Crystal structures and metastability of carbon-boron compounds C_3B and C_5B

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The recent discovery of the diamondlike C_3B and C_5B compounds has raised hopes of revealing interesting properties and also elicits questions about the stability of such compounds. Using our implementation of the evolutionary global space-group optimization method, we have found ordered structural models for C_3B (layered hexagonal) and C_5B (diamondlike) with lower energies than previously obtained and revealing unusual layer-stacking sequences. The compounds are less stable than a mixture of freestanding lowest-energy phases of B, C, and C_4B, thus C_3B and C_5B are not ground-state structures. Nevertheless, disordered diamondlike C_3B and C_5B can be formed exothermically at high temperature in the reaction [graphitelike C_3B] + 2C → [diamondlike C_5B] and [graphitelike C_3B] → [diamondlike C_3B]. Thus, the disorder on the C and B sites of diamondlike C_3B and C_5B is responsible for the observed phases.

Diamond has been the focus of attention for a very long time both because of its rare aesthetic appeal as well as for its unusual physical properties, including superhardness, thermal conductivity, wide band gap, and high hole mobility.[1] Elemental boron has also held the scientific community in constant fascination because, among others, of its unusual polymorphism, showing a multitude of polyhedral crystal structures.[2] Naturally, the reports that combine diamond and boron tend to stir much attention. Solid boron can accommodate as much as 20 atomic % of C in the stable C_3B_{12} (CB_4) phase, consisting of B_{12} icosahedra forming a hexagonal lattice surrounding a C-C-C chain located between the B_{12} icosahedra. In the opposite limit of carbon-rich phases, which are of interest here, boron has very low solid solubility, and B-doped diamond was predicted to attain a weakly $p-$type character.[3] However, it was suggested that incorporation of large amounts of boron into diamond would result in extreme enhancement of superconductivity.[4] B-doped diamond synthesized at 8–9 GPa and 2500–2800 K was reported to be a type-II superconductor with transition temperature $T_c = 5$ K,[5] while T_c of the heavily B-doped diamond (~ 20 at.% of B) was predicted, assuming simple hypothetical structural models,[4,5] to rise to $T_c = 55$ K,[5] prompting high-pressure experiments. However, most attempts to achieve high solubility of boron in diamond at extreme pressure (P) temperature (T) condition resulted in disordered $C_{1−x}B_x$ alloys with B content around 1–2 at.%. The two exceptions, which are of interest here, are C_3B and C_5B as they represent claimed stable phases.

C_3B was reported during chemical-vapor deposition (CVD) growth[6–8] of boron trichloride and benzene around 1000 K.[6] Its crystal structure has not been fully resolved, but C_3B was said to be graphitelike with uncertain distribution of C and B atoms.[6] Later on, the C_3B was grown epitaxially on the NbB_2 (0001) substrate.[7] Several theoretical studies have attempted to propose the crystal structure for C_3B[9] using intuitive models for distributing of B atoms in graphite-type supercells. The most recent experimental study[10] revealed another diamondlike phase with C_3B sto-ichiometry and unknown distribution of C and B atoms at 39 GPa and 2200 K. Theoretical study by Liu *et al.*[11] predicted, using a swarm-optimization algorithm, which was combined with the first-principles structural relaxations, three metallic diamond-based structural arrangements, which had lower energies than all previously considered intuitive models.

C_5B was reported very recently by Solozhenko *et al.*[12] in a course of the laser heating of samples in the diamond-anvil-cell and further quenching them from 24 GPa and ∼2200 K to ambient conditions. This C_5B phase was said to be diamond-like, showing high bulk modulus of 335 GPa, high thermal stability (up to 1900 K), and exhibiting extreme Vickers hardness (71 GPa). Indeed, the analysis of the x-ray diffraction spectrum of C_5B showed that C_5B is similar to diamond though more certain information of the crystal structure has been lacking. Several theoretical works have proposed ordered structural candidates for C_5B.[5,13–15] Two of the most stable structures were predicted by Li *et al.*[15] by combining the evolutionary algorithm with first-principles calculations. Surprisingly, comparative analysis of the theoretical stability of the proposed C_3B and C_5B phases with respect to the known stable phases, namely elemental C, B, and CB_4, has not been performed.

