A novel low compressible and superhard carbon nitride: Body-centered tetragonal CN₂

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A novel body-centered tetragonal CN₂ (4 units per cell), named as bct-CN₂, has been predicted here using our newly developed particle swarm optimization algorithm for crystal structure prediction. Bct-CN₂ is energetically much superior (3.022 eV per f.u.) to previously proposed pyrite structure and stable against decomposition into a mixture of diamond + N₂ or 1/3(C₃N₄ + N₂) above 45.4 GPa. No imaginary phonon frequencies in the whole Brillouin zone indicate bct-CN₂ is dynamically stable. The electronic calculations indicate that bct-CN₂ is a wide gap dielectric material with an indirect band gap of 3.6 eV. The ideal tensile, shear, and compressive strength at large strains of bct-CN₂ are examined to understand further the microscopic mechanism of the structural deformation. Strikingly, it is found that bct-CN₂ high calculated ideal strength, bulk modulus, shear modulus, and simulated hardness, indicating its very incompressible and superhard nature. The results provide new thoughts for designing and synthesizing novel superhard carbon nitrides, and insights for understanding the mechanical properties.

Introduction

Due to their importance in fundamental science and technological applications, the synthesis of new superhard materials is in high demand.1 The prediction of hexagonal β-C₃N₄2–4 with short interatomic distance and large bulk modulus has motivated intense experimental interest to synthesize and characterize this compound.5–15 Subsequently, other important dense polymorphs of C₃N₄, e.g., hexagonal γ-C₃N₄, cubic C₃N₄ (c-C₃N₄), cubic phase with defect zinc-blende structure (dzb-C₃N₄), and pseudo-cubic phase (pc-C₃N₄), have been further proposed and studied by theoretical calculations.16,17 Interestingly, c-C₃N₄ even has a zero pressure bulk modulus (449–496 GPa) exceeding the experimental value of diamond (442 GPa).18–22 Carbon nitrides are thus expected as competitive candidates in the superhard materials family. To date, carbon nitrides have been obtained either as thin films or as bulk forms.23,24 However, due to the similar and small atomic masses and ability to form sp-, sp²-, and sp³-hybridized bonds of C and N atoms,25 it remains a major challenge to determine the crystal structures of the synthesized carbon nitrides. Even the existence of crystalline stoichiometric C₃N₄ has not been clearly evidenced yet.26 Therefore, the discovery of other stable C₃N₄ polymorphs would contribute significantly to the exploration of superhard carbon nitrides. It is established that the formation of short and strong three-dimensional (3D) covalent bonds is a necessary condition for superhard materials.1–4,16,17,27–30 Carbon nitrides with high bulk modulus and hardness should have a four-coordinated carbon and a three-coordinated nitrogen.17 To form 3D covalent C₃N₄, the triple N≡N bond and N–N bond should be avoided, keeping just C–N bonds. It is known that the triply bonded state in nitrogen is the strongest bond known, however, the triply bonded molecular state in nitrogen collapses to form an N–N bond at a surprisingly modest pressure of 60 GPa,31–33 in contrast to 1920 GPa for oxygen34,35 and 500 GPa for hydrogen36 with much weaker covalent bonding. Thus, it might be possible to synthesize a new carbon nitride with a lower atomic ratio of C : N than 3 : 4 where the nitride contains both an N–N bond and C–N bonds at high pressure (e.g., 60 GPa).

In this paper, we have predicted the polytropic structures for carbon nitrides with an atomic ratio C : N of 1 : 2 (CN₂) under high pressure by our developed particle swarm optimization (PSO) algorithm37,39–46 on crystal structural prediction. Simulations uncovered a novel body-centered tetragonal CN₂ (4 units per cell) built up by strong covalent C–N bonds and N–N bonds, named as bct-CN₂, which is stable above 45.4 GPa with respect to decomposition. The electronic calculations indicate that bct-CN₂ is a semiconductor with an indirect band gap of 3.6 eV. To explore the pressure limit under extreme conditions, we have further performed first-principles calculations to study the atomistic deformation modes and the ideal strength of bct-CN₂ under tensile, shear and compressive strains.
Computational method

