_3N_4 peaks (indicating increasing yield) in longer shock-pressure pulse-duration sample.

tained from experiments performed with longer shock-pulse duration.

Acknowledgements

The authors acknowledge the help of Prof. Kent Barefield, for useful discussions with respect to precursor selection and preparation, and Prof. Z.L. Wang and Ms. Yolande Berta for their help with TEM and PEELS characterization. The infra-red spectroscopy analysis was performed at Allied-Signal, Inc. This research was funded by ARO Grants DAAH04-94-6-0192 and DAAG55-97-1-0163.

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