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# The phase diagram and hardness of carbon nitrides

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CRITICAL PHENOMENAHuafeng Dong<sup>1,2</sup>, Artem R. Oganov<sup>1,2,3,4</sup>, Qiang Zhu<sup>1,2</sup> & Guang-Rui Qian<sup>1,2</sup>

<sup>1</sup>Department of Geosciences, Stony Brook University, Stony Brook, New York 11794-2100, U.S.A., <sup>2</sup>Center for Materials by Design, Institute for Advanced Computational Science, Stony Brook University, Stony Brook, New York 11794-2100, U.S.A., <sup>3</sup>Moscow Institute of Physics and Technology, 9 Institutskiy Lane, Dolgoprudny City, Moscow Region 141700, Russia, <sup>4</sup>School of Materials Science, Northwestern Polytechnical University, Xi'an 710072, China.

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Correspondence and  
requests for materials  
should be addressed to  
A.R.O. (artem.  
oganov@stonybrook.  
edu)

Novel superhard materials, especially those with superior thermal and chemical stability, are needed to replace diamond. Carbon nitrides (C-N), which are likely to possess these characteristics and have even been expected to be harder than diamond, are excellent candidates. Here we report three new superhard and thermodynamically stable carbon nitride phases. Based on a systematic evolutionary structure searches, we report a complete phase diagram of the C-N system at 0–300 GPa and analyze the hardest metastable structures. Surprisingly, we find that at zero pressure, the earlier proposed graphitic-C<sub>3</sub>N<sub>4</sub> structure (*P6m2*) is dynamically unstable, and we find the lowest-energy structure based on s-triazine unit and s-heptazine unit.

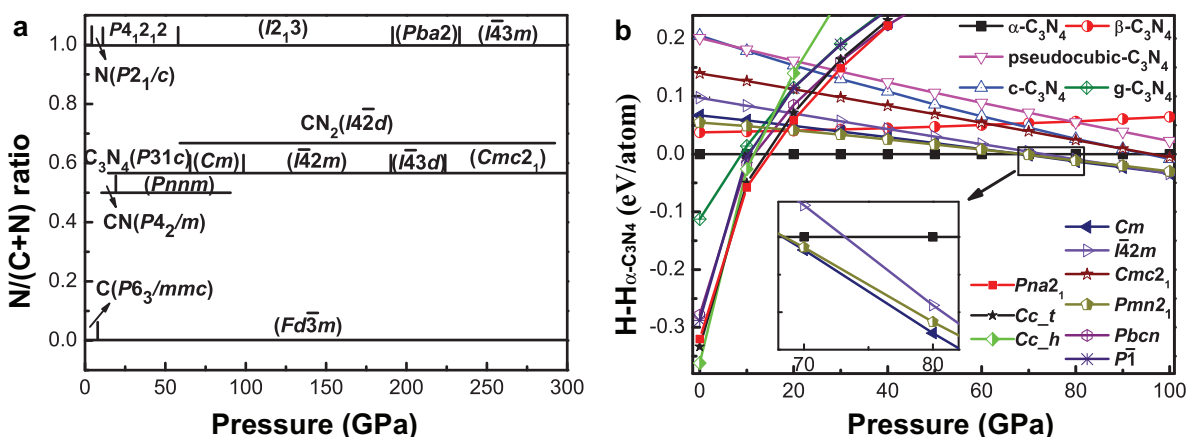
The carbon-nitrogen (C-N) system was long believed to have materials harder than diamond<sup>1</sup>. Recently, carbon nitrides attracted attention due to their potential applications in photocatalysis<sup>2</sup>, photodegradation<sup>3</sup> and photoelectrochemical anticorrosion<sup>4</sup> technology. However, studies of carbon nitrides under pressure face a big problem: neither from theory, nor from experiment it is clear which compositions (i.e., which C/N ratios) will be stable at high pressure, and which compositions will have optimal properties, such as hardness.

Experiments face challenges related to metastability, selection of precursors, determination of the crystal structures and chemical compositions from tiny samples<sup>5–7</sup>; theoretical calculations suffer from assumptions of certain stoichiometries, e.g., C<sub>3</sub>N<sub>4</sub><sup>1</sup>, CN<sup>8</sup>, C<sub>2</sub>N<sup>9,10</sup>, CN<sub>2</sub><sup>11</sup>, C<sub>11</sub>N<sub>4</sub><sup>12</sup>, C<sub>3</sub>N<sub>2</sub><sup>13</sup>, CN<sub>6</sub>.... Some of them are meaningful, while most of them are probably not.