The first-principles energetic calculations were carried out using the density functional theory with the Perdew–Burke–Ernzerh generalized gradient approximation (GGA) exchange-correlation potential as implemented in the VASP code. The projector augmented wave (PAW) pseudopotential with 2s2p6 and 2s2p3 valence electrons was adopted for C and N atoms, respectively. The use of a plane-wave kinetic-energy cutoff of 600 eV was shown to give excellent convergence on the total energies and structural parameters. The search of high-pressure structures (0–100 GPa) was performed with variable-cell PSO simulations with the CALYPSO code and up to 24 atoms in the unit cell. During the subsequent geometrical optimization, all forces on atoms were converged to less than 0.0001 eV Å⁻¹ and the total stress tensor was reduced to the order of 0.001 GPa. The phonon frequencies were calculated using direct supercell method, which uses the forces obtained by the Hellmann–Feynman theorem. Elastic constants were calculated by the strain-stress method, and the polycrystalline bulk modulus and shear modulus were thus derived from the calculated by applying shear deformations in the easy-slip plane. The critical shear stresses along various crystallographic directions were calculated. The critical shear stresses along various directions were then determined using a method described previously. The lattice vectors were incrementally deformed in the direction of the applied strains. At each step, the atomic positions of the stress tensor orthogonal to the applied strains were less than 0.1 GPa. To identify the weakest tensile direction, the tensile stresses along various crystallographic directions were calculated. The calculated compressive stresses along various crystallographic directions were calculated. The critical shear stresses along various crystallographic directions were then calculated by applying shear deformations in the easy-slip plane perpendicular to the weakest tensile direction. Furthermore, we calculated the compressive stresses along various crystallographic directions to obtain the pressure limit under uniaxial compression.

Results

Variable-cell simulations with 1–8 formula units (f.u.) in the unit cell were performed at 0, 10, 30, 50, 80 and 100 GPa, respectively. Analysis of the predicted structures gave us a shortlist of candidate structures with space groups Pa3 (4 f.u. per cell), P421m (2 f.u. per cell), I42d (4 f.u. per cell), I4m2 (2 f.u. per cell), P3m1 (2 f.u. per cell), and Cmc21 (2 f.u. per cell), respectively, as shown in Fig. 1 and 2. Pa3 structure (pyrite structure) has been previously proposed by Weinrich through a substitution method with the knowledge of isoelectronic SiP2 structure in order to investigate the release of N2 from the CNx compounds. Four-coordinated N and six-coordinated C atoms form a 3D lattice in Pa3. In comparison with the structure of rock salt, the carbon atoms in the Pa3 structure maintain a face-centered-cubic close packing as do Na atoms, and the N atoms appear as N–N dimers centered at the CI positions. The other five structures are, to the best of our knowledge, for the first time reported here. Among the newly predicted structures, primitive tetragonal P421m (referred to as pc-CN2 in the text) with an N–C–N layered structure is most stable below 27.6 GPa, and then body-centered tetragonal I42d (referred to as bct-CN2 in the text) becomes energetically favorable over the other structures. The calculated enthalpy difference indicates that pc-CN2 and bct-CN2 are 3.661 eV per f.u. and 3.022 eV per f.u. more stable than the earlier proposed pyrite structure at zero pressure, respectively. In both pc-CN2 and bct-CN2 structures, all carbon atoms are tetrahedrally bonded with clear sp3 hybridization (4 C–N bonds) and nitrogen atoms are three-coordinated (2 C–N bonds and 1 N–N bond). Intriguingly, the N–C–N “sandwiches”
stacks in order with a C–N bond length of 1.468 Å and N–N bond length of 1.447 Å in the pc-CN$_2$ structure. The distance (3.221 Å) between the N–C–N sandwiches in pc-CN$_2$ structure is close to the inter-layer distance of graphite (3.438 Å). Therefore, the only attractive forces between the adjacent sandwiches in pc-CN$_2$ structure are weak van der Waals interactions, and thus the sandwich layers can easily slip as in graphite. bct-CN$_2$ forms a 3D framework built up by C-N and N-N covalent bonds. As shown in Fig. 1 and 6, polyhedral views of bct-CN$_2$ reveals that fourfold coordinated carbon and threefold coordinated nitrogen atoms form CN$_4$ tetrahedra with one N-N bond (1.358 Å) and two nearly equal C–N bonds (1.479 and 1.482 Å). Interestingly, if substituting C atoms for N–N dimers at its center, bct-CN$_2$ transforms into a diamond-like structure. It is very important to note that the bond lengths in both pc-CN$_2$ and bct-CN$_2$ are shorter than the C–C bond in diamond (1.54 Å), suggesting that bct-CN$_2$ may exhibit high hardness and bulk modulus.

