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High-energy-density and superhard nitrogen-rich B-N compounds

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The pressure-induced transformation of diatomic nitrogen into non-molecular 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 ~ 3.44 kJ/g makes it a potential high-energy-density material. In addition, stress–strain calculations estimate a Vicker’s hardness of ~ 44 GPa. Structure searching reveals a new clathrate sodalite-like 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 non-molecular 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 meta-stable 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 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 B_3N_5 ; the enthalpy of the energetically most stable structure (*h*- B_3N_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 $P-6m2$, $P6_3/mmc$, 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 $P\bar{6}m2-2$ in Fig. 2) and $P3_1$. All six layered structures consist of flat planes of B_3N_3 hexagons (Fig. 2), with the only differences among them being the patterns in the stacking of the layers, which are $ABA\dots$ in h -BN and $AAA\dots$ in the new $P\bar{6}m2$ -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 meta-stable 3D structures—the experimentally observed c -BN, w -BN structures and the previously 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 B_3N_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 B_3N_3 hexagons and B_2N_2 squares form $B_{12}N_{12}$ sodalite-like 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° or 120°.

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[40]. 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. S3a[39]), which lies between those of h -BN (5.2 eV) and c -BN (6.4 eV). A sodalite-like $B_{12}N_{12}$ nanocage cluster has been synthesized[41], which is the building block of the $Pm\bar{3}n$ structure. Interestingly, a similar sodalite-like cage structure has been proposed in carbon[42], and is regarded as the best candidate structure for synthesized “superdense” carbon[43]. We found that at 0 GPa C-sodalite is 0.38 eV/atom higher in energy than diamond. In comparison, 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.

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[44]) 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 (1-10) 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 [45]. 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. S3b and S3c [39]).

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. S3d[39]).

The calculated phonon dispersions (Supplemental Material, Fig. S1b [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 ~ 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–N₂ (2.2 kJ/g) [6]. Remarkably, *C222*₁-B₃N₅ is thermodynamically stable at 15 GPa, which is much lower than the formation pressures of *cg*-N (110 GPa) and polymeric CO–N₂ (52 GPa). This stability at a relatively low pressure suggests that *C222*₁-B₃N₅ 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 (sodalite-like *Pm* $\bar{3}$ *n*-BN and *C222*₁-B₃N₅) 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-B₃N₅ were estimated with the microscopic hardness model[46-48], 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-B₃N₅ (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-B₃N₅. The results presented in Fig. 5 (a) show weakness in the $\langle 011 \rangle$ direction, with a 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 a 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-B₃N₅, 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 C222₁-B₃N₅ 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 B₃N₅, which at ambient pressure has a layered structure with freely rotating N₂ molecules intercalated between the layers. Layered B₃N₅ should transform into C222₁-B₃N₅ above 15 GPa with the dissociation of triple N≡N bonds into single N–N bonds. Therefore, the C222₁ phase is a potential high-energy-density material. Calculations also revealed C222₁-B₃N₅ to be superhard. These results provide a promising new area of synthesis for nitrogen-rich high-energy-density materials *via* the intercalation of N₂ molecules into the BN layers.

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Figure Captions

Fig. 1. Convex hull diagram for the BN system at ambient pressure. Formation enthalpy, ΔH , is defined as $\Delta H = H(\text{B}_x\text{N}_y) - (xH(\text{B}) + yH(\text{N}))$. Alpha-B phase and alpha-N₂ phase are used in the calculation. Only stoichiometries with formation enthalpies close to the convex hull are presented.

Fig. 2. 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.

Fig. 3. Illustrations of four predicted low-enthalpy structures of B₃N₅ at ambient pressure. Dashed rectangles in the left two structures represent the different orientations of N₂ molecules.

Fig. 4. (a) Total energies as a function of N₂ orientation at ambient pressure in (110) and (1-10) planes of *h*-B₃N₅. Insets in (a) illustrate N₂ rotations. Blue atoms represent rotated N₂ molecules. (b) Enthalpy curves of C222₁ and R3m structures relative to *h*-B₃N₅ as a function of pressure.

Fig. 5. (a) Calculated tensile stress–strain relations for C222₁-B₃N₅ in various directions. (b) Calculated shear stress–strain relations for C222₁-B₃N₅ in the (011) easy cleavage plane.