It is difficult to solve this problem because numerous compositions must be tested at each pressure point. For example, at  $P = 0$  GPa, one needs to test compositions of 1 : 1, 1 : 2, 1 : 3, ...; 2 : 1, 3 : 1, 4 : 1, ...; 2 : 3, 2 : 5, 2 : 7, ... When the pressure changes, e.g.  $P = 5, 10, 20$ ... GPa, this needs to be re-checked. Therefore, it becomes a major effort.

To solve this problem, we used the *ab initio* evolutionary algorithm USPEX<sup>14–17</sup>, which can simultaneously find stable stoichiometries and the corresponding structures in multicomponent systems. First, we carried out variable-composition calculations at pressures of 1 atm, 30, 60, 80, 100, 150, 200, and 300 GPa to find the stable and nearly stable compositions (found compositions: C<sub>11</sub>N<sub>4</sub>, C<sub>2</sub>N, CN, C<sub>3</sub>N<sub>4</sub>, CN<sub>2</sub>, CN<sub>6</sub>). Then, for each of these compositions, we performed fixed-composition calculations with different numbers of formula units at different pressures. We not only obtained the stable compositions and structures at each pressure, we also analyzed the hardness of all the stable and metastable structures and found out the hardest structures and compositions, which provide a solid basis for future synthesis of promising ultrahard materials, stable or metastable. Moreover, we have three other novel findings:

1. We uncovered three new superhard phases which are more stable than previous proposals.
2. Graphitic-C<sub>3</sub>N<sub>4</sub> (space group: *P6m2*, based on s-triazine unit)<sup>18–20</sup> was reported to be stable at ambient pressure and has rich potential applications in photocatalysis<sup>2</sup>, photodegradation<sup>3</sup> and photoelectrochemical anticorrosion<sup>4</sup>. However, we found graphitic-C<sub>3</sub>N<sub>4</sub> is not dynamically stable and we uncovered two new structures based on s-triazine unit and s-heptazine unit, which are more stable at ambient pressure.
3. We determined a complete pressure-composition phase diagram of the C-N system at 0–300 GPa, which provides basis to guide the future experimental synthesis of superhard C-N materials.



**Figure 1** | (A) Pressure-composition phase diagram of the C-N system. (B) Enthalpy curves (relative to  $\alpha$ - $C_3N_4$ ) of the five earlier proposed structures<sup>18</sup> and the newly predicted structures.

## Results

**Phase diagram.** Detailed enthalpy calculations for the most stable structures allowed us to reconstruct the pressure-composition phase diagram (Fig. 1). The first thermodynamically stable carbon nitride,  $P4_2/m$ -CN, appears at the pressure of just 14 GPa. This is a superhard 3D-polymorphic structure, as all the other stable carbon nitrides. The predicted phase diagram indicates that  $I\bar{4}2d$ - $CN_2$  is stable at 59–298 GPa;  $P31c$ - $C_3N_4$  (i.e.,  $\alpha$ - $C_3N_4$ ) at 22–68 GPa;  $Cm$ - $C_3N_4$  at 68–98 GPa (reported for the first time);  $I\bar{4}2m$ - $C_3N_4$  at 98–187 GPa (reported for the first time);  $I\bar{4}3d$ - $C_3N_4$  (i.e., cubic- $C_3N_4$ ) at 187–231 GPa;  $Cmc2_1$ - $C_3N_4$  at 224–300 GPa (reported for the first time);  $P4_2/m$ -CN at 14–22 GPa; and  $Pnm$ -CN, stable at 22–97 GPa (see Supplementary Table S1 online for details of structure detailed structural information). These stable structures have lower free energy than any isochemical mixture of other compounds or pure elements (see Supplementary Fig. S1 online). Their main features are the presence of only single C-C, C-N and N-N bonds, with fourfold (tetrahedral) coordination of all C atoms and threefold coordination of all N atoms. For all the stable structures, we computed phonons (see Supplementary Fig. S2 online) and elastic constants (see Supplementary Table S1 online) at ambient pressure, and found them to be dynamically and mechanically stable. Their band structures exhibit wide band gaps as a consequence of strongly localized electrons (see Supplementary Fig. S3 online). Remarkably, all of these phases have three-dimensional frameworks of short covalent bonds, which are responsible for their extreme hardness (Table 1).