This paper reports a structure search with the evolutionary method called global space-group optimization (GSGO), using first-principles calculations. Starting from a set of randomly generated structures, we find ordered structures for C_3B (layered hexagonal) and C_5B (diamondlike), which have lower total energies than all previously proposed structural models. We perform a systematic analysis of thermodynamics for bulk C_3B and C_5B phases, finding that at low temperature they are *not* ground state structures (i.e., would decompose to the stable phases C, B, and CB4). However, disordered diamondlike phases of C_3B and C_5B can be formed exothermically at high temperature in the reaction [graphitelike C_3B] + 2C → [diamondlike C_5B] and [graphitelike C_3B] → [diamondlike C_5B].

Method of calculations. We have performed an evolutionary search of the structures for the C_3B and C_5B phases using implementation to the GSGO method,[16] which determines the lowest-energy structure starting from unbiased random lattice vectors and random atomic positions in a supercell of given maximal size. A comparative discussion of different optimization approaches can be found in Ref. 17. To minimize the risk of getting trapped into high-energy local minima, we restarted the evolutionary search a few times, starting from independent sets of random structures. The electronic-structure calculations were performed in the framework of the density functional theory (DFT),[18] using the projector augmented wave (PAW) method[19] with exchange and correlation treated within the generalized gradient approximation (GGA)[20] as implemented in the VASP code[21] (previous studies Refs. 11 and 15, which predicted the lowest-energy structures for C_3B and C_5B, respectively, also used GGA). The structural search for the C_5B candidates was done at pressure of 20 GPa since the synthesis of the phase was reported at similar pressure conditions.[12] The search for the C_3B candidates was done at the same pressure. For more details see Supplemental Material.[22]

Results of the evolutionary structural search. C_3B: The GSGO procedure identifies a structural candidate for the ordered C_3B [see Fig. 1(b)], which has positive formation enthalpy, yet lower than all other structural candidates known in the literature [see Figs. 1(c)–1(e)]. Figure 1(a) shows the results of the calculated formation enthalpies (ΔH_{form}) vs pressure for our best candidate and for the most competitive structural models of Ref. 11, using the same GGA calculation parameters. Remarkably, all previously suggested structures

from Ref. 11 represent diamondlike carbon networks with different substitutions of C by B. In contrast, our best candidate for the C_3B phase represents a layered hexagonal structure with unusual stacking along the close-packed [111] direction. It has a hexagonal unit cell, which consists of 12 atoms (coordinates are listed in Ref. 23). Three bilayers of C and three bilayers of C/B form the structure. The central C-B bilayer has graphitelike environment with 3-coordinated B and C in plane. The adjacent bilayer of C/B and other C bilayers have diamondlike environment and with fourfold coordination. The stacking of the fourfold coordinated bilayers of C/B and C differs from diamond. Our C_3B model can be viewed as tetrahedral-based with the tetrahedra oriented along (111) direction. Interestingly, the tetrahedra are oriented opposite from both sides of the graphitelike C/B bilayer. The C_3B structure represents a semimetal with rather low occupancy of the density of states (DOS) at the Fermi level [see Fig. (S1)]. Experimentally the crystal structure of C_3B has not been resolved.[6] By assumption from Ref. 6 C_3B may have a graphitelike structure with unknown distribution of C and B atoms, and, in principle, our structural model would fit such description. However, complete structural refinement requires further experimental analysis.

