



First-principles investigation of high pressure Pbca phase of carbon mononitride



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ABSTRACT

A theoretical investigations on the stability, mechanical and electronic properties of Pbca-CN was performed by using first principle calculations. According to our calculations, Pbca-CN exhibits a large elastic anisotropy. The further mechanical calculations demonstrated that Pbca-CN shows high elastic moduli. Young's modulus of Pbca-CN is found to reach a maximum along [001] direction and a minimum along [100] direction. The ideal tensile and shear strength at large strains of Pbca-CN are also examined. The ideal shear strength along the weakest (100)[010] slip system is about 20 GPa, which shows Pbca-CN is not an intrinsic superhard material.

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1. Introduction

Light element nitrides [1–8] and transition metal nitrides [9–12] have been proved to be potential incompressible and superhard materials. Because of short C–N bond length, carbon nitrides are expected as potential superhard materials. The known C_3N_4 of α -, β -, and the cubic spinel phases are widely investigated theoretically and experimentally [13–15]. The bulk modulus of β - C_3N_4 (419 GPa) is predicted to be comparable to that of diamond (439 GPa) [14]. Excitingly, the bulk modulus of c - C_3N_4 (449 GPa) is slightly larger than that of diamond, and the hardness of c - C_3N_4 (92 GPa) is comparable to that of diamond (97 GPa) [14]. This motivates researchers to search more superhard C–N materials. Other than C_3N_4 , more novel superhard materials in C–N system, such as CN [6–8,16–18], CN_2 [19], C_3N [18,20], C_3N_2 [21,22], and $C_{11}N_4$ [23], have been predicted. For C–N 1:1 compound composition, carbon can be either in sp^2 or sp^3 configuration. Khazaei et al. [8] proposed a high pressure Pbca phase of CN, in which carbon atoms have sp^3 -like hybridization with their nearest-neighboring C and N atoms. This is similar to that in Pnm-CN and $P4_2/m$ -CN. Recently, Oganov's group [5,24] studied the phase diagram and hardness of carbon nitrides. They theoretically confirmed the $P4_2/m$ phase proposed by Zhang et al. [6] is the most stable phase of CN at 0 GPa, and experimentally synthesized the high pressure phase

Pnm-CN at 55 GPa and 7000 K. The detailed properties of $P4_2/m$ and Pnm phases of CN have been systematically studied [6,7,16]. The stability, mechanical and electronic properties of high pressure phase Pbca-CN have not been studied, hitherto. In this work, we present a systematic first-principles calculations on Pbca-CN. The semiempirical hardness calculations show that Pbca-CN is a superhard material. Since semiempirical models have over-exaggerated the hardness of several C–N compounds [16], the stain-stress calculations are performed to obtain the weakest ideal tensile and shear strengths of Pbca-CN.

2. Computational methods

The theoretical calculations were carried out using first-principles density functional theory (DFT) [25]. The Perdew–Burke–Ernzerhof (PBE) [26] exchange–correlation functional and projector-augmented wave (PAW) [27] potentials were employed for the self-consistent total energy calculations and geometry optimization. The C: $2s^2 2p^2$ and N: $2s^2 2p^3$ electrons are explicitly treated as valence electrons. The calculations were performed using the Vienna Ab-initio Simulation Package (VASP) [28]. The kinetic energy cutoff for the plane wave basis set was chosen to be 900 eV. The conjugate gradient method was used for the relaxation of structural parameters. The k-point samplings with $9 \times 11 \times 11$ in the Brillouin zone were performed using the Monkhorst–Pack scheme. The energy convergence criteria for electronic and ionic iterations were set to be 10^{-5} eV and 10^{-4} eV, respectively. With this parameter setting, the calculations were converged within 1 meV in

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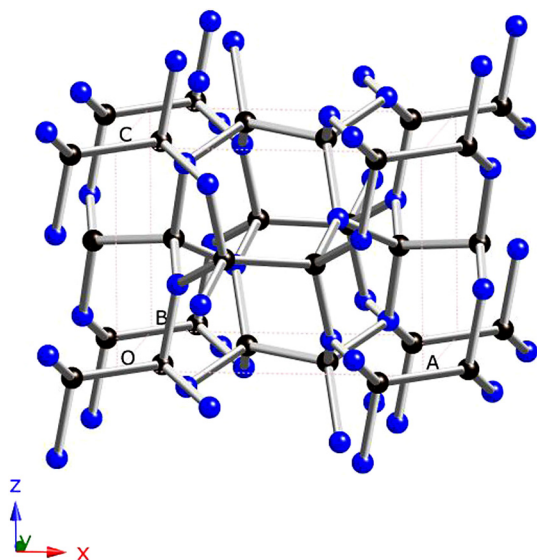


Fig. 1. Crystal structure of Pbca-CN. The blue and black spheres represent N and C atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

total energy per atom. The elastic constants were determined from evaluation of stress tensor generated small strain. Bulk modulus, shear modulus, Young's modulus, and Poisson's ratio were estimated by using Voigt–Reuss–Hill approximation [29].

