

## High-Energy Density and Superhard Nitrogen-Rich B-N Compounds

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The pressure-induced transformation of diatomic nitrogen into nonmolecular polymeric phases may produce potentially useful high-energy-density materials. We combine first-principles calculations with structure searching to predict a new class of nitrogen-rich boron nitrides with a stoichiometry of  $B_3N_5$  that are stable or metastable relative to solid  $N_2$  and  $h$ -BN at ambient pressure. The most stable phase at ambient pressure has a layered structure ( $h$ - $B_3N_5$ ) containing hexagonal  $B_3N_3$  layers sandwiched with intercalated freely rotating  $N_2$  molecules. At 15 GPa, a three-dimensional  $C222_1$  structure with single N-N bonds becomes the most stable. This pressure is much lower than that required for triple-to-single bond transformation in pure solid nitrogen (110 GPa). More importantly,  $C222_1$ - $B_3N_5$  is metastable, and can be recovered under ambient conditions. Its energy density of  $\sim 3.44$  kJ/g makes it a potential high-energy-density material. In addition, stress-strain calculations estimate a Vicker's hardness of  $\sim 44$  GPa. Structure searching reveals a new clathrate sodalitelike BN structure that is metastable under ambient conditions.

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Triple-bonded diatomic nitrogen ( $N_2$ ) has the highest bond energy of all diatomic molecules. Previous experiments have shown that molecular nitrogen can only be transformed into a singly bonded polymeric phase at pressures greater than 100 GPa [1–3]. The preservation of such a nonmolecular structure and its recovery under ambient conditions would provide a useful high-energy-density material. However, polymeric N has never been formed at ambient pressure [1–3], precluding its practical applicability. Therefore, other nitrogen-rich compounds with substantially lower dissociation pressures of the triple  $N \equiv N$  bond have been sought such as  $LiN_3$  [4],  $NaN_3$  [5], a  $CO-N_2$  [6] mixture, and  $C_3N_{12}$  [7]. In particular, Raza *et al.* [6] reported a  $CO-N_2$  system where the triple  $N \equiv N$  bond dissociated at 52 GPa.

Boron nitride (BN) is the only known stable compound in the BN system. It is isoelectronic to carbon, and forms analogues to various carbon structures ( $h$ -BN [8],  $r$ -BN [9],  $c$ -BN [10],  $w$ -BN [11], amorphous BN [12], BN nanotubes [13], and BN nanomesh [14]). These polymorphs exhibit exceptional mechanical, thermal, optical, and catalytic properties. They have featured in various efforts to find superhard materials, with polymorphs developed by substituting B and N for C in different carbon allotropes. Structural searches from first principles have also been used to develop superhard materials, uncovering a new family of thermodynamically metastable BN polymorphs that includes  $bct$ -BN [15] (or  $pct$ -BN [16]),  $Z$ -BN [17],  $P$ -BN [18],  $T$ -BN [19],  $cT_8$ -BN [20],  $I$ -BN [21],  $O$ -BN [22,23],  $Pbca$ -BN [24],  $B_4N_4$  [25],  $M$ -BN [26],  $Z'$ -BN [26], and  $BC_8$ -BN [26]. A common property shared between

these BN polymorphs is their predicted superhardness, with estimated Vicker's hardnesses between 47 and 66.8 GPa.

*Ab initio* structural prediction can reliably search for unknown structures. A recent example is the prediction of  $NaCl_3$  and  $Na_3Cl$  compounds, which have been confirmed experimentally [27]. Experiments have also demonstrated that molecular  $H_2$  can interact readily with closed-shell molecules at easily accessible pressures ( $< 20$  GPa) in the formation of van der Waals compounds, such as  $SiH_4-H_2$  [28] and  $H_2S-H_2$  [29]. If B-N compounds with unusual properties could be stabilized, they could be used in superhard and high-energy-density materials.

In this study, stable compounds in the  $B_xN_y$  ( $x, y = 1-6$ ) system are investigated by *ab initio* structure prediction [30,31]. In addition to the known compound BN, several thermodynamically stable and metastable BN and  $B_3N_5$  compounds are found. The newly predicted  $B_3N_5$  polymer is a hard and high-energy-density material that is metastable under ambient temperature and pressure, and thus might be recoverable.

