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Quantum chemical modeling of solid-state B_4X structures containing tetrahedral B_4 units with X = B, C, Al, Si

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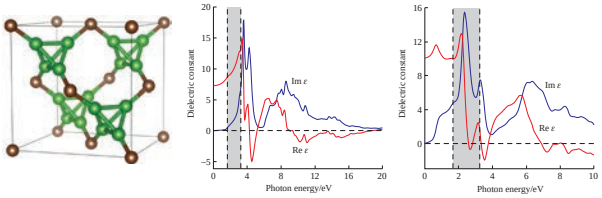
The quantum chemical modeling of new solid state structures based on a diamond lattice in which pairs of carbon atoms are replaced by B_4X fragments (where B_4 is a tetrahedron and X are B, C, Al or Si atoms) has been performed using density functional calculations.



The acquisition of new materials with unusual structures for micro- and nanoelectronics is a problem of modern materials science. An important role in the search for these materials and underlying basic substances belongs to computational design,[1–3] which is efficient for the prediction and theoretical characterization of various crystalline forms of carbon[4] and new allotropic forms of boron.[5–10] Previously, by analogy with supertetrahedral carbon (T-carbon, dia-a and their motifs and so on),[11–13] we have proposed supertetrahedral boron as a new allotropic form of boron.[8–10] As an electron-deficient element, boron is enforced to use multi-center bonds in order to form polyatomic crystalline structures, which not only are lighter than carbon-based analogs but also can have other attractive physical and chemical properties (hardness, electrical conductivity or semiconducting properties, *etc*.).

Here, we computationally studied the geometric and electronic structures of solids constructed on the basis of a diamond lattice in which pairs of neighboring carbon atoms are replaced by the fragments B_4–X (X = B, C, Al, Si) using density functional theory (DFT) quantum chemical calculations with imposing periodic boundary conditions. The corresponding crystal structures are denoted as *cF*-B_4X. The calculations were carried out using the Vienna *ab initio* Simulations Package (VASP)[14–17] with PAW pseudopotentials[18,19] and the PBEsol exchange-correlation functional.[20] The plane-wave cutoff energy of 750 eV of the associated pseudopotentials was used. The Brillouin zone was sampled by the Monkhorst–Pack method[21] with an automatically generated grid 25×25×25. The convergence criteria for total energies and forces on atoms were 10^{-8} eV per atom and 10^{-6} eV Å^{-1}, respectively. The unit cell of *cF*-B_4X was plotted using the VESTA software.[22]

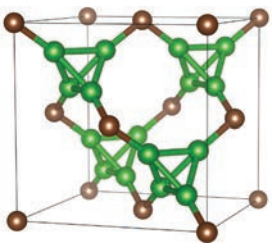


Figure 1 Conventional unit cell of the supertetrahedral crystal structure of *cF*-B_4X. Boron tetrahedrons and X atoms are shown green and brown, respectively.

Table 1 Calculated lattice constants *a*, Wyckoff position coordinates *x* for B atoms, X–B bond lengths d_1, B–B bond lengths d_2, density ρ and cohesive energy E_{coh} for *cF*-B_4X (X = B, C, Al, Si) structures.

Structure	*a*/Å	*x*	d_1/Å	d_2/Å	ρ/g cm^{-3}	E_{coh}/eV per atom
cF-B_5	6.255	0.15304	1.658	1.715	1.47	–5.75
cF-B_4C	6.003	0.15042	1.564	1.691	1.70	–6.50
cF-B_4Al	7.321	0.16784	2.128	1.701	1.19	–4.75
cF-B_4Si	6.995	0.16465	1.995	1.689	1.38	–5.47

The crystal structures of *cF*-B_4X have a face-centered cubic lattice with four B atoms and one X atom in the primitive unit cell (Figure 1). The space group is $F\bar{4}3m$ (number 216). Atoms X occupy the Wyckoff position 4*a* with the coordinates (0, 0, 0), and atoms B occupy the Wyckoff position 16*e* with the coordinates (*x*, *x*, *x*). All the structures have a negative cohesive energy (Table 1); therefore, they are thermodynamically stable.

