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Crystallographic and spectral equivalence of boron-carbide polymorphs

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ABSTRACT

The extraordinary properties of boron carbide originate from the collection of polymorphs that comprise fabricated samples. However, traditional nomenclature that differentiates and describes these crystal structures often restricts the ability to fully model variations in material properties and performance. To highlight and transcend these limitations, this study introduces a modified nomenclature and defines new groups of equivalent polymorphs based on quantum-mechanical simulations. Trends in lattice parameters, total energy, and Raman spectra are explained in terms of the unique covalent-bonding environments of boron-carbide polymorphs.

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For boron carbide, polymorphism affords large variability in both carbon percentage (from 8.0 to 20 at.%) and atomic arrangement to strongly influence physical, mechanical, and electronic properties [1–11]. Further, the closeness of formation energies of these crystal structures induces many polymorphs to form in the same fabricated sample [10]. Unfortunately, limitations in experimental techniques and naming conventions obscure the identity and distribution of these crystal structures. Hence, the current investigation introduces a highly specific nomenclature and models polymorphs through quantum-mechanical simulations.

The simplest unit cell for each boron-carbide polymorph comprises a three-atom chain and a twelve-atom icosahedron [see Fig. 1(a)]. Within each icosahedron, six polar (p) atoms connect multiple icosahedra directly, and six equatorial (e) atoms connect multiple icosahedra through the chains [see Fig. 1(b) and (c)]. Traditionally [1], researchers differentiate boron-carbide crystal structures with the following notation: $(B_mC_{nfo})ijk$ where (B_mC_{nfo}) represents the icosahedron (sites 1–12), and ijk represents the chain (sites i, j, and k) [see Fig. 1(a)]. Subscripts "m" and "n" indicate the number of boron atoms and carbon atoms, respectively, in the icosahedron. If $n = 0$, C_{nfo} is excluded. Subscript "f" marks the family of the icosahedral carbons as either polar (p) or equatorial (e). If $n = 2$ and $f = p$, "o" is often included to describe the relative orientation of polar carbons [1]. The simplest example of this traditional nomenclature is $(B_{12})CCC$, which has a CCC chain and a twelve-boron icosahedron. Here, the six equatorial boron atoms represent one $6h$ Wyckoff site of space group 166 ($R\overline{3}m$), and the six polar boron atoms

represent another [12,13]. Thus, there is no need to differentiate within polar sites or within equatorial sites for $(B_{12})CCC$. However, an icosahedron with a carbon atom [i.e., $(B_{11}C_{1f})ijk$] no longer exhibits the aforementioned symmetry. Depending on chain composition, the location of this icosahedral carbon may need to be explicitly specified in the nomenclature to differentiate unique crystal structures. Adding a second icosahedral carbon atom poses similar issues. Consider $(B_{10}C_{2p,antipodal})BCB$, which has one carbon atom in polar site 1, 2, or 3 and another carbon atom in the polar site 4, 5, or 6. Because the distance between pairs of antipodal atoms varies, additional specificity in the nomenclature is required to describe variability in properties.

A comprehensive understanding of material performance and the full tailoring of properties mandate the differentiation of all unique polymorphs. Unfortunately, the commonly adopted nomenclature does not always differentiate polymorphs with the same stoichiometry. Further, while fabricated boron carbide may exhibit $R\overline{3}m$ symmetry on average, constituent polymorphs may not. For these reasons, this manuscript modifies nomenclature from $(B_mC_{nfo})ijk$ to $(B_mC_{fz})ijk$. Here, "z" specifies location(s) of icosahedral carbon atom(s) in the unit cell according to Fig. 1(a). Reduced coordinates may slightly change with position and/or number of carbon atoms. The "C_{fz}" is excluded if no icosahedral carbons are present [e.g., $(B_{12})CCC$], and site numbers are separated by commas if multiple icosahedral carbons are present [e.g., $(B_{10}C_{p2,5})BCB$]. Subscript "f" is retained to avoid confusing "z" (site number) for "n" (number of atoms). Unlike traditional nomenclature, this modified scheme can model differences due to icosahedral carbon position within polar sites and within equatorial sites [e.g., $(B_{11}C_{p1})BCC$ vs. $(B_{11}C_{p4})BCC$] and can also differentiate a chain from its mirror [e.g., $(B_{11}C_{p1})BCC$ vs. $(B_{11}C_{p1})CCB$]. Hence, this new