Structure predictions for  $B_xN_y$  are performed using the particle swarm optimization technique implemented in the CALYPSO code [30,31] and the Vienna *ab initio* simulation package [32]. CALYPSO has been used to investigate a great variety of materials at high pressures [33–38]. Detailed information on the calculations is provided in the Supplemental Material [39].

We first perform structure searches on  $B_xN_y$  ( $x, y = 1-6$ ) at ambient pressure. Figure 1 summarizes the formation enthalpies calculated at a high level of accuracy and

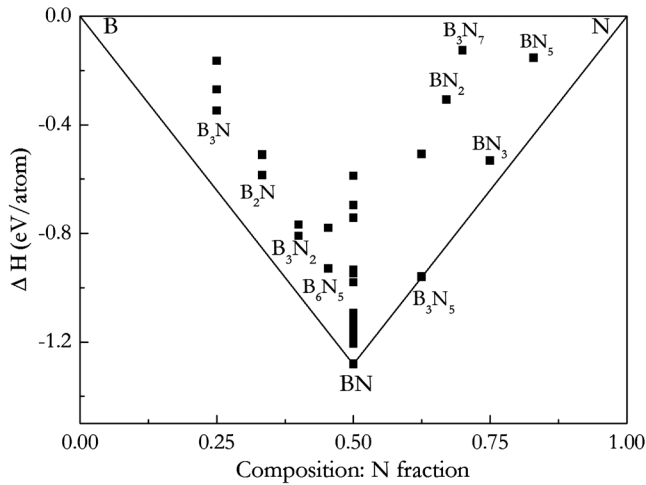


FIG. 1. Convex hull diagram for the BN system at ambient pressure. Formation enthalpy,  $\Delta H$ , is defined as  $\Delta H = H(\text{B}_x\text{N}_y) - [xH(\text{B}) + yH(\text{N})]$ . The alpha-B phase and alpha- $\text{N}_2$  phase are used in the calculation. Only stoichiometries with formation enthalpies close to the convex hull are presented.

normalized on a per-atom basis for the most energetically favorable of the structures. The stable compositions form a convex hull, where a point lying on the tie line corresponds to a thermodynamically stable phase. As expected, BN has the lowest formation enthalpy. On the B-rich side, all the stoichiometries have significant negative enthalpies with respect to dissociation into elemental B and N. However, the enthalpies are all above the tie line connecting BN and B. Therefore, these B-rich polymorphs are only thermodynamically metastable, and are susceptible to decomposition into *h*-BN and B. The N-rich region includes a thermodynamically stable compound with stoichiometry of  $\text{B}_3\text{N}_5$ ; the enthalpy of the energetically most stable structure (*h*- $\text{B}_3\text{N}_5$ ) is nearly equal to  $3(\text{BN}) + \text{N}_2$  calculated with both the PAW-PBE and vdW-DF functionals.

Figure 2 shows 10 predicted low-enthalpy structures of BN at ambient pressure, which can be categorized as 2D layered, 3D, and cage-like structures. The most stable crystalline forms of BN predicted here have layered structures. These include the experimentally known *h*-BN [8] (with space groups  $P\bar{6}m2$ ,  $P6_3/mmc$ , and  $P\bar{3}m1$ ), *r*-BN [9] (space group  $R\bar{3}m$ ), and two new structures with space groups  $P\bar{6}m2$  (denoted as  $P\bar{6}m2\text{-}2$  in Fig. 2) and  $P3_1$ . All six layered structures consist of flat planes of  $\text{B}_3\text{N}_3$  hexagons (Fig. 2), with the only differences among them being the patterns in the stacking of the layers, which are *ABA*... in *h*-BN and *AAA*... in the new  $P\bar{6}m2\text{-}2$ -BN. The layers are held together by weak van der Waals forces with a large average interlayer distance of 4.2 Å based on the PAW-PBE calculation, which decreases to 3.5 Å when vdW-DF functionals are included. Consequently, the six layered structures possess nearly identical enthalpies.