According to the calculations of the phonon spectra of four structures, which are shown in Figures 2, 3 and S1–S2 (Online Supplementary Materials), only two of them with X = C and X = Si between boron tetrahedrons possess dynamic stability. With X = B and X= Al atoms, the systems are dynamically unstable; therefore, their properties have not been studied. The geometric characteristics of solids found by the calculations are given in Table 1. According to the calculations, the length of the intra-tetrahedral B–B bond is 1.689–1.715 Å (Table 1), which is close to that (1.680 Å determined by X-ray crystallography[23]) of a similar bond in B_4Cl_4. According to the NBO[24] and AdNDP[25] analyzes, these in tetrahedron B–B bonds represent three-center two-electron (3*c*–2*e*) bonds. The B–X bonds in all of the compounds conform to the two-electron two-center (2*c*–2*e*) bonds and, in terms of the NBO theory, correspond to covalent bonds. The calculated lengths of the B–C bonds in the *cF*-B_4C structure are 1.564 Å, which is close to the lengths of similar bonds in *closo*-carboranes[26–29] and super-tetrahedral carboranes.[10] The length of the covalent B–Si bond in the *cF*-B_4Si structure is 1.995 Å, which is close to the calculated length of such a bond in a silicon cluster (~1.88–2.09 Å) doped with a boron atom[30] and a two-dimensional borosilicon flat sheet.[31] The calculations of the electronic band structures of the test compounds showed that the *cF*-B_4C and *cF*-B_4Si systems are semiconductors (Figures 4 and 5). Both systems have a small band gap between the valence and

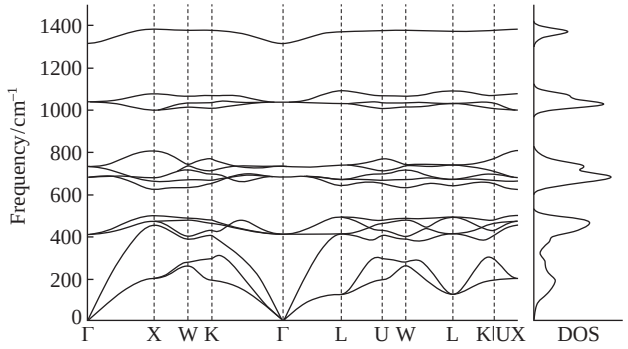


Figure 2 Calculated phonon dispersion curves along high-symmetry lines in the first Brillouin zone (left) and phonon density of states (right) for *cF*-B_4C.

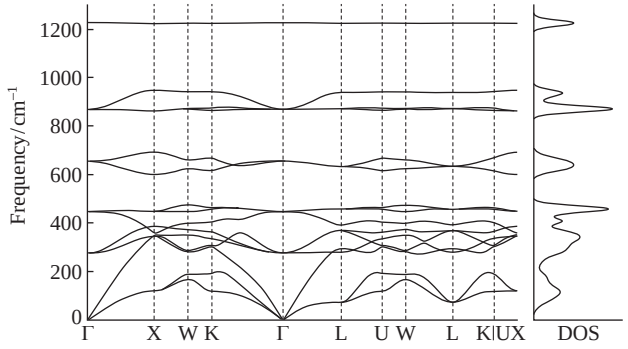


Figure 3 Calculated phonon dispersion curves along high-symmetry lines in the first Brillouin zone (left) and phonon density of states (right) for *cF*-B_4Si.

conduction bands, which in the case of silicon decreases to 0.62 eV.

The calculated values of elastic constants, bulk modulus, shear modulus, Young's modulus and Poisson's ratio for *cF*-B_4C and *cF*-B_4Si structures are given in Table 2. For both the structures, the bulk and shear modulus values are smaller than those of super-tetrahedral carbon (K = 169 GPa, G = 70 GPa)[12] but greater than those of super-tetrahedral boron (K = 68 GPa, G = = 16 GPa).[8] The bulk modulus for the *cF*-B_4Si structure is smaller than that of crystalline silicon.[32] The elastic constants of *cF*-B_4C and *cF*-B_4Si suggest high plasticity of the materials.

