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First-principle study of orthorhombic CN as a potential superhard material

Xiao Tang, Jian Hao*, and Yinwei Li

Using first-principle calculations, we have investigated the structural, electronic, dynamical and mechanical properties of a recently synthesized Pnnm-CN. Phonon dispersion and elastic constant calculations demonstrate the dynamical and mechanical stabilities of the Pnnm structure of CN at ambient pressure. The electronic band structure suggests that Pnnm-CN is an insulator with an indirect band gap of about 3.7 eV. First-principle strain-stress relations at large strains were also simulated to examine the structural and mechanical properties of Pnnm-CN. The established ideal tensile strength of ~ 41 GPa in the <100> direction suggests that CN is a potential superhard material. The present results provide deep insights for understanding the mechanical properties of CN and thus are helpful to explore the potential industrial applications of CN.

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Computational methods

Calculations were performed using density functional theory (DFT) within the Perdew–Burke–Ernzerhof (PBE)\textsuperscript{37} generalized gradient approximation (GGA) as implemented in the Vienna \textit{ab initio} simulation package (VASP).\textsuperscript{38, 39} The all-electron projector augmented wave (PAW) method\textsuperscript{40} was adopted for C and N atoms with valence electrons of 2s²2p² and 2s²2p³, respectively. An energy cutoff of 600 eV and a Monkhorst-Pack Brillouin zone sampling grid with a resolution of 0.2 Å\textsuperscript{-1} were used, resulting in total energy convergence better than 1 meV/atom. The phonon dispersions were computed based on the supercell approach using the PHONOPY\textsuperscript{42} code with 2×2×3 supercell for \textit{Pnnm}-CN. Elastic constants were calculated by the strain-stress method, and the polycrystalline bulk modulus and shear modulus were thus derived from the Voigt–Reuss–Hill averaging scheme.\textsuperscript{41} The ideal tensile and shear strengths in the various directions were obtained by calculating strain-stress relations under large structural deformation using a method described previously.\textsuperscript{17, 42} Metadynamics simulation for \textit{Pnnm}-CN was applied by using the PAW method as implemented in the VASP code.\textsuperscript{38, 39} Molecular dynamics simulation for \textit{Pnnm}-CN was applied by using the PAW method as implemented in the VASP code.\textsuperscript{38, 39} The simulation cell was constructed by using 48 C and 48 N atoms and k-mesh of 2×2×2. The canonical \textit{NVT} (N-number of particles, V-volume, T-temperature) ensemble was used for molecular dynamics runs with time step of 1.0 fs.

Results and discussion

![Image](Fig. 1) Crystal structures of \textit{Pnnm}-CN (a) and \textit{d-ZB}-\textit{C}_{3}\textit{N}_{4} (b). The black and blue spheres represent C and N atoms, respectively.

The \textit{Pnnm} structure of CN as well as the \textit{d-ZB}-type structure of \textit{C}_{3}\textit{N}_{4} were fully geometry optimized allowing simultaneous variations of unit cell and atomic positions at selected pressures. The theoretical equilibrium properties and equation of states (EOS) were determined by fitting the total energies as functions of volume to the Murnaghan EOS.\textsuperscript{44} The resultant equilibrium lattice parameters and atomic positions together with previous experimental\textsuperscript{3, 9, 11} or theoretical\textsuperscript{3, 9, 11} data have been listed in Table 1. A good agreement within a maximum 6% interval can be found between the current results and previous data.\textsuperscript{3, 9, 11} As shown in Fig. 1, The \textit{Pnnm} structure of CN has four formula units (f.u.) in a unit cell. Each C atom in the \textit{Pnnm} structure is bonded with three N atoms and one C atom, and each N atom is coordinated with three C atoms. The presence of sp²-hybridized C and sp³-hybridized N in \textit{Pnnm}-CN is similar to that in \textit{d-ZB}-\textit{C}_{3}\textit{N}_{4}, where each C atom is surrounded by four N atoms while each N atom is bonded with three C atoms (Fig. 1b). At ambient pressure, the C–C bond in \textit{Pnnm}-CN is calculated to be 1.606 Å, which is slightly longer than that (1.535 Å) in diamond. Meanwhile, we found the C–N bond lengths (1.433–1.487 Å) in \textit{Pnnm}-CN are slightly shorter than that (1.488 Å) in \textit{d-ZB}-\textit{C}_{3}\textit{N}_{4}. The electronic band structure shows that \textit{Pnnm}-CN is an insulator with a large indirect band gap of 3.7 eV at ambient pressure (Fig. 2a). The predicted gap for \textit{Pnnm}-CN is larger than that (2.9 eV) of cubic-\textit{C}_{3}\textit{N}_{4} and is comparable to that (3.85 eV) of \textit{d-ZB}-\textit{C}_{3}\textit{N}_{4}.