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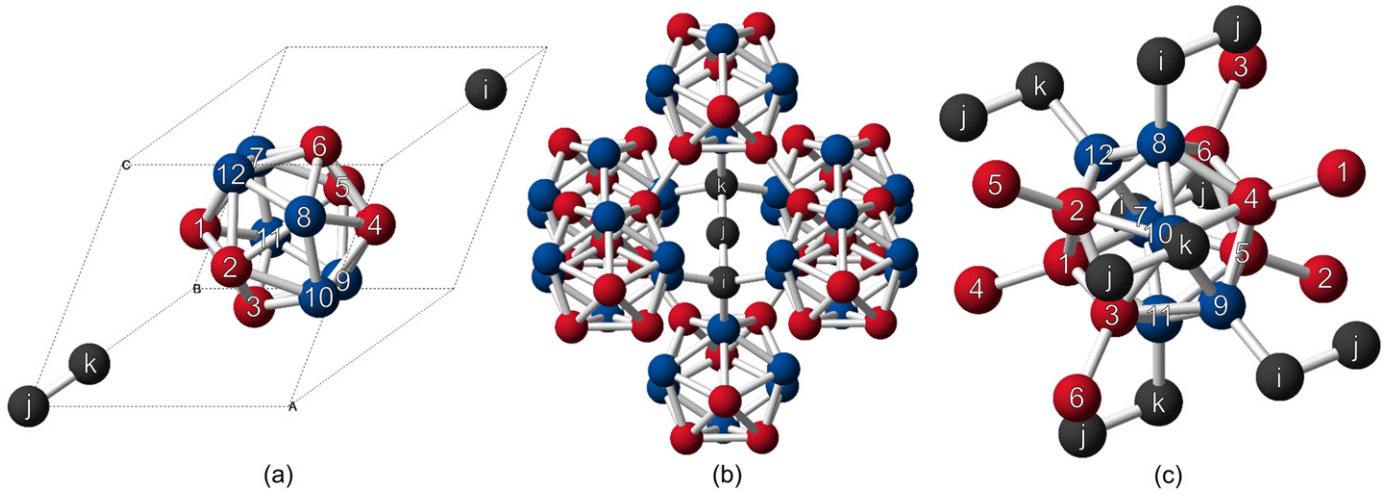E-mail address: subhash@ufl.edu (G. Subhash).

Fig 1. (a) Simplest boron-carbide unit cell color-coded by site family: polar (red, sites 1–6), equatorial (blue, sites 7–12), and chain (black, sites i, j, and k). (b) Connectivity of chain atoms. (c) Nearest neighbors of icosahedral atoms.

nomenclature lays a more robust foundation for understanding polymorphism and the corresponding variation in properties.

The current study employs ABINIT [14], a popular atomistic solver for density functional theory (DFT), to model all fifty-two variations of boron carbide commonly proposed in both experimental and theoretical investigations on boron carbide [1,8,10,15–17] except those with chain vacancies [18–21] or without Raman activity [11,22]. Single unit cells [Fig. 1(a)] with periodic-boundary conditions, a Monkhorst k-point mesh, and norm-conserving pseudopotentials with the Troullier–Martins scheme and Pulay mixing are utilized. The exchange-correlation functional is evaluated by both the Teter–Pade local-density approximation (LDA) [23] and the Perdew–Burke–Ernzerhof generalized-gradient approximation (GGA) [24]. From this energy-minimization process (accurate up to 10^{-14} eV), lattice parameters, mass densities, and relative energies per atom are calculated (see Table 1). Structures with the same properties are considered an "equivalent-lattice group," assigned a Roman numeral, and ordered by energy relative that of group i. All calculated lattice parameters and energies from the seven B_4C polymorphs modeled in a previous DFT study [9] have been replicated within 0.3% error in this investigation.