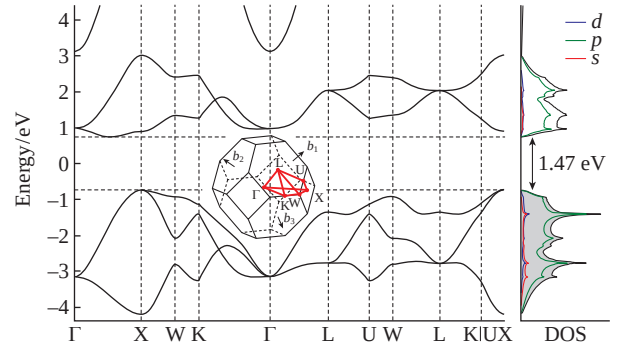


Figure 4 Calculated electronic band structure along high-symmetry lines in the first Brillouin zone (left) and electronic density of states (right) for *cF*-B_4C.

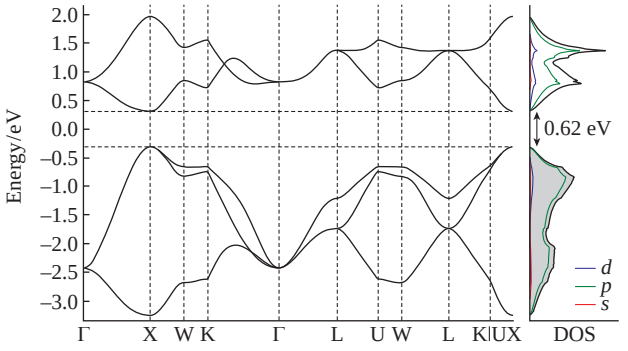


Figure 5 Calculated electronic band structure along high-symmetry lines in the first Brillouin zone (left) and electronic density of states (right) for *cF*-B_4Si.

Table 2 Calculated elastic constants c_{ij}, bulk modulus K, shear modulus G, Young's modulus E and Poisson's ratio ν for *cF*-B_4C and *cF*-B_4Si.

Structure	c_{11}/GPa	c_{12}/GPa	c_{44}/GPa	K/GPa	G/GPa	E/GPa	ν
cF-B_4C	201.57	121.86	50.50	148.43	45.93	124.91	0.3597
cF-B_4Si	109.97	66.87	25.79	81.24	24.00	65.56	0.3655

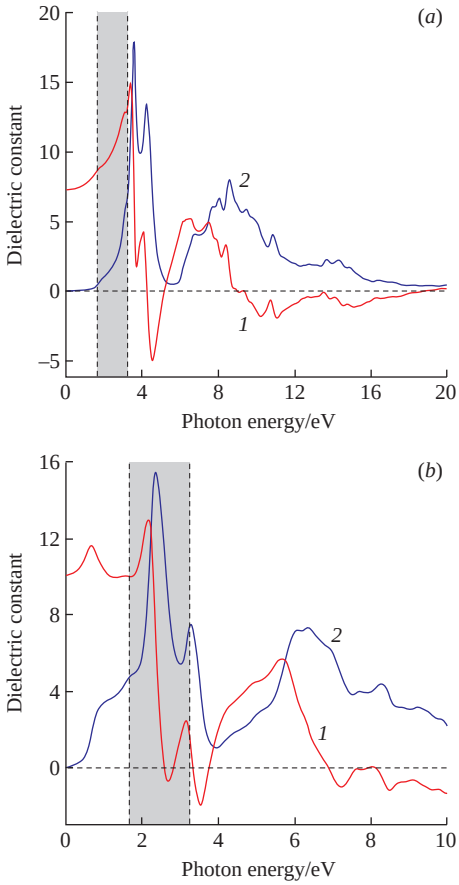


Figure 6 Frequency dependence of the (*1*) real and (*2*) imaginary parts of complex dielectric permittivity for (*a*) *cF*-B_4C and (*b*) *cF*-B_4Si.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.03.021.

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