![Image](Fig. 2) Electronic band structure and density of states (DOS) (a), phonon dispersion curves and phonon density of states (PDOS) (b) of \textit{Pnnm}-CN at ambient pressure.

The bulk modulus (\textit{B}_0) and shear modulus (\textit{G}_0) derived from the above elastic constants are listed in Table 2. The results of \textit{d-ZB}-\textit{C}_{3}\textit{N}_{4} and diamond are also listed for comparison. The bulk modulus is calculated to be 336 GPa for \textit{Pnnm}-CN, indicating the ultra-
incompressible nature. However, the bulk modulus of Pnnm-CN is still lower as compared to d-ZB-C$_4$N$_4$ and diamond. This is understandable since Pnnm-CN has relatively smaller C$_{12}$ and C$_{13}$. It is well-known that a superhard material should possess high bulk modulus as well as high shear modulus. Here, we also calculated the shear modulus and found that the G$_d$/B$_0$ value of Pnnm-CN is ~ 0.97 (Table 2). This value is identical to that calculated for d-ZB-C$_4$N$_4$ and lies in the range of the values (0.9-1.2) of typical covalent superhard materials, such as diamond, c-BN$^{41}$-68 and c-B$_4$N$_x$.$^{41,45}$ Therefore, Pnnm-CN is expected to be a superhard material.

Table 2 The calculated elastic constants C$_{ij}$ (GPa), bulk modulus B$_0$ (GPa), shear modulus G$_d$ (GPa), G$_v$/B$_0$ and Vickers hardness H$_v$ of Pnnm-CN, d-ZB-C$_4$N$_4$ and diamond.

<table>
<thead>
<tr>
<th>Phase</th>
<th>C$_{11}$</th>
<th>C$_{12}$</th>
<th>C$_{13}$</th>
<th>C$_{44}$</th>
<th>C$_{55}$</th>
<th>C$_{66}$</th>
<th>C$_{12}$</th>
<th>C$_{13}$</th>
<th>B$_0$</th>
<th>G$_d$</th>
<th>G$_v$/B$_0$</th>
<th>H$_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pnnm-CN</td>
<td>506</td>
<td>643</td>
<td>1183</td>
<td>442</td>
<td>275</td>
<td>372</td>
<td>191</td>
<td>80</td>
<td>140</td>
<td>336</td>
<td>326</td>
<td>0.97</td>
</tr>
<tr>
<td>Pnnm-CN$^a$</td>
<td>518</td>
<td>767</td>
<td>1227</td>
<td>534</td>
<td>277</td>
<td>379</td>
<td>203</td>
<td>83</td>
<td>201</td>
<td>369</td>
<td>351</td>
<td>0.95</td>
</tr>
<tr>
<td>d-ZB-C$_4$N$_4$</td>
<td>794</td>
<td></td>
<td>431</td>
<td></td>
<td></td>
<td></td>
<td>184</td>
<td></td>
<td></td>
<td>387</td>
<td>375</td>
<td>0.97</td>
</tr>
<tr>
<td>c-BN$^c$</td>
<td>820</td>
<td></td>
<td>480</td>
<td></td>
<td></td>
<td></td>
<td>190</td>
<td></td>
<td></td>
<td>400</td>
<td>0.9-1.2$^d$</td>
<td>47-68$^e$</td>
</tr>
<tr>
<td>Diamond</td>
<td>1050</td>
<td></td>
<td>561</td>
<td></td>
<td></td>
<td></td>
<td>124</td>
<td></td>
<td></td>
<td>433</td>
<td>519</td>
<td>1.20</td>
</tr>
</tbody>
</table>

We then calculated the Vickers hardness of Pnnm-CN, d-ZB-C$_4$N$_4$ and diamond using the microscopic hardness model.$^{27,28}$ According to this model, the hardness of a covalent crystal can be calculated from $H = 740P_0(v_i^0)^{-5.3}$, where $P_0$ and $v_i^0$ are Mulliken overlap population and volume of $u$-type bond, respectively. Using this model, remarkably high hardness of 62.5 GPa was estimated for Pnnm-CN, in excellent agreement with a previous prediction (62.3 GPa$^{17}$) based on the same hardness model. The hardness predicted for Pnnm-CN is close to that (63.3 GPa) of d-ZB-C$_4$N$_4$. According to this result, both Pnnm-CN and d-ZB-C$_4$N$_4$ can be classified as superhard materials.

