Fused borophenes: a new family of superhard materials

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The search of new superhard materials has received a strong impulse by industrial demands for low-cost alternatives to diamond and c-BN, such as metal borides. In this Letter we introduce a new family of superhard materials, "fused borophenes", containing 2D boron layers which are interlinked to form a 3D network. These materials, identified through a high-throughput scan of B$_x$C$_{1-x}$ structures, exhibit Vicker’s hardnesses comparable to those of the best commercial metal borides. Due to their low formation enthalpies, fused borophenes could be synthesized by high-temperature methods, starting from appropriate precursors, or through quenching of high-pressure phases.

Introduction

The revamped interest in superhard materials has been driven not only by scientific curiosity, but also by the increasing technological interest, in several industrial applications. 

Due to their low formation enthalpies, fused borophenes could be synthesized by high-temperature methods, starting from appropriate precursors, or through quenching of high-pressure phases.

In this paper, applying a combination of crystal structure prediction (minima hopping) and high-throughput screening techniques to the boron-carbon (B–C) phase diagram, we uncover a new family of metastable boron and boron-rich carbon structures, "fused borophenes" (FB) with hardness and elastic properties comparable to those of the best metal borides.

Fused Borophenes in the B–C Phase Diagram

Fused borophenes were identified through a HT search of hard materials on a database of ~2700 distinct B–C structures, obtained through an unbiased minima hopping search, on 8–15 atoms unit cells, with variable B/C composition. Fig. 1 shows the location of all resulting structures in formation energy (ΔE) vs Boron fraction plane; C-graphite and α-B12 were used to compute the reference energy.

Among these 72 superhard materials, 40 are diamond-like carbon-rich structures (filled diamonds). Based on the atomic arrangement, the remaining 31 boron-rich compounds can be classified in two groups: 4 are icosahedron-like (filled inverted pentagons), while 27 of them can neither be classified as B12 icosahedra nor triangular/hexagonal 2D boron sheets (borophenes). We termed this new class of boron-rich B-C structures as "fused borophenes" (FB), and indicate them in the plot as black inverted triangles. FBs appear in the B-C phase diagram at a minimum boron concentration B$_{7/12}$C$_{5/12}$, with relative energies ΔE ≥ 293 meV/atom and become gradually more stable as the B fraction increases. There is a total of 306 FB structures in the whole database of 2700 B-C structures. Among them only 27 have V$_H$ ≥ 40 GPa, i.e. ~9 % of FB structures are superhard materials.

The inset of Fig 1 displays a plot of the Vicker’s Hardness V$_H$ (GPa) against relative energy of the 27 FB superhard structures. The merged plot of the bulk modulus B (GPa) along with the Vicker’s Hardness V$_H$ (GPa) against relative energy of the 27 FB superhard structures is provided in the supplementary material (SM). The colour of the symbols indicates the boron fraction in the structure, from pure boron (red) to the minimum
B concentration (blue). Depending on the nature and relative arrangement of the boron layers, FB have been divided into three families: α (triangles), β (circles) and γ (squares). There is no evident correlation between the formation energy $\Delta E$ and the $V_H$ of the FB in the inset of Fig.1.

It is encouraging to observe that all superhard FBs shown in the plot have formation energies $\Delta E \leq 500$ meV/atom, which implies that they could be synthesized under appropriate conditions \[27, 28\]. For a reference, among the different borophene phases synthesized till date on Ag/Au substrates, the lowest-energy borophene is 2-Pmmn phase with 555 meV/atom w.r.t. α-B$_{12}$ \[29\].

As for the hardness, most structures have a $V_H$ close to the threshold value of 40 GPa. A few structures, however, stand out as exceptional, with $V_H$ exceeding 45 GPa: among these, we selected one structure per prototype, indicated as $\alpha^*$, $\beta^*$ and $\gamma^*$ in Fig.1 which will be discussed in detail in the following.

**Classification of Fused Borophenes in Different Families** - Like other known boron polymorphs, Fused Borophenes exhibit a large diversity of motifs, reflecting the electron-deficient nature of this element \[30\]. Fused borophenes identified in our search may contain: (i) boron layers (BL) of different types and (ii) single or V-shaped double bonds connecting one atom in a layer to two atoms in another layer. Furthermore, (iii) a structure may comprise BL all of the same type or of different types, and (iv) their stacking along the vertical axis may also be different. \[31\]

In order to uniquely identify all structures generated we assigned each FB a unique alphanumeric ID, of the form: "TYPE-XYZ(HH)-XYZ(HH)". Here, TYPE indicates the family – $\alpha$, $\beta$ or $\gamma$; the XYZ numerals denote the polygonal motif present in each of the two BL, while HH is the hexagonal-hole concentration of the BL if applicable. The XYZ(HH) notation is introduced for each BL in the structure; the unconventional BL precedes the
conventional BL. The family prototype, $\alpha$, $\beta$ or $\gamma$, is assigned on the basis of the type and sequence of stacked boron layers (BL):

- $\alpha$: FBs formed by stacking conventional BL only.
- $\beta$: FB consisting of both conventional and unconventional BL.
- $\gamma$: FB made of unconventional BL only.

Boron layers are termed conventional, if they exhibit only triangular and hexagonal patterns, as quasi-2D BLs synthesized in mono- and bilayer form (borophenes); unconventional if they contain other polygonal motifs. Within this classification scheme, the $\alpha$-Ga structure, formed by stacking two triangular BLs with 0 HH concentration would be assigned the ID $\alpha$-3(0)-3(0).