C_5B: Our best candidate for the C_5B structure obtained with the GSGO is shown in Fig. 2(b). Its formation enthalpy is positive, but lower than the best candidates from the literature,[15] shown in Figs. 2(c)–2(d). The crystal structure of our best candidate is diamondlike unlike the case we find for C_3B. C_5B has fourfold coordination [see Fig. 2(a)] with 10 layers of C and two nearby B layers stacked along [111]
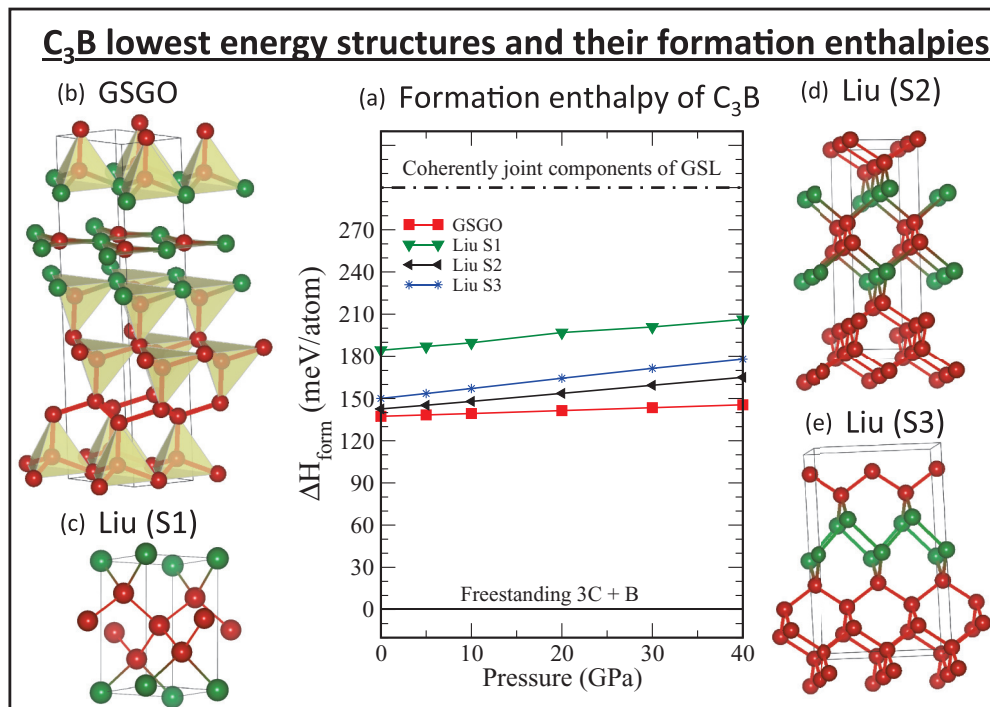

C_3B lowest energy structures and their formation enthalpies

(b) GSGO

(a) Formation enthalpy of C_3B

(d) Liu (S2)

(c) Liu (S1)

(e) Liu (S3)

Coherently joint components of GSL

GSGO
Liu S1
Liu S2
Liu S3

ΔH_{form} (meV/atom)

Freestanding 3C + B

Pressure (GPa)