$CN_2$  is stable in the tetragonal  $I\bar{4}2d$  structure at 59–298 GPa (Fig. 2a)<sup>11</sup>. In this structure, each C atom is tetrahedrally bonded with four N atoms and each N atom is three-coordinate (2 C-N bonds and 1 N-N bond). Notably, under normal conditions, the  $I\bar{4}2d$ - $CN_2$  structure has an atomic number density of 0.167 atoms/ $\text{\AA}^3$ , which is just a little lower than that of diamond (GGA result: 0.176 atoms/ $\text{\AA}^3$ ; experimental result: 0.178 atoms/ $\text{\AA}^3$ )<sup>18</sup> (Table 1). Moreover, its N-N bond length is only 1.359  $\text{\AA}$ , and C-N bond length is 1.480  $\text{\AA}$ . Both are shorter than the C-C bond length of diamond (1.547  $\text{\AA}$ ) (Table 1).

$C_3N_4$  has attracted much attention for more than 20 years<sup>1,18</sup>. It is not only because the predicted bulk modulus of the cubic- $C_3N_4$  structure is higher than that of diamond<sup>21,22</sup>, but also because of the rich potential applications of the graphitic- $C_3N_4$  in water splitting, organic photosynthesis and environmental remediation<sup>23</sup>. The two most important graphitic carbon nitrides discussed in the literature are based on s-triazine<sup>24</sup> and s-heptazine (i.e. tri-s-triazine)<sup>25</sup> units. The graphitic- $C_3N_4$  (space group:  $P\bar{6}m2$ , based on s-triazine unit) was reported to be stable at ambient conditions,

and there are numerous reports in the literature that approach the synthesis of this material<sup>18–20</sup>. Besides, many theoretical studies are based on this structure<sup>26</sup>. However, we found it to be dynamically unstable (see Supplementary Fig. S2 online). This is in agreement with the prior prediction of Deifallah *et al.*<sup>27</sup> and Bojdys *et al.*<sup>28</sup>, which reported a buckled-graphitic- $C_3N_4$  to be more stable than the planar graphitic- $C_3N_4$ . In addition, we found the most stable structures based on s-triazine unit or s-heptazine unit are not just a buckled structure, all their layers are connected by one nitrogen atom with  $sp^2$  C-N bonds<sup>29</sup>, as shown in Supplementary Fig. S4. We found that the lowest-energy form of structures based on s-triazine unit and s-heptazine unit are almost the same. They have similar topology and belong to the same space group  $Cc$  (No. 9). The s-heptazine-based structures were postulated on the basis of density-functional calculations<sup>25</sup> and experiments<sup>28</sup> to be more stable at ambient conditions. Our predictions support this conclusion:  $Cc$ - $C_3N_4$  (s-heptazine) is lower in energy than  $Cc$ - $C_3N_4$  (s-triazine). Moreover, we have compared their energy with other theoretical proposals<sup>25,29</sup>, as shown in Supplementary Table S5 online. The newly found structures have lower energies than the previously proposed structures. We must emphasize that all calculations on zero-pressure phases of  $C_3N_4$  took account of van der Waals interactions (see Methods).

At 22–68 GPa, the  $\alpha$ - $C_3N_4$  structure is the most stable. The  $\alpha$ - $C_3N_4$  structure is a three-dimensional framework, where each C atom has four inequivalent bonds to N atoms, and each N atom has three inequivalent bonds to C atoms (Fig. 2b). This kind of framework can very easily lead to an asymmetric charge distribution and weak piezoelectricity, which has been confirmed by our calculations (see Supplementary Table S2 online) and recent experimental work<sup>30</sup>. At 68–98 GPa, the  $Cm$ - $C_3N_4$  structure is more stable than any other known  $C_3N_4$  polymorph, and also consists of corner-sharing  $CN_4$  tetrahedron (Fig. 2c). We also found another new structure at the same pressure range,  $Pmn2_1$ - $C_3N_4$  (see Supplementary Fig. S4 online), which is just 2 meV/atom higher in enthalpy than the  $Cm$ - $C_3N_4$  structure. The  $I\bar{4}2m$ - $C_3N_4$  structure (Fig. 2d) is stable at 98–187 GPa. However, at pressures above 187 GPa this structure gives way to a high-density structure, cubic- $C_3N_4$ , which is denser and less compressible (i.e. has higher bulk modulus) than diamond. Besides, it has the largest shear modulus and Young's modulus among all stable carbon nitrides (Table 2). At > 224 GPa (and at least to 300 GPa), the orthorhombic  $Cmc2_1$ - $C_3N_4$  structure, which has not been reported before, is stable. Its structure (Fig. 2f) can be described as an ABAB sequence of puckered graphitic- $C_3N_4$  layers with strong covalent bonds formed between the layers.