Ideal strength, the peak stress in the strain-stress curves in the weakest tensile stretch or shear slip direction, provides an assessment of the upper limit of the material strength that can be directly compared to nanoindentation measurement.$^{49}$ Therefore, strain-stress calculation is known as a method more accurate in predicting hardness of materials. Encouraged by the extremely high hardness estimated from semiempirical model, we have performed more exact first-principle strain-stress calculations on Pnnm-CN and d-ZB-C$_4$N$_4$. As shown in Fig. 3 (a), Pnnm-CN has high peak stresses of 41, 42, 94, 47.6, 46, 57 and 53 GPa in the <001>, <100>, <110>, <110>, <011> and <111> directions, respectively. The weakest peak tensile stress (ie. ideal tensile strength) of 41 GPa in the <100> direction for Pnnm-CN is comparable to the ideal tensile strength of 45 GPa established here for d-ZB-C$_4$N$_4$ (top panel of Fig. 3b), but still much smaller than that (66 GPa$^{39}$) of c-BN. Meanwhile, we found the strongest peak stress of 94 GPa occurs in the <001> direction, which is larger than the ideal tensile strength (93 GPa$^{50}$) of diamond. The presence of largest and lowest peak stresses in the <001> and <100> directions, respectively, is consistent with the large C$_{12}$ and small C$_{13}$ observed in the elastic constant calculations.

The weakest peak tensile stress of Pnnm-CN in the <100> direction suggests that the (100) planes are the easy cleavage planes. We then evaluate the shear stress response in the (100) planes by applying [001], [011] and [010] shear deformations. The lowest peak shear stress (ie. ideal shear strength) of 51 GPa in the (100)[011] shear direction is larger than the ideal tensile strength. We also examined the shear stress in the (010) secondly easy cleavage planes, and the resultant minimal peak shear stress is 54 GPa in the (010)[100] shear direction. The ideal tensile and shear strengths are both above the threshold (40 GPa) for a superhard material, indicating the superhard nature of Pnnm-CN. Interestingly, we found the ideal shear strength ([111][111] shear direction) of d-ZB-C$_4$N$_4$ is only 39 GPa, excluding it as a superhard material. The Vickers hardness of 41 GPa for Pnnm-CN deduced from ideal tensile strength is much lower than that (62.5 GPa) estimated by semiempirical hardness model. The discrepancy is not surprising as semiempirical model is known to over-exaggerate the hardness for open framework structures.$^{51}$ Even though the hardness is lower than c-BN (47-68 GPa$^{39,30}$), Pnnm-CN may still be an industrially useful material.
In Fig. 4, we show the structural snapshots of the Pnnm structure of CN at selected strains in the <100> direction to understand the local bond deformation and breaking mechanism. The Pnnm structure can be viewed as puckered layers of CN hexagons in the (001) planes bridged by covalent C-C bonds nearly along the <100> direction. We found that the ideal tensile strength of Pnnm-CN coincides with the onset of sudden increase of elongation of C-C bonds at the tensile strain of 0.17 (Fig. 4f). However, it is surprisingly to find that the <100> tensile stress decreases very gradually over a wide range of tensile strain (0.17-0.21) past the peak tensile stress, which is different from the sharply drop behaviour found in superhard c-BN and diamond. Interestingly, hardening of C-N bonds was found with the continuously elongation of C-C bonds at the tensile strain of 0.17 (Fig. 4f). This is understandable since weakening C-C bond as indicated by the slightly decreased C-N bond length from the strain of 0.15 (Fig. 4f). This is understandable since each C atom is surrounded by three N atoms and one C atom, forming three C-N and one C-C bonds. C atoms will be inevitably dragged close to N atom as a result of the weakening of the C-C bonds. As shown in Fig. 4(e), the C-C bonds have been broken at the strains after 0.21 in view of the absence of ELF between two neighboring C atoms. These results demonstrate that C-C bonds are the main load bearing component relating to the structural stability of Pnnm-CN.

Conclusion

In summary, we have performed systematic first-principle calculations to study the structural, electronic, dynamical and mechanical properties of Pnnm-CN. Results show that Pnnm-CN synthesized at high pressure and temperature is dynamically and mechanically stable at ambient pressure established from the phonon dispersion and elastic constants calculations. Significantly, Pnnm-CN possesses high ideal tensile (41 GPa) and shear (51 GPa) strengths obtained from the strain-stress relations, indicating its superhard nature. Analysis of the local bond deformation at the strains in the <100> direction demonstrates that C-C bonds are the main component relating to the structural stability of Pnnm-CN. We believe that the current study will advance the understanding of properties of Pnnm-CN and simulate its potential industrial applications.

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