



Unexpected ground-state structures and properties of carbon nitride C_3N at ambient and high pressures

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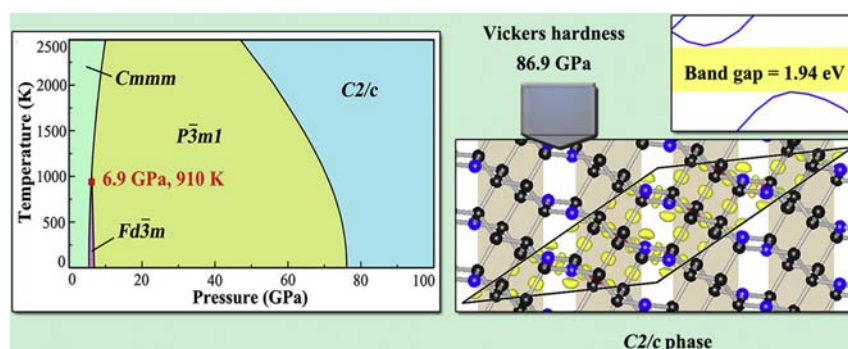
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HIGHLIGHTS

- Four stable C_3N phases were uncovered and pressure-induced phase transition were determined.
- Vickers hardness for the $C2/c$ C_3N can reach up to 86.9 GPa.
- Uncovered C_3N phases are semiconductors with diverse band gaps.
- Pressure-temperature phase diagram was established and high temperature can decrease synthesis pressures of $C2/c$ C_3N .

GRAPHICAL ABSTRACT



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ABSTRACT

Thermodynamically stable C_3N phases in the pressure range of 0–100 GPa are searched and calculated by *ab initio* evolutionary algorithm and density functional theory. Ground-state C_3N phase at ambient pressure is predicted to be a layered structure with $Cmmm$ space group. The previously reported $Fd\bar{3}m$ phase exists only in the narrow pressure range of 6.1–7.4 GPa, which transforms into a $P\bar{3}m1$ phase at 7.4 GPa and then into a $R\bar{3}m$ phase at 40.7 GPa. The increasing pressure drives the $R\bar{3}m$ phase to a $C2/c$ phase at 76.9 GPa. Dynamical and mechanical stabilities of C_3N phases are checked and confirmed by phonon dispersion and elastic constant calculations. It is diverse of the electronic properties of C_3N with $Cmmm$ (zero band gap), $P\bar{3}m1$ (wide gap of 4.55 eV), $R\bar{3}m$ (wide gap of 4.54 eV) and $C2/c$ (narrow gap of 1.94 eV). The three-dimensional strong covalent $C2/c$ C_3N is superhard with high hardness of 79.5 and 86.9 GPa calculated by Chen and Gao models. Pressure-temperature phase diagram of C_3N is firstly established and shows high temperature can significantly decrease synthesis pressures of $C2/c$ phase, which gives a theoretical guidance for further experimental synthesis.

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1. Introduction

Searching for superhard materials (Vickers hardness > 40 GPa) is not only of fundamental research interests on the understanding of hardness nature, but also of their wide technical applications in modern industry areas, such as wear-resistant coating, abrasives, polishing and cutting tools. The intrinsic superhard materials can be classified into

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two groups [1]: a) light-element (B, C, N, and O) compounds or elementary substance (diamond) with short and strong covalent bonds [2]; b) compounds formed by transition metals and light elements [3,4]. The former group includes some well-established compounds, such as cubic-BN, B₆O, BC₅ and BC₂N [2,5,6].

Except for the above light-element compounds, carbon nitride crystals with C₃N₄ stoichiometry have attracted more attentions since their hardnesses were predicted to be comparable to that of diamond [7]. Considering similar atomic radii and bonding characters between C and N atoms, it is undoubtedly logical that there should exist other stoichiometric carbon nitride compounds. Many efforts have been devoted to the studies of different stoichiometries in C-N system experimentally [8–13] and theoretically [7,14–20]. For C₃N₄ stoichiometry, Dong et al. [14] found the most stable form at ambient pressure should be Cc-C₃N₄ structure rather than the earlier proposed graphitic C₃N₄ structure. Recently the mechanical and electronic properties of two thermodynamically metastable C₃N₄ (monoclinic and tetragonal phases) were investigated [21], whose structures are built by carbon replacing silicon in *m*-Si₃N₄ and *t*-Si₃N₄ respectively [22]. Pressure-composition phase diagram of C-N system shows that the CN₂ stoichiometry with tetragonal $I\bar{4}2d$ symmetry becomes stable above 59 GPa [14], agreeing with an earlier calculation [19]. In recent several years, CN stoichiometry has attracted particular interests due to the successful synthesis [8], which is consistent with theoretical predictions [14–16].

Because N atoms in C-N compounds prefer to form N₂ molecules, it is a common phenomenon that the nitrogen content is low in the products of attempting to synthesize C₃N₄ stoichiometry [23,24]. Thus it is reasonable that some carbon-rich C-N phases should exist. A previous paper [25] also confirmed that low-nitrogen C-N phases should be easier synthesized than C₃N₄. Due to high carbon contents, C₃N stoichiometry has been paid more attentions in carbon-rich C-N phases. By a solvothermal process, graphitic C₃N powders were synthesized experimentally using CaCN₂ and C₂Cl₆ as starting materials [26]. Sun et al. also got some small C₃N particles by a low-temperature reaction [27]. Recently bulk C₃N flakes have been synthesized by thermolysis of *m*-phenylenediamine under vacuum [13]. However the above obtained samples are of poor crystallinity, and meanwhile the atomic masses of C and N atoms are similar and small. Therefore it is a challenge by experimental measurements to completely resolve the crystal structure of the synthesized C₃N samples.