Three metastable 3D structures—the experimentally observed *c*-BN, *w*-BN structures and the previously

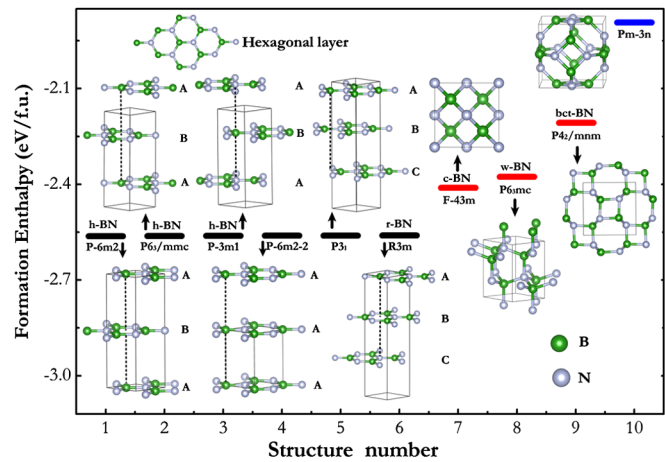


FIG. 2 (color online). Ten predicted low-enthalpy structures for BN at ambient pressure. Horizontal bars beside each structure represent formation enthalpies with respect to elemental B and N; the color represents the type of structure. Dashed vertical lines in the first six layered structures are shown to distinguish the stacking sequence of the layers.

predicted *bct*-BN structure [15,16]—are also found in the structure search (Fig. 2). We also find a sodalite structure with the cubic  $Pm\bar{3}n$  space group at a higher negative formation enthalpy (Fig. 2). The  $Pm\bar{3}n$  structure, which is constructed from planar  $\text{B}_3\text{N}_3$  hexagonal faces with B–N bond lengths of 1.57 Å, is identical to that of *c*-BN. Eight hexagons in the unit cell are linked to each other by sharing B–N edges. Consequently, planar  $\text{B}_3\text{N}_3$  hexagons and  $\text{B}_2\text{N}_2$  squares form  $\text{B}_{12}\text{N}_{12}$  sodalitelike cages (Fig. 2). The B and N atoms form a tetragonally bonded structure with both B–N–B and N–B–N forming bond angles of either  $90^\circ$  or  $120^\circ$ .

The  $Pm\bar{3}n$  structure is stable at ambient pressure because all phonon frequencies are positive definite (Supplemental Material, Fig. S1 [39]) and the calculated elastic constants [39] satisfy the Born stability criteria [53]. The results indicate that  $Pm\bar{3}n$ -BN is metastable and may be recoverable once formed. The electronic band structure calculated with the HSE06 functional shows that  $Pm\bar{3}n$ -BN is an insulator with a large indirect band gap of 5.9 eV (Supplemental Material, Fig. S3(a) [39]), which lies between those of *h*-BN (5.2 eV) and *c*-BN (6.4 eV). A sodalitelike  $\text{B}_{12}\text{N}_{12}$  nanocage cluster has been synthesized [54], which is the building block of the  $Pm\bar{3}n$  structure. Interestingly, a similar sodalitelike cage structure has been proposed in carbon [55], and is regarded as the best candidate structure for synthesized “superdense” carbon [56]. We found that at 0 GPa C-sodalite is 0.38 eV/atom higher in energy than diamond. In comparison,  $\text{C}_{60}$  is 0.30 eV/atom higher in energy than graphite. In this case, the total energy difference of  $Pm\bar{3}n$ -BN with respect to *c*-BN is only 0.26 eV/atom. Therefore, if C-sodalite is indeed the synthesized “superdense” carbon, we believe that BN-sodalite can also be synthesized.