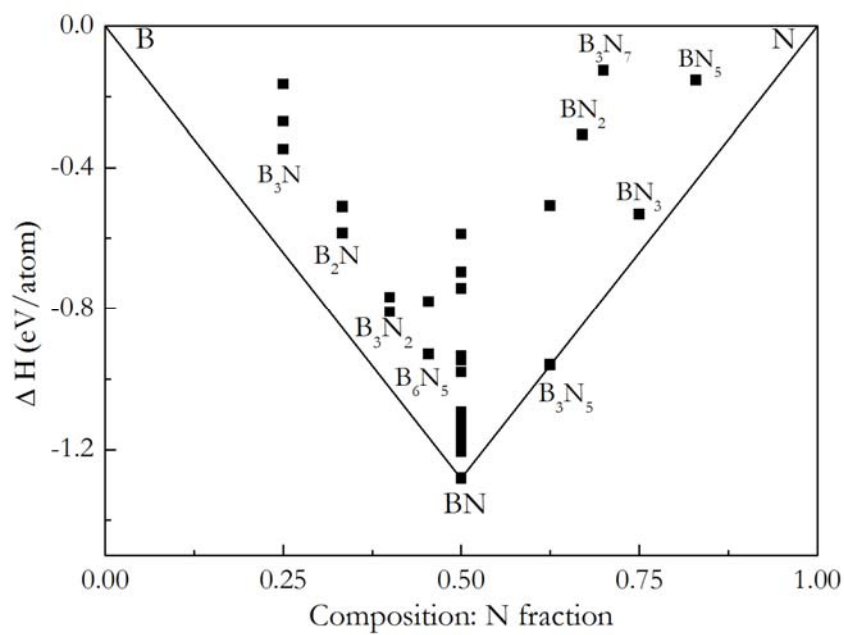


Figure 1

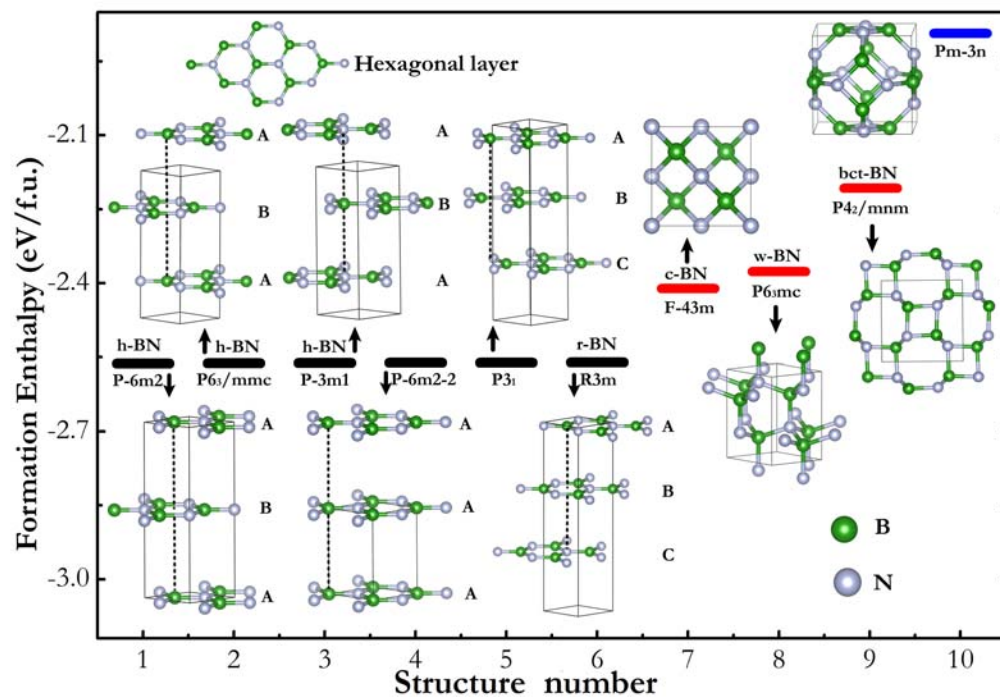


Figure 2

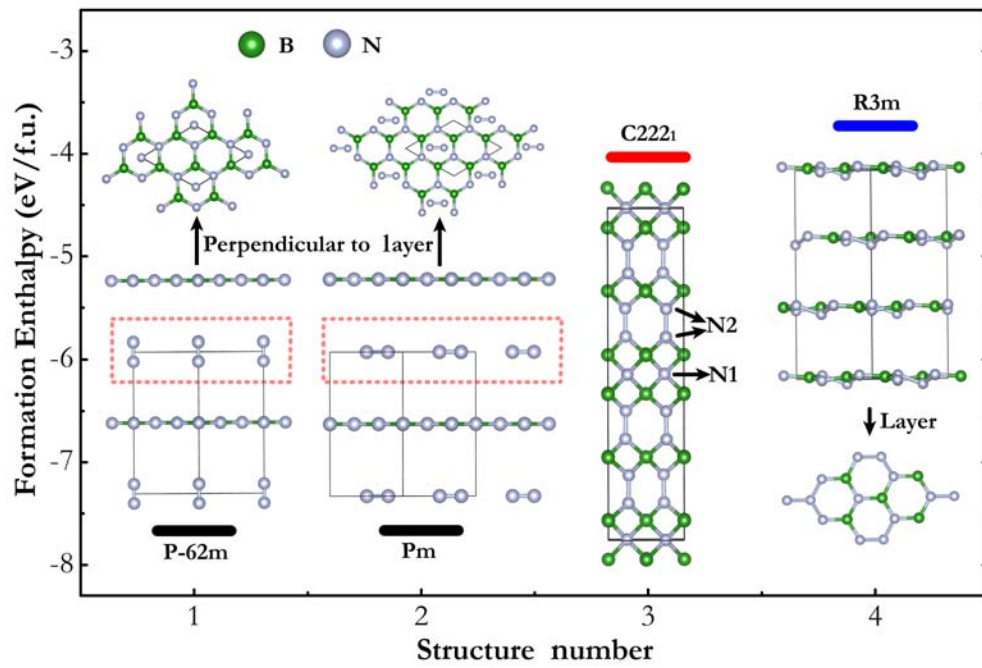