The thermodynamic stability of the various predicted structures at a large pressure range from 0 to 100 GPa with respect to the decomposition, was quantified in terms of the formation enthalpies of two different reaction routes:

$$\Delta H = H_{\text{CN}_2} - (H_C + H_{\text{N}_2})$$

$$\Delta H' = H_{\text{C}_3\text{N}_4} - \frac{1}{2}(3H_{\text{C}_3\text{N}_4} + H_{\text{N}_2})$$

The diamond, cubic gauche (cg) nitrogen and $\alpha$-phase (Pa$\bar{3}$) N$_2$, $\alpha$-C$_3$N$_4$, $\beta$-C$_3$N$_4$, and $c$-C$_3$N$_4$ were chosen as the reference phases. Fig. 2 shows the enthalpy curves for various structures and the decomposition with respect to our predicted Cmc$_2$$_1$ structure. Like diamond and $c$-BN, C$_3$N$_4$ are metastable compounds under atmospheric pressure. At a wide pressure range of 0–14.8 GPa, superhard C$_3$N$_4$ is thermodynamically unstable relative to diamond (Fd$\bar{3}$m) and $\alpha$-phase N$_2$ (Pa$\bar{3}$). Thus, C$_3$N$_4$ is very difficult to synthesize experimentally under normal conditions. Instead, the preparation requires rather extreme conditions, e.g., high temperature and high pressure. Furthermore, C$_3$N$_4$ is thermodynamically unstable, again relative to the current predicted bct-CN$_2$ (I$\bar{4}$m2) and $\alpha$-phase N$_2$ (Pa$\bar{3}$) above 45.4 GPa. Therefore, the optimum pressure range for the synthesis of superhard C$_3$N$_4$ in bulk form is 15–45 GPa. It should be mentioned that the reaction pressure and reaction time would be reduced under high temperature. The use of high temperature is the classical way to improve both diffusion processes and the reactivity of precursors for materials synthesis of bulk forms or thin films$^{5,23}$ e.g., CN films with high thermal stability have been prepared at 600°C by rf. plasma pulsed laser deposition, and a transformation from the sp$^3$ C–N to the sp$^3$ C–N binding state was observed$^{23,60,61}$ Studies on the thermodynamic stability and physical properties of CN compounds under high temperature would also improve understanding of the synthesis. However, these studies are beyond the scope of the current work. Notably, the calculated formation enthalpies for bct-CN$_2$ are negative above 45.4 GPa for the above two different reaction routes, indicating that the bct-CN$_2$ is thermodynamically stable against decomposition into a mixture of diamond + N$_2$ or 1/3(C$_3$N$_4$ + N$_2$) above this pressure. Interestingly, pressure-induced dissociation of N$_2$ molecules ($N\equiv N \rightarrow N-N$) has been theoretically predicted and experimentally observed at $\sim 60$ GPa.$^{27,31}$ Furthermore, a recent exciting diffraction experiment shows that the synthesized $c\gamma$-nitrogen with monatomic N–N bonds can be stabilized down to at least 25 GPa as a metastable phase, but below that pressure the sample escaped owing to rupturing of the gasket.$^{62}$ Therefore, a technique may be developed to recover this nonmolecular sample at ambient pressure. Note that the energy difference between the $N\equiv N$ and N–N bond reaches 1.499 eV per atom$^{43}$ at zero pressure, which is much larger than the decomposition energies of bct-CN$_2$ (0.761 eV per atom) and $\beta$-C$_3$N$_4$ (0.383 eV per atom). Therefore, more experimental and theoretical studies are needed to face the challenge in prediction and synthesis of new superhard carbon nitrides as metastable materials at ambient pressure, or stabilized by introducing impurities or chemical pressure.

To get further insights into the predicted carbon nitrides, the calculated band structures at zero pressure have been presented in Fig. 3. All the structures show nonmetallic features since they obey the following simple rule$^{64}$ $mZ_C + nZ_N = 4l$. The values $m$, $n$, and $l$ are integers, and $Z_C$ and $Z_N$ are the atomic valence states (2s and 2p) for C, and N, respectively. The electronic calculations indicate that pc-CN$_2$ and bct-CN$_2$ are wide gap dielectric materials characterized by indirect large energy gaps of 4.8 eV and 3.6 eV, respectively. Since density functional calculations typically underestimate the energy gap by 30%–50%, the true band gap might be in the range of 6.9–9.6 eV and 5.1–7.2 eV, respectively, leading to potential optical applications. The total energies as a function of volume are fitted to the Murnaghan equation of state to

\begin{align*}
\Delta H &= H_{\text{CN}_2} - (H_C + H_{\text{N}_2}) \\
\Delta H' &= H_{\text{C}_3\text{N}_4} - \frac{1}{2}(3H_{\text{C}_3\text{N}_4} + H_{\text{N}_2})
\end{align*}