Two competing effects seem to drive the ordering of the polymorphs by energy in Table 1. First, small distances between carbon atoms generally were found to correlate with large energies. Carbon has higher electronegativity than boron, so spatially concentrating carbon atoms concentrates charge and raises potential energy. Hence, groups i and ii (CBC chain) have lower energy than groups iii–vii (CCC, BCC, or CCB chain). Groups i (0 meV) and iii (166 meV) have lower energy than groups ii (36 meV) and iv (174 meV), respectively, because the icosahedral carbon of the former two groups are not directly bound

to chain carbons as in the latter two groups. Likewise, group viii (304 meV) has lower energy than group x (346 meV) because the icosahedral carbons are bonded to icosahedral borons in the former but to icosahedral carbons in the latter [see Fig. 1(c)]. Second, the number of icosahedral carbon atoms was found to correlate with energy. That (B_{12}) is the lowest-energy icosahedron is consistent with the fact that boron icosahedra can form without chains [25,26]. Energy increases from group iii (zero icosahedral carbons) to groups iv–vii (one icosahedral carbon) to groups viii–x (two icosahedral carbons). Polymorphs with a CBC chain and a single icosahedral carbon atom (groups i and ii) have lower energy than $(B_{12})CCC$ (group iii) simply as a result of the competition of these two effects. In group iii, the rise in energy due to the direct bonding of the carbons in the CCC chains supersedes the low energy of the (B_{12}) icosahedron. In groups i and ii, however, the chain carbons are favorably separated by a boron atom.

After fully relaxing lattice parameters and atomic positions, density functional perturbation theory (DFPT) in ABINIT [27] is employed to calculate natural frequencies, phonon eigenvectors, and dielectric tensors. Intensities of the Raman-active natural frequencies can then be computed from a well-established post-processing method [28]. Because this manuscript seeks to establish the equivalencies of polymorphs, Raman-peak widths, which result from anharmonic effects [29], are beyond the scope of this study and are therefore not included. With a temperature of 300 K and an excitation wavelength of 532 nm, this analysis provides the first high-fidelity simulations for numerous boron-carbide polymorphs. Each row of Table 2 lists the top-five Raman peaks (natural frequency; normalized intensity) for polymorphs that exhibit identical Raman spectra. Most importantly, these "equivalent-Raman groups" are found identical to the equivalent-lattice groups and are therefore

Table 1

Lattice parameters, mass densities, and relative energies per atom of B_4C (20 at.%) polymorphs for the LDA (GGA). Structures with the same energy and combination of lattice parameters are listed on the same row and assigned a Roman numeral.

Group	Equivalent B_4C polymorph(s)	Permutation of lattice parameters	Mass density	Rel. Energy
–	zijk of $(B_mC_{fz})ijk$	Å	g/cm³	meV
i	1CBC | 2CBC | 3CBC | 4CBC | 5CBC | 6CBC	{5.00, 5.16, 5.16} ({5.04, 5.19, 5.19})	2.60 (2.56)	0 (0)
ii	7CBC | 8CBC | 9CBC | 10CBC | 11CBC | 12CBC	{5.11, 5.15, 5.15} ({5.15, 5.18, 5.18})	2.59 (2.55)	36 (36)
iii	CCC	{5.14, 5.14, 5.14} ({5.17, 5.17, 5.17})	2.55 (2.50)	77 (71)
iv	7BCC | 10CCB | 8BCC | 11CCB | 9BCC | 12CCB	{5.05, 5.16, 5.16} ({5.10, 5.19, 5.19})	2.55 (2.50)	166 (161)
v	4BCC | 1CCB | 5BCC | 2CCB | 6BCC | 3CCB	{4.98, 5.17, 5.17} ({5.02, 5.20, 5.20})	2.54 (2.50)	169 (164)
vi	1BCC | 4CCB | 2BCC | 5CCB | 3BCC | 6CCB	{4.96, 5.17, 5.17} ({5.00, 5.20, 5.20})	2.55 (2.50)	174 (169)
vii	10BCC | 7CCB | 11BCC | 8CCB | 12BCC | 9CCB	{5.10, 5.16, 5.16} ({5.13, 5.19, 5.19})	2.53 (2.49)	225 (219)
viii	3,5BCB | 2,6BCB | 3,4BCB | 1,6BCB | 1,5BCB | 2,4BCB	{5.01, 5.01, 5.21} ({5.05, 5.05, 5.24})	2.54 (2.59)	304 (299)
ix	5,6BCB | 2,3BCB | 4,6BCB | 1,3BCB | 4,5BCB | 1,2BCB	{5.01, 5.01, 5.23} ({5.05, 5.05, 5.25})	2.52 (2.47)	328 (322)
x	1,4BCB | 2,5BCB | 3,6BCB	{4.81, 5.22, 5.22} ({4.85, 5.25, 5.25})	2.55 (2.50)	346 (342)