Figure 3

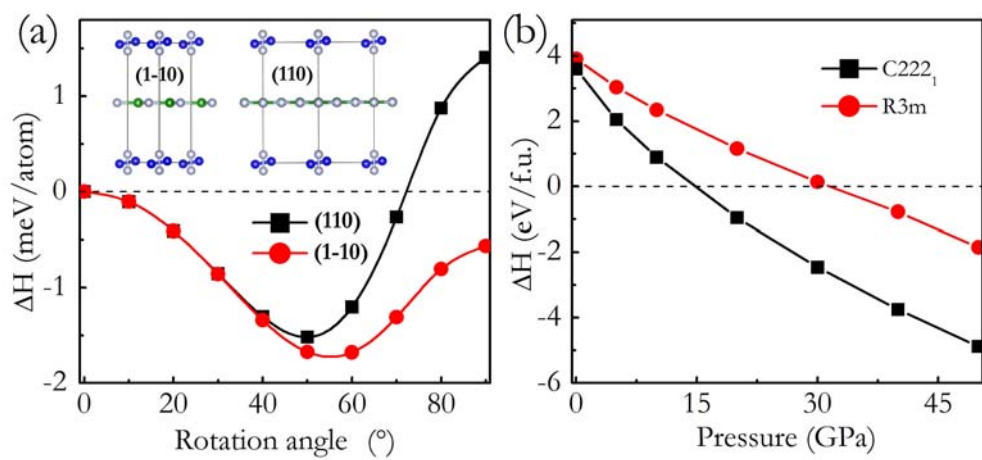


Figure 4

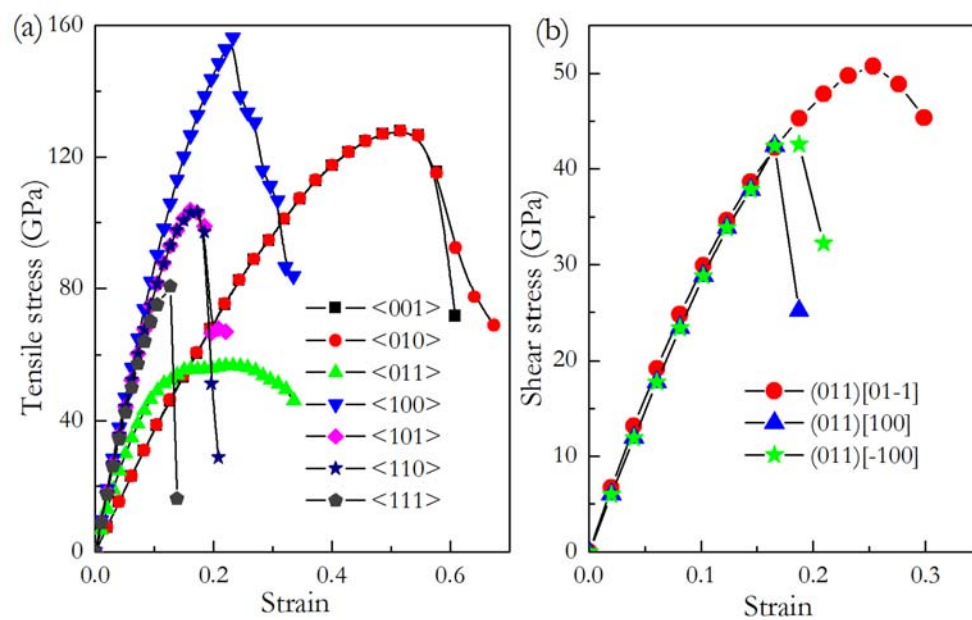


Figure 5