Fig. 3 Electronic band structures for (a) Pa$\bar{3}$, (b) pc-CN$_2$, (c) bct-CN$_2$, (d) $I\bar{4}$m2, (e) $P\bar{3}$m1, and (f) Cmc$_2$$_1$, at 0 GPa. The horizontal dashed lines represent the Fermi level.
obtain the theoretical bulk modulus ($B_{\text{soc}}$), as listed in Table 1. For comparison, the results of diamond, α-C$_3$N$_4$ and β-C$_3$N$_4$ and c-C$_3$N$_4$ are also listed. The current results support the previous conclusion\cite{17,18} that the calculated bulk modulus of c-C$_3$N$_4$ (437 GPa) is larger than that of diamond (423 GPa). The theoretical bulk modulus of bct-CN$_2$ reaches 392 GPa, close to α-C$_3$N$_4$ (396 GPa) and β-C$_3$N$_4$ (406 GPa). Pa$\bar{3}$, bct-CN$_2$, Cmc$_2$$_1$, and I$\bar{4}$m$_2$ have a large bulk modulus, indicating that these structures are very incompressible as expected from their short and strong 3D chemical bondings, while P$\bar{3}$m$_1$ and pc-CN$_2$ have very small bulk modulus due to the layered structures.

To check the structural stabilities of the predicted CN$_2$ polymorphs, the phonon dispersions were calculated. As shown in Fig. 4, no imaginary phonon frequencies are observed in the whole Brillouin zone, indicating pc-CN$_2$, bct-CN$_2$, Cmc$_2$$_1$, I$\bar{4}$m$_2$, and P$\bar{3}$m$_1$ are dynamically stable. However, the Pa$\bar{3}$ structure is unstable with a wide range of imaginary frequencies [Fig. 4(a)]. The lattice dynamics of Pa$\bar{3}$ structure were confirmed by the density-functional linear-response method\cite{65} as implemented in the Quantum-ESPRESSO code.\cite{66} As shown in Fig. 4(b) and (e), the flat dispersions of the optical branches along A–M, Γ–Z and R–X directions for pc-CN$_2$ and Γ–A, H–K, and M–L directions for P$\bar{3}$m$_1$ reflect the layered structural characteristics, which are attributed to the weak interaction between the adjacent sandwich layers. In fact, the flat dispersion along those directions for pc-CN$_2$ and P$\bar{3}$m$_1$ can also be seen in the electronic band structures [Fig. 3b and e]. The nearly zero frequencies along Γ–Z and Γ–A directions in pc-CN$_2$ and Γ–A, respectively, make it very easy for the atoms to move about along the c axis.

To study the mechanical properties of bct-CN$_2$, the elastic constants were calculated. Table 2 lists the theoretical results on the mechanical properties. For comparison, the results of α-C$_3$N$_4$, β-C$_3$N$_4$, c-C$_3$N$_4$, and diamond are also shown. All the five structures satisfy the mechanical stability criteria. From the calculated elastic constants, we further estimate the polycrystalline bulk modulus $B$ and shear modulus $G$ using the Voigt–Reuss–Hill approximation.\cite{52} Since the hardness is deduced from the size of the indentation after deformation, a hard material typically requires a high bulk modulus to support the volume decrease created by the applied pressure, and a low Poisson’s ratio ($\nu$) or high shear modulus (such that the material will not deform in a direction different from the applied load).\cite{67}
tensile deformation show that $bct$-CN$_2$ has strong stress responses in the [100], [001], [011], [110], and [111] directions with the peak tensile stresses at 80.0, 117.1, 62.0, 46.6 and 50.8 GPa, respectively. It is important to note that all the tensile stresses are larger than 40 GPa in $bct$-CN$_2$, indicating its superhard nature. The weakest peak tensile stress occurs in the [110] direction, which indicates that under tensile loadings, $bct$-CN$_2$ would first cleave in the (110) plane. The critical shear stress in the $bct$-CN$_2$ was then calculated by applying [001], [110], and [111] shear deformations in the (110) easy cleavage plane perpendicular to the weakest tensile direction, as shown in Fig. 5 and Fig. 6. The lowest shear strength appears in the (110)[001] direction with a peak shear stress of 51.1 GPa, which is 9.7% higher than the tensile strength along the [110] direction. The obtained tensile (46.6 GPa) and shear strength (51.1 GPa) of $bct$-CN$_2$ are lower than those of diamond (92.9 and 96.3 GPa) and $c$-BN (65.6 and 70.5 GPa) but comparable to those of pc-C$_3$N$_4$ (55.5 and 45.2 GPa) and $b$-C$_3$N$_4$ (62.2 and 60.5 GPa). The current results demonstrate that the failure mode in $bct$-CN$_2$ is dominated by the tensile type, which is different from that in pc-C$_3$N$_4$ and $b$-C$_3$N$_4$. 