3. Results and discussions

The crystal structure of Pbca-CN was obtained by full relaxations of both lattice constants and internal atomic coordination without any restrictions at ambient pressure. The optimized lattice constants are $a_0 = 5.5140$ Å, $b_0 = 4.3956$ Å, and $c_0 = 4.0409$ Å, which are in good agreement with Ref. [8]. The C and N atoms are located at Wyckoff 8c (0.1399, 0.0724, 0.0207) and 8c (0.8158, 0.8665, 0.6313) sites, respectively. The crystal structure is illustrated in Fig. 1. Every C atom is bonded with 1 C atom and 3 N atoms, which has a sp^3 -like hybridization. Every N atom is sp^2 -like hybridization bonded with 3 C atoms. The bond lengths of C–C and C–N are 1.677 Å and 1.455 Å, respectively. The C–C bond length is longer than $P4_2/m$ phase (1.584 Å) and Pnm phase (1.606 Å).

At ambient pressure, phonon calculations have verified the Pbca-CN is dynamically stable [8]. To check its stability under high pressures, the phonon dispersion curve of Pbca-CN at 0 GPa and 100 GPa were calculated, as shown in Fig. 2. There is no imaginary frequency in the whole Brillouin zone, which means Pbca-CN can be dynamically stable in the pressure range 0–100 GPa. The validity of DFT calculations at high pressures have been widely confirmed [30,31], so our calculated results at ambient and high pressures should be reasonable. The formation enthalpy of Pbca-CN can be obtained by

$$\Delta H = H_{CN} - H_C - \frac{1}{2}H_{\alpha-N_2} \quad (1)$$

Table 1
Calculated elastic constants C_{ij} (GPa), bulk modulus B (GPa), shear modulus G (GPa), and Young's modulus E (GPa) of Pbca-CN at 0 GPa and 100 GPa. Also shown are G/B ratio and Poisson's ratio ν .

Phase	Pressure	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}	B	G	E	G/B	ν
Pbca ^a	0	495	934	1112	465	313	243	174	145	124	363	326	754	0.899	0.154
	100	937	1450	1615	650	388	345	542	402	444	733	430	1081	0.587	0.255
$P4_2/m$ ^b	0	596	1156	370	326	172	116	341	328	745	0.96	0.136			
Pnm ^b	0	518	767	1227	534	277	379	203	83	201	369	351	799	0.95	0.139

^a This work.

^b Ref. [6].

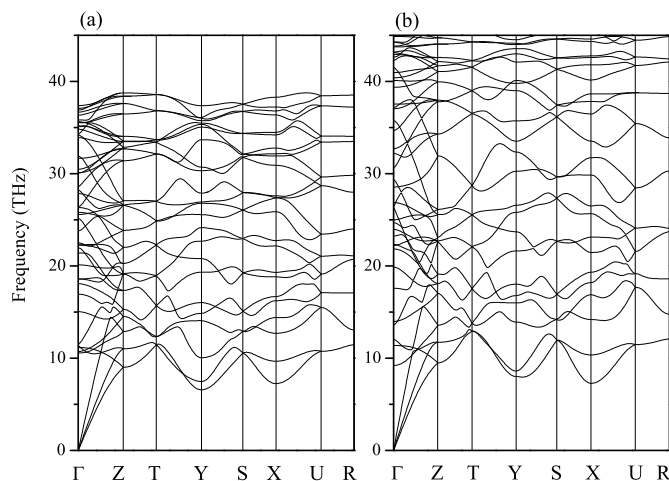


Fig. 2. Phonon dispersion curves of Pbca-CN at 0 GPa (a) and 100 GPa (b).

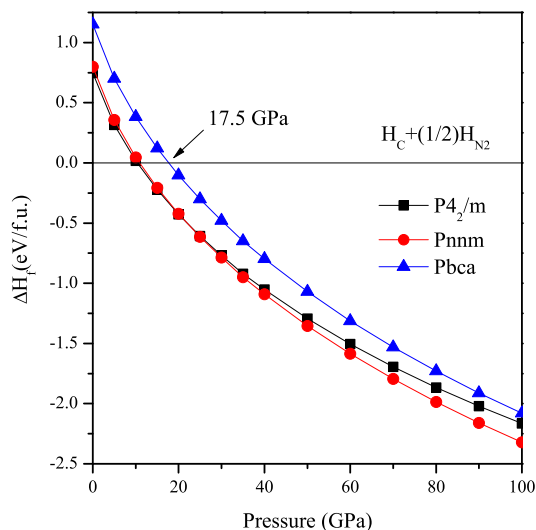


Fig. 3. Formation enthalpies of Pbca-CN, $P4_2/m$ -CN, and Pnm-CN relative to diamond and nitrogen as a function of pressure.

where H_{CN} , H_C and $H_{\alpha-N_2}$ are the enthalpies of CN, diamond and $\alpha-N_2$, respectively. The calculated formation enthalpy of Pbca-CN are shown in Fig. 3 along with that of $P4_2/m$ -CN and Pnm-CN for comparison. It is found that, in the whole pressure range, the enthalpy of Pbca phase is higher than $P4_2/m$ and Pnm phases. This means Pbca phase is a thermodynamically metastable phase, which becomes thermodynamically stable above 17.5 GPa. The mechanical stability of a structure can be confirmed by using the elastic constants. For orthorhombic structure, the criteria of mechanical stability are [32]: $C_{11} > 0$, $C_{22} > 0$, $C_{33} > 0$, $C_{44} > 0$, $C_{55} > 0$, $C_{66} > 0$, $C_{11}C_{22} - C_{12}^2 > 0$, $C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 > 0$. The elastic constants of Pbca-CN are shown in Table 1. Clearly, Pbca-CN is stable under ambient pressure. The

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