Examples of structures belonging to each of the three families are shown in Fig.2. In particular, the figure depicts the three structures indicated as $\alpha$, $\beta$ and $\gamma$. $\alpha^*$ FB (36/25-36/25) - comprises two identical conventional BL with 2/25 HH concentration, interconnected through V-shaped double bonds (Fig.2c); $\beta^*$ FB, with composition B$_{7/8}$C$_{1/8}$ (356-36/1/5) comprises an unconventional BL (Fig.2d) with a triangular-pentagonal-hexagonal motif and a conventional BL (Fig.2e) with 1/5 HH concentration. These two BL are connected by single bonds as shown in Fig.2f. $\gamma^*$ FB (34-34) comprises two unconventional BL of the same type, interconnected through a V-shaped double bond (Fig.2g)-(i).

In all three structures, bonds within and between the BLs are of comparable length. The isosurfaces of the Electronic Localization Function (ELF) - $\eta \approx 0.7$ - superimposed to the three structures show that the electronic charge tends to accumulate both along the bonds connecting atoms in the same BLs and between different layers. Thus, FBs should be described rather as a bulk-like interconnected network of boron layers, and not as a collection of weakly-bound layers, quasi-2D van-der-Waals systems. This peculiar structural arrangement of FBs is at the heart of their remarkable elastic properties.

**Thermodynamical and Mechanical Properties of $\alpha^*$, $\beta^*$ and $\gamma^*$ fused borophenes**

Table 1 contains selected thermodynamic, geometric and elastic properties of $\alpha^*$, $\beta^*$, and $\gamma^*$ FBs, calculated at the LDA-DFT level [36]. The table also reports for comparison, the same properties calculated for other well-known superhard covalent materials and metal borides, as well as for graphite, as a representative example of quasi-2D van-der-Waals system.

With the exception of diamond and c-BN, the calculated $V_H$ of $\alpha^*$, $\beta^*$, and $\gamma^*$ FBs is larger than other superhard materials listed in the table. Their formation energies are relatively low ($\Delta E \leq 280$ meV/atom). Furthermore, the three phases satisfy the general stability criteria, i.e. the elastic tensor $C_{ij}$ is positive definite and has positive eigenvalues, and are dynamically stable. While $\alpha^*$ and $\beta^*$ FBs are both metallic, $\gamma^*$ is a semiconductor, with a small gap of 0.46 eV. Additional details on the calculations are reported in the SM, together with electronic and phononic spectra.

The three elastic moduli, i.e. the bulk ($B$), shear ($G$) and Young’s ($Y$) moduli, are considerably smaller than the covalent superhard materials with a $sp^3$ tetragonal arrangement, such as C-Diamond (C-Dia) and c-BN, but comparable or larger than the other hard non-tetragonal covalent systems ($\alpha$-B$_{12}$ and B$_6$O), and hard metal borides. The Poisson’s ratio $\nu$ and universal elastic anisotropy index $A_U$ [37] are in line with those of other bulk systems, but sensibly different than in graphite, confirming that FBs have substantially a bulk nature.

Having established that FBs are competitive compared to other classes of widely-used superhard materials, two obvious questions remain to be asked: What is the origin of their record hardness? What strategies can be used to synthesize them?

The reasons underlying the exceptional hardness of superhard materials have been extensively investigated, re-
Table I. Summary of the calculated properties of the three structures generated in a minima-hopping run. FB can be seen as a stacking of 2D boron-layers, interconnected through either a single or V-shaped double covalent bonds, which makes them distinct from other known 2D boron materials (borophenes) reported in literature. The spatial distribution of the Electronic Localization Function and the low universal elastic anisotropy index $A^U$ clearly show that, due the presence of covalent bonds between the atoms of the interconnected BLs, FBs effectively behave as 3D bulk structures, although they are composed of 2D BLs.

Due to their relatively low formation energies, these systems, which are strong contenders to hard metal borides as superhard materials for industrial applications, may be synthesizable through high-temperature synthesis, starting from appropriate precursors. Furthermore, our calculations hint that the structure labeled as $\gamma^*$ in this work, which, with a predicted $V_H$ of 53 GPa, second only to C-diamond and $c$-BN, may be synthesized by quenching from high pressures.

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Note added: While completing the present manuscript, a preprint has appeared [41], which reports layered structures of boron, discovered by crystal structure prediction with evolutionary algorithms. The authors propose a different classification scheme of fused borophenes into derivatives of the $\alpha$-$Ga$ and channel structures. The Channel-I structure is analogous to our $\gamma^*$ structure. The main results of that work, which is totally independent from ours, are in good agreement with ours.

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Computational details of elastic properties calculations: The elastic properties of the enlisted systems in Table I were estimated from the elastic tensor based on the Voigt-Reuss-Hill approximation. The Chen’s model was used to estimate the hardness. The elastic tensor was calculated with a two step displacement of $\delta = \pm 0.005 \, \text{Å}, \pm 0.01 \, \text{Å}$. The crystal structures of other hard covalent systems and metal borides in Table I were obtained from Materials Project database. These structures were further geometrically relaxed and their different properties were reevaluated. Details of the calculations can be found in the Supplementary Material(SM).