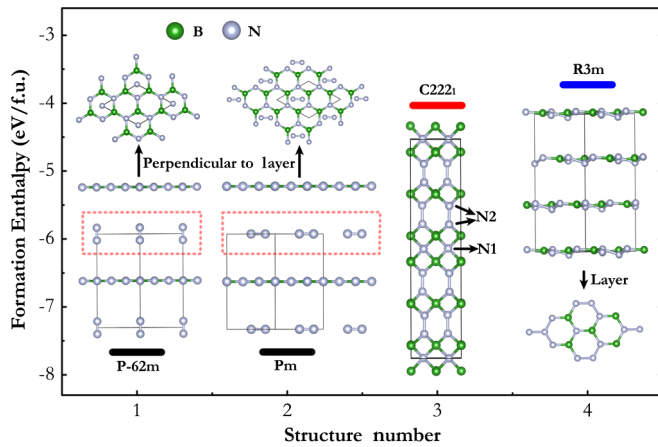


FIG. 3 (color online). Illustrations of four predicted low-enthalpy structures of  $B_3N_5$  at ambient pressure. Dashed rectangles in the left two structures represent the different orientations of  $N_2$  molecules.

The stability of N-rich  $B_3N_5$  is surprising. Its most stable form at ambient pressure has a layered structure (Fig. 3). Interestingly, the two energetically comparable  $P\bar{6}2m$  and  $Pm$  structures (referred to as  $h$ - $B_3N_5$  hereafter) are constructed from the same planar hexagonal BN layers sandwiched with  $N_2$  molecules  $[(BN)_3N_2]$ . Each BN layer in  $h$ - $B_3N_5$  consists of a network of hexagonal  $B_3N_3$  with B-N bond lengths of 1.45 Å, identical to those in  $h$ -BN. The N-N bond length of the  $N_2$  molecule in the two layered structures is 1.11 Å, which is only slightly longer than that (1.07 Å [57]) of pure  $N_2$  and much shorter than that (1.21 Å) of a typical N=N double bond in  $N_2F_2$ . Therefore, the intercalated  $N_2$  in  $h$ - $B_3N_5$  is nominally triple bonded ( $N \equiv N$ ).

Both the  $P\bar{6}2m$  and  $Pm$  structures have the same AA... stacking of BN layers with  $N_2$  molecules sandwiched between pairs of adjacent planes. The only difference between them is the orientation of the  $N_2$  molecules, which are perpendicular to the layers in  $P\bar{6}2m$  but parallel in  $Pm$  (dashed rectangles in Fig. 3). Removal of  $N_2$  molecules from the two structures results in a simple layered structure of  $P\bar{6}m2$ -BN (Fig. 2), suggesting that the  $N_2$  molecules are loosely bound between the BN hexagonal layers. To test this suggestion, total energy calculations are performed by rotating the  $N_2$  incrementally in the (110) and (1 $\bar{1}$ 0) planes (Fig. 3) while fixing each molecule's center of mass. Plots of the calculated energy versus  $N_2$  orientation are compared in Fig. 4(a). The maximum energy change during the  $N_2$  rotation is only 1.7 meV/atom, even smaller than the estimated energy barrier (6 meV/atom) of  $H_2$  rotation in orientationally disordered hcp- $H_2$  [58]. Therefore, the  $N_2$  molecules in  $h$ - $B_3N_5$  are almost certainly freely rotating at finite temperature. Surprisingly, we find that the band gap of  $h$ - $B_3N_5$  changes appreciably with the  $N_2$  orientation: from 4.74 eV in the  $P\bar{6}2m$  structure to 5.02 eV in the  $Pm$  structure (Supplemental Material, Figs. S3(b) and S3(c) [39]).

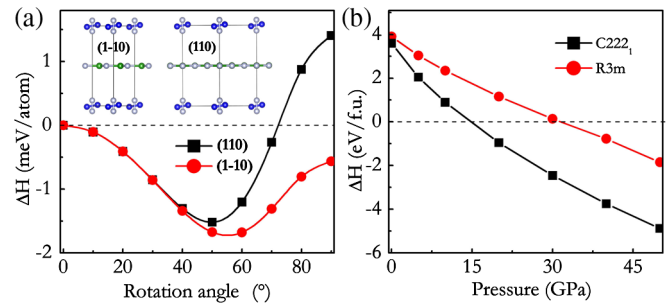


FIG. 4 (color online). (a) Total energies as a function of  $N_2$  orientation at ambient pressure in the (110) and (1 $\bar{1}$ 0) planes of  $h$ - $B_3N_5$ . Insets in (a) illustrate  $N_2$  rotations. Blue atoms represent rotated  $N_2$  molecules. (b) Enthalpy curves of  $C222_1$  and  $R3m$  structures relative to  $h$ - $B_3N_5$  as a function of pressure.

