Superhard pseudocubic BC_2N superlattices

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Abstract: It is currently under debate whether diamond-like BC_2N may be harder than the second-hardest material, cubic BN (c-BN). Using the bond counting rule, which states that for a non-isovalent semiconductor alloy such as BC_2N, the low energy configurations should have a minimum of "wrong bonds", we have performed an unconstrained search and identified a series of short period (111) superlattice structures that have much lower total energy than previously proposed structures. According to the larger ideal strength of this BC_2N superlattice, it is harder than c-BN. Our results are consistent with recent experimental findings, but in contrast to a recent theoretical study, which claimed that the optimal BC_2N structure is less hard than c-BN.

I. Motivation

Finding superhard material:

- Diamond is the hardest.
- c-BN is the second, but with better thermal and chemical stability.

New material harder than c-BN, more stable than diamond

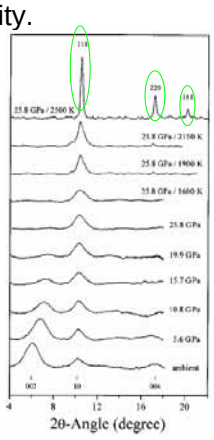
Synthesis of cubic BC_2N and its structure:

Experiment: large bulk modulus and shear modulus, high Vickers hardness: 76 GPa (Diamond: 115 GPa, c-BN: 62 GPa.) still unknown atomic configuration.

V. L. Solozhenko et al, Appl. Phys. Lett.78, 1385 (2001)

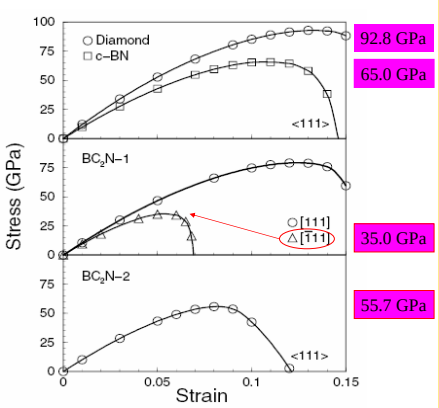
Theory: a number of structures proposed with bulk and shear modulus larger than c-BN.

Which one is the most stable ?



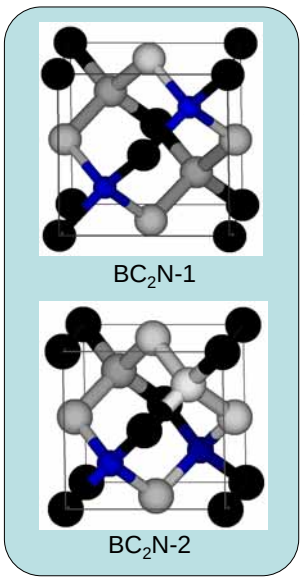
Ideal strength of BC2N:

Ideal strength: the tensile or shear stress at which a perfect crystal becomes mechanically unstable, that sets an upper bound for material strength.



Y. Zhang, et al, Phys. Rev. Lett. 93, 195504 (2004).

Although previous BC_2N structures have larger bulk modulus, but they have lower ideal strength than c-BN.



Is there a BC_2N structure with bulk modulus and ideal strength both bigger than c-BN?

II. Calculation details

- DFT, ABINIT code, plane wave basis, Energy cutoff 80 Ry;
- Troullier-Martins pseudopotential;
- LDA, Perdew-Wang exchange-correlation functional parameterized by Goedecker,
- k-points: 8x8x8 Monkhorst-Pack grid for an eight-atom cubic unit cell or equivalent.

Ideal stress: Hellymann-Feynman stress tensor orthogonal to the applied stress less than 0.1 GPa after relaxation. [D. Roundy, et al. Philos. Mag. A 81, 1725 (2001).

III. <111> (C2)*n*(BN)*n* Superlattices

We propose < 111 > (C2)*n*(BN)*n* superlattices, BC_2Nnxn (n = 1, 2, 3), which are more stable than all previous structures due to less wrong bonds, and have larger bulk modulus.

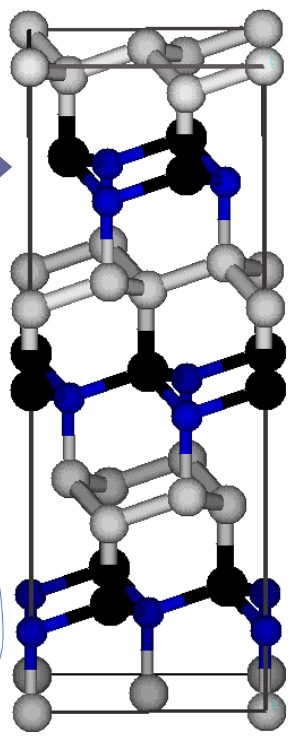
Ratio of the bond numbers

More stable bonds Less stable bonds Least stable bonds

B-N : C-C : B-C : N-C : N-N : B-B

3 : 3 : 1 : 1 : 0 : 0

1 : 1 : 1 : 1 : 0 : 0



Calculated volume *V*, bulk modulus *B*, and formation energy $\Delta E = E(BC2N) - E(C2) - E(BN)$.