Furthermore, to determine whether $bct$-CN$_2$ can be used under nonhydrostatic conditions, such as the creation of high-pressure devices for investigating the properties of various materials under pressure, and an indenter in the nanoindentation test, the compressive stresses along various crystallographic directions were calculated to obtain the pressure limit under uniaxial compression. From Fig. 5, it is seen that the limit compressive stresses of $bct$-CN$_2$ are $-210.0$, $-149.5$, $-161.6$, $-291.3$ and $-271.0$ GPa with the corresponding strain of $-0.305$, $-0.170$, $-0.275$, $-0.260$ and $-0.245$, along the [100], [001], [011], [110], and [111] directions, respectively. The [100], [111] and [110] directions are good choices for producing pressures above 200 GPa.

According to the semiempirical microscopic hardness model by Tian et al., the simulated hardness of $bct$-CN$_2$ is 77.4 GPa, which is close to those of pc-C$_3$N$_4$ (81.0 GPa) and $b$-C$_3$N$_4$ (77.7 GPa) at equilibrium. It is known that this semiempirical microscopic model and ideal strength are widely confirmed and generally accepted as efficient ways to describe hardness. However, in the current $bct$-CN$_2$, the ideal strength (46.6 GPa) is much lower than the simulated hardness (77.4 GPa). In order to understand this disparity, we have examined the charge density distribution and the electron localization function (ELF) that enables an effective and reliable analysis of the nature of covalent bonding. The calculated charge density at a value of 1.5 e Å$^{-3}$ and isosurface of ELF = 0.82 in Fig. 7(a) (b). ELF is not a measure of electron density but is a measure of the Pauli principle. It is useful in distinguishing ionic, covalent, and metallic bonding. High ELF (≥0.8) indicates the formation of covalent bonds. The high electron localization can be seen in the region between adjacent C and N atoms, indicative of strong covalent bonding. We found an important feature in $bct$-CN$_2$ that is not shared by diamond, namely the distribution of the excess electrons on the N atoms that do not form bonds, but form a stable and localized lone-pair nonbonding state. Although the nitrogen atoms in $bct$-CN$_2$ are threefold-coordinated, the electronic state is actually characterized by the 3D tetrahedral-like electronic state. From the calculated charge density distribution at a value of 1 e Å$^{-3}$ in the energy range from $-6$ eV to the Fermi energy (Fig. 7(c)), the energy band structure (Fig. 3(c)) and density of state (Fig. 7(d)), we note that these localized lone-pair nonbonding states are degenerate and occupy the highest energy level. The strong covalent C–N bonds, N–N bonds and lone-pair nonbonding are together the driving force for its high bulk shear modulus and simulated hardness at equilibrium. Under large strain, the mobility of lone-pair nonbonding states...
is much more flexible than that of covalent bonds, and thus has a relatively lower ideal strength under large strain.

Conclusions

In summary, a novel body-centered tetragonal CN$_2$ (4 units per cell), named as bct-CN$_2$, has been predicted to be the thermodynamically preferred structure for carbon nitrides under hydrostatic pressures above 45.4 GPa. Fourfold coordinated carbon linking threefold coordinated nitrogen atoms form CN$_4$ tetrahedra with three bond lengths of 1.479, 1.482, and 1.358 Å, which are much shorter than the C-C bond of diamond (1.545 Å). No imaginary phonon frequencies for are observed in the whole Brillouin zone, indicating bct-CN$_2$ is dynamically stable. The electronic calculations indicate that bct-CN$_2$ is a wide gap dielectric material characterized by indirect large energy gaps of 3.6 eV. Strikingly, this new polymorph of carbon nitride has a high calculated ideal strength, shear modulus, bulk modulus and simulated hardness, indicative of its excellent incompressible and superhard property. The electronic origin has been examined to understand this disparity between the ideal strength and simulated hardness. We believe that the current study will advance the understanding of chemistry and stimulate future experimental synthesis and determination of carbon nitrides.

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References


Fig. 7 The calculated (a) charge density at a value of 1.5 e Å$^{-3}$, (b) isosurface of ELF = 0.82, (c) isosurface of constant charge density at a value of 1 e Å$^{-3}$ for the states in the energy range from –6 eV to the fermi energy (0 eV), and (d) density of state at zero pressure for bct-CN$_2$. The electronic origin has been examined to understand this disparity between the ideal strength and simulated hardness. We believe that the current study will advance the understanding of chemistry and stimulate future experimental synthesis and determination of carbon nitrides.