In addition to  $h$ - $B_3N_5$ , we find another layered structure with a  $R\bar{3}m$  space group. In contrast to the free  $N_2$  in  $h$ - $B_3N_5$ , the  $N_2$  units here participate in forming the puckered  $B_3N_5$  layers containing edge-sharing  $B_3N_3$  and  $B_2N_4$  hexagons (Fig. 3). Consequently, the N-N bond distance of 1.48 Å is much longer than that in  $h$ - $B_3N_5$ , and is closer in length to a single N-N bond. The B-N bond distance of 1.44 Å is similar to that in  $h$ - $B_3N_5$ . The  $B_2N_4$  hexagon is less stable than the  $B_3N_3$  hexagon because the  $R\bar{3}m$  structure has a much higher enthalpy than  $h$ - $B_3N_5$  (Fig. 3).

The structure search also yields an orthorhombic 3D  $B_3N_5$  structure with the space group  $C222_1$ . This structure is metastable relative to  $h$ - $B_3N_5$  at 0 GPa, but is the most stable structure in the structure searches performed at 50 GPa. The calculated equation of states predicts that the phase transition from  $h$ - $B_3N_5$  to  $C222_1$  occurs at 15 GPa (Fig. 4b). In the  $C222_1$  structure, each B atom is tetragonally bonded to two different N atoms (N1 and N2) with B-N1 and B-N2 bond lengths of 1.58 and 1.53 Å, respectively. The  $sp^3$  N1 is bonded to four B atoms, and  $sp^2$  N2 is bonded to two B atoms and one N2 atom; both combine to form planar  $B_2N_4$  hexagons with two equal N-N bonds 1.33 Å in length. In the  $C222_1$  structure, the N2-N2 bond of two  $sp^2$  N atoms indicates a single bond. In contrast to the large band gap of  $h$ - $B_3N_5$  and the various crystalline forms of BN, the presence of  $sp^2$  and  $sp^3$  N atoms make  $C222_1$ - $B_3N_5$  a semiconductor with a small band gap of 0.775 eV (Supplemental Material, Fig. S3(d) [39]).

The calculated phonon dispersions (Supplemental Material, Fig. S1(b) [39]) and elastic constants (Supplemental Material, Table S3 [39]) confirm that  $C222_1$ - $B_3N_5$  is dynamically and mechanically stable at ambient pressure. Owing to the large difference in the bond strengths between single N-N (160 kJ/mol) and triple  $N \equiv N$  (954 kJ/mol) bonds [2], the transformation from polymeric nitrogen back to diatomic nitrogen is expected to be highly exothermic. The energy involved in the decomposition of  $C222_1$ - $B_3N_5$  into solid 3BN and gaseous  $N_2$  at ambient pressure was

calculated. The contribution of  $PV$  to the enthalpy of gaseous  $N_2$  was considered in view of its large volume (22.4 L/mol) under ambient conditions. At the PBE-GGA level, the energy difference of 3.57 eV corresponds to an energy density of  $\sim 3.44$  kJ/g, which is lower than that predicted for  $cg$ -N (9.7 kJ/g), but higher than that predicted recently for  $CO-N_2$  (2.2 kJ/g) [6]. Remarkably,  $C222_1$ - $B_3N_5$  is thermodynamically stable at 15 GPa, which is much lower than the formation pressures of  $cg$ -N (110 GPa) and polymeric  $CO-N_2$  (52 GPa). This stability at a relatively low pressure suggests that  $C222_1$ - $B_3N_5$  might be synthesized by high-pressure high-temperature techniques. If it can be made, the compound will be a good high-energy-density material. The energy and phonon calculations predict two BN polymorphs (sodalitelike  $Pm\bar{3}n$ -BN and  $C222_1$ - $B_3N_5$ ) that may be quenched and recovered at ambient pressure. The stabilities of both compounds at ambient pressure and temperature are investigated by metadynamics simulations at 1 bar and 300 K (Supplemental Material, Fig. S2 [39]). No structural changes are observed after 200 metasteps, indicating that both compounds are metastable under ambient conditions.