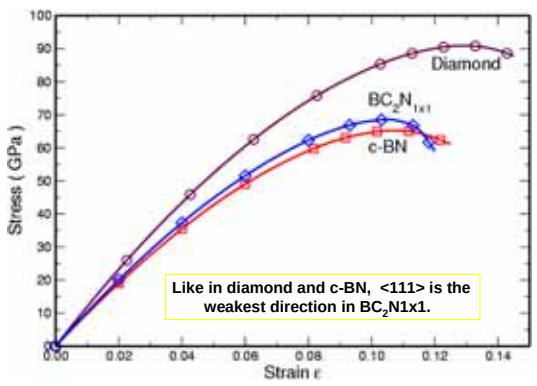
Structure	V (Å³/4-atoms)	B (GPa)	⊿E (eV/4-atoms)
Diamond	22.22	453.7	-
c-BN	23.19	392.0	-
BC_2N_{1x1}	22.92	419.5	0.76
BC_2N_{2x2}	22.84	419.5	0.52
BC_2N_{3x3}	22.80	421.9	0.39
BC_2N-1	23.06	397.6	1.78
BC_2N-2	23.06	400.2	1.80

Phase segregation to diamond and c-BN

The calculated structure factors of BC_2Nnxn superlattices show weak 200 Bragg line and intensive 111, 221, 311 lines, indicating BC_2Nnxn are diamond-like pseudocubic structures.

IV. Ideal strength of <111> BC_2N superlattices

<111> BC_2N superlattice have bigger ideal strength than c-BN, in contrast with previous study.



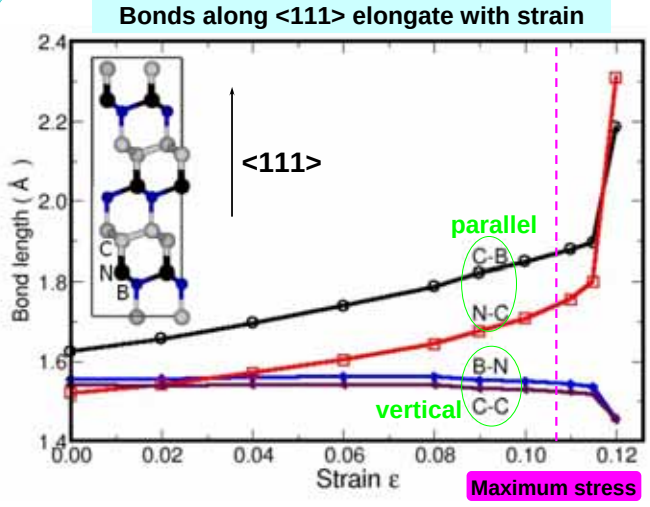
Like in diamond and c-BN, <111> is the weakest direction in BC_2N1x1.

Calculated ideal tensile strength and the corresponding strain at which the maximum stress (in GPa) occurs.

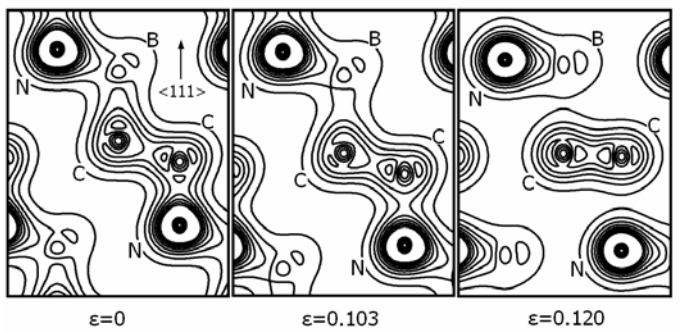
Structure	Direction	Strain	Stress	Stress*
Diamond	<111>	0.130	90.8	92.8
c-BN	<111>	0.108	65.2	65.0
BC_2N_{1x1}	<111>	0.103	68.4	
BC_2N-1	<$\bar{1}$11>	0.053	33.0	35.0
BC_2N-2	<111>	0.078	53.4	55.7

* : From Y. Zhang, et al, Phys. Rev. Lett. 93, 195504 (2004).

Bonds along <111> elongate with strain



Charge distribution at different <111> strains



B-C and N-C along <111> elongate significantly after the stress reaches its top. N-C bond length increases faster than C-B and breaks first. After both bonds break, the system converts into alternating graphite and hexagonal BN layers.

V. Summary:

We have identified the short period (C2)*n*(BN)*n* (111) superlattice structures with larger bulk modulus and ideal strength than c-BN, indicating that BC_2N could be harder than c-BN. This is consistent with experimental findings.

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