FIG. 1. (Color online) (a) The formation enthalpy ΔH_{form} of the structural models of C_3B with respect to freestanding diamond plus α-boron (3C + B) as a function of pressure. The structural models show carbon as red and boron as green spheres. The models include (b) the lowest-energy crystal structure, obtained with GSGO; (c)–(e), respectively, the Liu (S1), Liu (S2), and Liu (S3) structures proposed in Ref. 11, which were considered as most stable in previous studies.
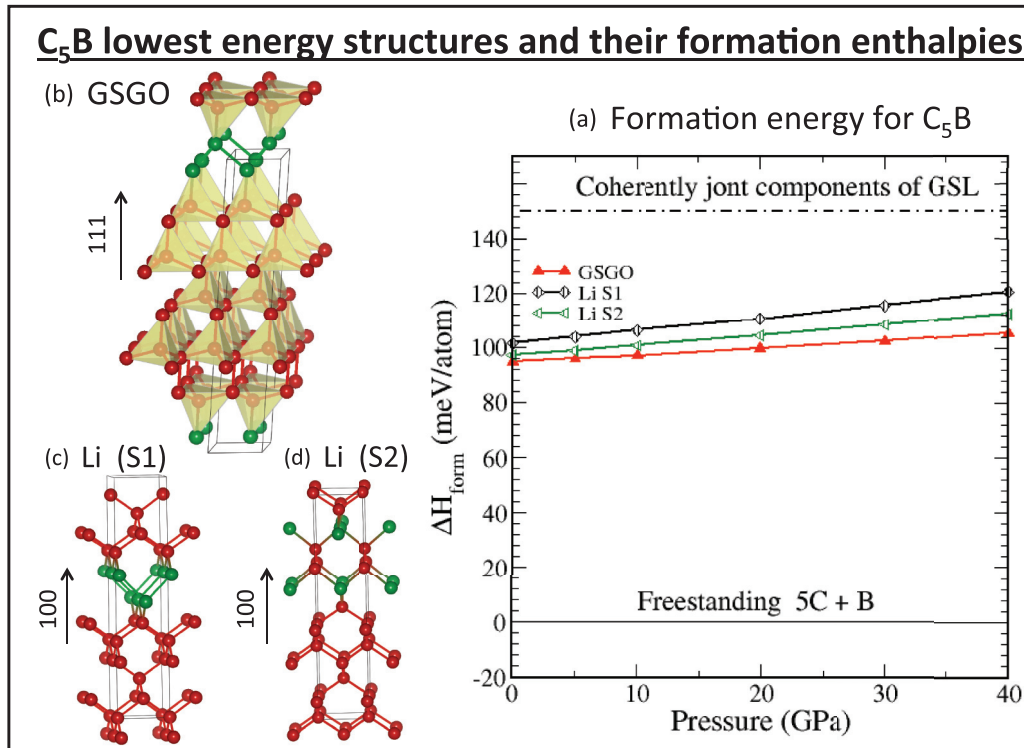
FIG. 2. (Color online) (a) The formation enthalpy ΔH_{form} of the C_5B with respect to the freestanding diamond plus α-boron (5C + B) as a function of pressure. The structural models show carbon as red and boron as green spheres; (b) the lowest-energy crystal structure, obtained with GSGO; (c) and (d), respectively, the Li (S1) and Li (S2) structures proposed in Ref. 15, which were considered as most stable in the previous studies.

diamond direction (12 atoms per unit cell; coordinates are listed in Ref. 24). The structure forms tetrahedra, oriented along [111] diamond direction in such a way that they produce twin chain with a period of three tetrahedra. The bonds are separated in three groups. The B-B bonds are longest: $\sim$1.79 Å, the C-B bonds are $\sim$1.58–1.59 Å, and the C-C bonds are $\sim$1.54 Å. Both structures from Ref. 15 have also diamond−based structures [see Figs. 2(b)–2(b)]. However, in contrast to our model, they have layer stacking along the [100] diamond direction. C_5B is found here to be semimetallic. The electron deficiency in the C_5B diamondlike structure results in small occupancy of the DOS at the Fermi level and above in the pseudogap [see Supplemental Material[22] and Fig. 1(S2) for more details.] The structural model, suggested in the present work, as well as two other diamond-based models[15] fit the experimental proposal of a diamondlike framework.[12] It is interesting that the structural differences between the three models of C_5B result only in a subtle energetic difference; this opens the possibility of their coexistence at high-temperature conditions of synthesis.

CB_4: This is the only stable compound in the observed phase diagram of C-B.[25] We calculated the total energy of the stoichiometric CB_4 phase employing the experimentally known structure prototype.[26] After relaxation of the shape of the unit cell and atom positions, the values for the lattice parameters were $a = 5.640$ Å and $c/a = 2.147$, in good agreement with experiment ($a = 5.60$ Å and $c/a = 2.164$). At ambient pressure the formation enthalpy ΔH_{form} (with respect to equivalent amounts of freestanding elemental C

and B) is negative [see Fig. 3(a)] unlike C_3B and C_5B. But with increasing pressure, ΔH_{form} of CB_4 gradually increases and at pressure above $\sim$20 GPa it becomes unstable [Fig. 3(b)]. It would be expected to decompose or transform into a more stable phase. However, we did not find confirmation of this effect in the literature. Instead, the CB_4 is stable to the highest applied pressure of 40 GPa.

Basic thermodynamic analysis. We discuss the stability of these structures in three levels of theory to clearly delineate the factors leading to stability.