Theoretical calculations are a feasible method to predict the structures and properties of C₃N. The first theoretical work for C₃N was conducted by Mizuno [28], in which a C₃N monolayer model is constructed by N atoms replacing one of four carbon atoms in a single graphite layer (graphene). Sandré et al. [29] proposed four C₃N bulk structures, in which a flat C₃N model possesses the lowest energy at ambient pressure. Subsequently, one M2 structure [25] with *Pbam* space group was calculated to be more stable at ambient pressure than the reported flat C₃N model in Ref. [29]. Later a C₃N model [30] constructed from hexagonal BN was found to possess lower energy than the M2 structure. Recently, a C₃N model [17] with *P6/mmm* symmetry was constructed based on hexagonal B₃N₅ structure [31]. The *P6/mmm* C₃N was calculated to be more energetically favorable at ambient pressure than all previously proposed structures. The above researches mainly focus on searching the ground-state structure of C₃N at ambient pressure. Superhard materials are dense phase with short bonds, which could be synthesized usually under high pressures. For high-pressure phase transition of C₃N, Hao et al. [17] found when pressure is above 9 GPa, the *P6/mmm* C₃N structure will transform into a C222₁ phase constructed from C222₁ B₃N₅ structure [31].

The above predictions of new C₃N structures take a conventional method to construct structural models by replacing atoms in known phases. In recent years, several state-of-the-art global optimization packages, such as USPEX [32–34], CALYPSO [35] and MUFE [36], were developed to uncover structures with minimum free energy under ambient or high pressures and have been successfully applied in various

systems [37–40]. Using the particle swarm optimization technique as implemented in CALYPSO, Wei et al. uncovered a stable cubic *Fd\bar{3}m* C₃N phase. Though previously several calculations have been done, an extensive and systematical research is still essential to reveal the energetically stable C₃N phases at ambient and high pressures. In order to systematically investigate the structure evolution of C₃N under high pressures, thorough and careful searches for the structures of C₃N stoichiometry at ambient and high pressures (up to 100 GPa) were conducted in the present work by using the evolutionary algorithm USPEX. Four thermodynamically stable C₃N phases (*Cmmm*, *P\bar{3}m1*, *R\bar{3}m* and *C2/c*) are uncovered, and then their mechanical and electronic properties are investigated. In order to determine the phase boundaries, phase transition sequences and critical pressure points of C₃N are given, and especially a detailed pressure-temperature (*P-T*) phase diagram for C₃N is established to guide next experimental syntheses.

2. Computational methods

The fixed-composition searches for C₃N ground-state structures were performed using the ab initio evolutionary algorithm as implemented in the USPEX package [32–34]. Variable-cell structure searches for C₃N with one to four formula units (f.u.) were performed at 0, 10, 30, 60 and 100 GPa without any symmetry constraints. The first-generation structures were randomly obtained. Then each subsequent generation was generated from the lowest-enthalpy 60% structures of the last generation by applying variation operators including heredity (45%), random (25%), lattice mutation (20%), and atomic permutation (10%). Structural relaxations of the C₃N structures created by USPEX were carried out using density functional theory within the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional as implemented in the VASP code [42]. All electron projector-augmented wave method (PAW) was taken with 2s²2p² (carbon) and 2s²2p³ (nitrogen) treated as valence electrons. The plane-wave kinetic-energy cutoff was set to be 600 eV and the Brillouin zone was sampled by Monkhorst-Pack meshed with the resolution 2π × 0.03 Å⁻¹ to ensure that the enthalpy calculations are converged to better than 1 meV/atom. Calculated total energies were corrected by considering van der Waals (vdW) interactions through the D2 method of Grimme [43]. Phonon calculations were carried out by using a finite displacement approach in the PHONOPY code [44]. Elastic constants were calculated by the strain-stress method [45], and then the polycrystalline bulk modulus, shear modulus, Young's modulus, and Poisson's ratio were estimated by using the Voigt-Reuss-Hill averaging scheme [46].

3. Results and discussion

3.1. Stable structures under different pressures

The C₃N ground state at ambient pressure revealed by our structure searches is to be a layered phase. As shown in Fig. 1a, the C₃N layered structure can be identified as N₂ molecules sandwiched between the graphite layers. This layered structure of C₃N is similar to the *P6/mmm* structure predicted in Ref. [17]. For layered structure calculations, long-range vdW interactions should not be ignored. In this work, the vdW corrections were taken into account to acquire accurate lattice parameters of C₃N and exact orientations of N₂, which were not considered in previous C₃N calculations [17,41]. The N₂ molecule was rotated in the two neighboring carbon layers to acquire the optimal orientation of N₂. Considering the graphite-like layered structure feature of C₃N, N₂ rotation in the (001) plane was firstly taken. Then with the most stable orientation of N₂ in the (001) plane as the starting, the N₂ rotation out of the (001) plane was performed. This rotating plane is determined to be (110) plane. During the N₂ rotating, the center of N₂ molecule was fixed. The calculated enthalpies as a function of N₂ rotation angles were plotted in Fig. 1b. For comparison, no-vdW correction results were also

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