A strong three-dimensional covalent bond network is a key feature of superhard materials. The hardness values of  $Pm\bar{3}n$ -BN and  $C222_1$ - $B_3N_5$  were estimated with the microscopic hardness model [59–61], which calculates the hardness of a covalent crystal as  $H_v^u = 740P^u(v_b^u)^{-5/3}$ , where  $P^u$  and  $v_b^u$  are the Mulliken overlap population and the volume of  $u$ -type bonding, respectively. This model predicts remarkably high hardnesses for  $Pm\bar{3}n$ -BN (58.4 GPa) and  $C222_1$ - $B_3N_5$  (78.5 GPa) (Supplemental Material, Table S4). Their high hardnesses compared with  $c$ -BN (65 GPa) allow both to be classified as superhard materials. These encouraging results are verified through more exact *ab initio* stress-strain calculations for  $C222_1$ - $B_3N_5$ . The results presented in Fig. 5 (a) show weakness in the  $\langle 011 \rangle$  direction, with an ideal tensile strength of 56 GPa; therefore, the (011) planes allow easy cleavage. We then evaluate the shear stress response in the (011) planes and an ideal shear strength of 44 GPa is obtained in the (011)[100] shear direction. This suggests a theoretical hardness of 44 GPa for  $C222_1$ - $B_3N_5$ , much lower than that estimated by the microscopic hardness model. The discrepancy is not surprising as this empirical model is known to exaggerate hardness for open-framework structures. Despite the hardness being lower than that of  $c$ -BN, quenched recovered  $C222_1$ - $B_3N_5$  may still be an industrially useful material.

In conclusion, we performed a systematic search for stable compounds in the BN system. In addition to BN, the search found a new stable N-rich compound with stoichiometry of  $B_3N_5$ , which at ambient pressure has a layered structure with freely rotating  $N_2$  molecules intercalated between the layers. Layered  $B_3N_5$  should transform into  $C222_1$ - $B_3N_5$  above 15 GPa with the dissociation of

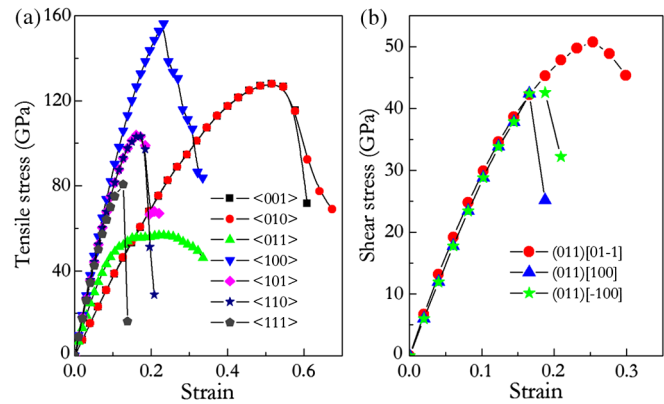


FIG. 5 (color online). (a) Calculated tensile stress-strain relations for  $C222_1$ - $B_3N_5$  in various directions. (b) Calculated shear stress-strain relations for  $C222_1$ - $B_3N_5$  in the (011) easy cleavage plane.

triple  $N \equiv N$  bonds into single  $N-N$  bonds. Therefore, the  $C222_1$  phase is a potential high-energy-density material. Calculations also revealed  $C222_1$ - $B_3N_5$  to be superhard. These results provide a promising new area of synthesis for nitrogen-rich high-energy-density materials *via* the intercalation of  $N_2$  molecules into the BN layers.

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