(i) *Level 1 description: T = 0 K stability of individual phases of ordered* C_3B *and* C_5B. In the literature on C_3B and C_5B, stability was often argued on the basis of the sign of the formation enthalpy ΔH_{form}, i.e., relative to equivalent amounts of freestanding elemental constituents C and B at $T = 0$ K. However, to establish thermodynamic stability additional decomposition reactions need to be considered. These can be conveniently viewed by inspecting the ΔH vs X ground state line, i.e., the convex line connecting all lowest-energy phases at different compositions X (i.e., B–CB_4–C), which is shown by the black line connecting red dots in Fig. 3. We observe that at $T = 0$ K both C_3B and C_5B are situated above the ground state line in the entire considered pressure range (Fig. 3). This implies the instability of both C_3B and C_5B with respect to decomposition into alternative phases. Thus, level 1 theory does not provide an explanation for the formation of these structures.

(ii) *Level 2 description: finite T free energies of individual phases of disordered* C_3B *and* C_5B. A possible explanation
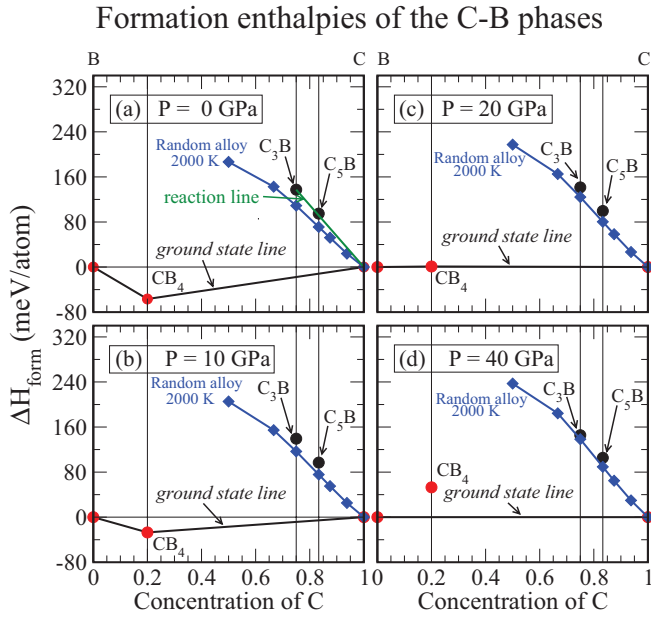
Formation enthalpies of the C-B phases

FIG. 3. (Color online) Black line shows the formation enthalpy ΔH_{form} of the binary phases in B-C system at T = 0 K and various pressures. The ground state line is shown as black solid line, connecting lowest-energy phases (red circles). Black circles correspond to C_3B and C_5B, obtained in this work by the GSGO method. Notably, black circles are above the ground state line. Blue line is the energy of random alloy phases at T = 2000 K. The green line is a sum of energies of the proportionally taken freestanding initial components of the reaction [graphitelike C_3B] + n C → [diamondlike C_xB] (x is a proportion between C and B in the alloy; n is amount of C).

for the apparent disagreement between experiment and level 1 theory would be disorder effects, which may take place at high-temperature synthesis[10,12] and change phase equilibrium in comparison to low temperatures. The configuration entropy serves an agent to stabilize disordered phases over ordered ones at high temperatures. To estimate the effects of disorder at about 2000 K we considered a structural model of random C_xB alloys with various proportions x between amounts of C and B in the alloy. The model is inspired by the fact that the atomic environments of C and B in the crystal lattice of our diamondlike C_5B are similar, so these sites can be interchanged [see Fig. 2(b)].

The energy cost of such exchange of the C and B atoms in this lattice, which is in fact realized in the models of the Li *et al.*[15] [Figs. 2(c)–2(d)], is relatively small [see Fig. 2(a)]. Consequently, the C_5B can carry configurationally entropy associated with such cross substitutions. In contrast, the local environments of C and B atoms in the ordered layered hexagonal C_3B structure are markedly different [Fig. 2(b)]. So cross substitution and its associated entropy is unlikely. Thus, we consider only diamondlike random alloys C_xB as an alternative to the ordered C_3B and C_5B phases. We simulated such disordered diamondlike C_xB alloys for several concentrations, using the special quasirandom structure (SQS) model[27] for the distribution of C and B atoms on the fully relaxed diamond-based 196-atom supercells (see more details in the Supplemental Material,[22] Sec. S.I). The configuration

entropy was estimated within a mean-field approach: $S_{conf} = -k_B T [x \ln(x) + (1-x) \ln(1-x)]$. The calculated ΔH_{form} of the disordered alloys at 0 K were very high at all considered pressures, but increasing the temperature increases the configuration entropy for the disordered phases. At 2000 K $\Delta H_{form} - T\Delta S_{conf}$ of the disordered alloys (see blue line in Fig. 3) are lower than the ΔH_{form} of the ordered C_3B and C_5B compounds, but they are still very positive. Thus, configuration entropy for single phases is not enough to stabilize disordered C_3B and C_5B.

(iii) *Level 3 description: Configuration disorder effect for the compound generating reaction.* The experiments that produced the diamondlike C_3B[11] and C_5B[15] at high-pressure and high-temperature conditions used the graphitelike phase as a precursor starting material. For the ordered C_5B such a process can be described by the reaction

$$\text{[ordered graphitic } C_3B] + 2C \text{ (graphite)}$$
$$\rightarrow \text{[ordered diamondlike } C_5B].$$
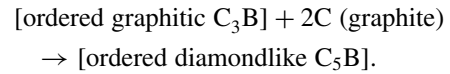
The sum of energies of the proportionally taken freestanding initial components of the reaction is shown in Fig. 3 (green line).

Such a reaction was examined in Ref. 14 by means of the GGA calculation at $T = 0$ K. It was shown that at ambient pressure the enthalpy of that reaction at $T = 0$ K is positive [see Fig. 1 (S3)], and, hence, the stabilization of C_5B is not possible. But with compression the reaction enthalpy becomes negative and in favor of the stabilization of C_5B. However, Ref. 14 considered very high-energy structures for the C_3B and C_5B and used the GGA functional for graphite, which severely overestimated the energy of this phase. We have recalculated the reaction enthalpy at $T = 0$ K, using our ordered GSGO structural models and avoiding the large GGA error for graphite by using instead the diamond phase of C. We found a small positive reaction enthalpy in the entire considered pressure range up to 40 GPa [Fig. 1 (S3)], i.e., the ordered C_5B phase is not stabilized by the reaction.

However, if we calculate the reaction free energy ΔF_{react} by considering the effect of configuration entropy on the disordered C_3B and C_5B, we find (see Fig. 4 that shows the free energy of the reaction ΔF_{react} as a function of temperature at various pressures) that (i) at 0 K ΔF_{react} of both reactions are positive at all considered pressures, indicating that the reactions does not go forward. (ii) But as soon as temperature approaches 2000 K ΔF_{react} of both reactions becomes negative, and, consequently, the reactions could go forward, stabilizing the disordered diamondlike C_3B and C_5B phases. Thus, the disagreement between experiment and level 1 theory regarding synthesis of the diamondlike C_3B and C_5B phases at high pressure and temperature can be explained by the metastable precursor reaction (level 3 theory) between metastable graphitelike C_3B and diamond and assisting by the effects of disorder. Besides, our prediction that the synthesized diamondlike C_3B and C_5B represent disordered alloys between C and B may also explain the experimental difficulties in determining unique positions for C and B atoms.

In summary, we discovered via DFT evolutionary GSGO calculations ordered structures for graphitelike C_3B and diamondlike C_5B phases, which have lower energies than the
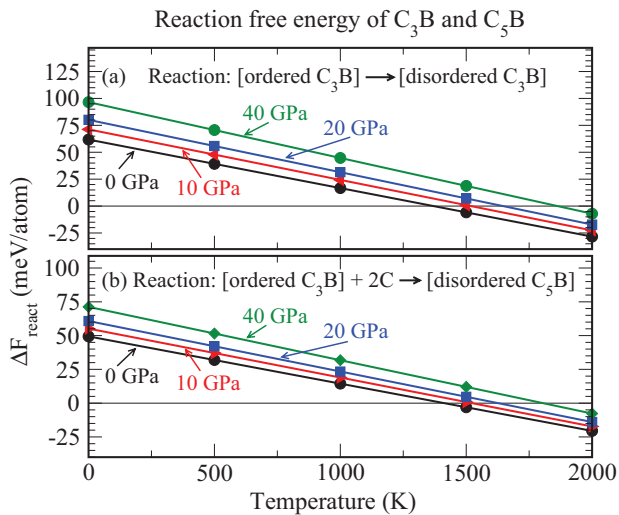
Reaction free energy of C_3B and C_5B

FIG. 4. (Color online) Free energy of the reactions (ΔF_{react}) at various pressures. In the upper panel (a) the energy reference is the ordered graphitelike C_3B phase. In the lower panel (b) the energy reference is a mixture of freestanding ordered graphitelike C_3B phase and diamond-C.

previously proposed structural models. Both C_3B and C_5B have positive formation enthalpies and structures with unusual layer-stacking sequences. (i) We examined $T = 0$ K stability of individual phases of ordered C_3B and C_5B relatively to the other stable phases at different concentration (convex hull, consisting of B - CB_4–C) and found that C_3B and C_5B have very high energy and would decompose. (ii) We calculated finite-T free energies of individual phases of disordered C_3B and C_5B. It turns out that while at high temperature the disordered structures have lower energy than that of ordered ones, but the formation enthalpy of the disordered phases are still very positive. (iii) Since the starting material in the experiment is graphitelike carbo-boride, we considered the finite temperature formation reactions: [graphitelike C_3B] + 2C → [diamondlike C_5B] and [graphitelike C_3B] → [diamondlike C_3B]. We showed that the reactions go forward only at high temperature stabilizing the disordered C_3B and C_5B. The disordering between C and B atoms in diamondlike C_3B and C_5 may explain experimental difficulty to resolve the crystal structure of these phases.

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[22]See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.87.094103 for more details on C_3B candidates.

[23]Information of crystal structure of the GSGO C_3B: Space Group: No. 160, R3m, C3v-5, Hexagonal lattice: a = 2.608 A, c = 37.402 A; atomic positions: C 3a (0, 0, 0.304), C 3a (0, 0, -0.459), C 3a (0, 0, -0.307), C 3a (0, 0, -0.418), C 3a (0, 0, -0.181), C 3a (0, 0, 0.263), C 3a (0, 0, -0.140), C 3a (0, 0, 0.089), C 3a (0, 0, -0.348), B 3a (0, 0, 0.423), B 3a (0, 0, 0.041), B 3a (0, 0, 0.138); alternatively the structure can be represented as follows, rhombohedral lattice: a = 2.608 A, c = 12.558 A, $\alpha = 90°$, $\beta = 84.04°$, $\Upsilon = 120°$; atomic positions: C (0.391, 0.696, 0.913), C (0.918, 0.459, 0.623), C (0.615, 0.307, 0.078), C (0.836, 0.418, 0.746), C (0.361, 0.181, 0.458), C (0.475, 0.737, 0.788), C (0.280, 0.140, 0.580), C (0.821, 0.911, 0.268), C (0.696, 0.348, 0.956), B (0.155, 0.577, 0.268), B (0.918, 0.959, 0.122), B (0.724, 0.862, 0.414).

[24]Information of crystal structure of the GSGO C_5B: Space Group: No. 156, P3m1, C3v-1; hexagonal lattice: a = 2.52(2) A, c = 13.03(6) A, atom positions: C 1a (0,0,0.353), C 1a (0,0,0.672), C 1c (2/3,1/3,0.154), C 1a (0,0,0.790), C 1c (2/3,1/3,0.511), C 1b (1/3,2/3,0.194), C 1c (2/3,1/3,0.632), C 1b (1/3,2/3,0.313), C 1b (1/3,2/3,0.830), C 1a (0,0,0.471), B 1c (2/3,1/3,0.0321), B 1b (1/3,2/3,0.952).

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