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New insights into the enigma of boron carbide inverse molecular behavior

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ABSTRACT

Equation of state and compression mechanism of nearly stoichiometric boron carbide B_4C were investigated using diamond anvil cell single crystal synchrotron X-ray diffraction technique up to a maximum quasi-hydrostatic pressure of 74.0(1) GPa in neon pressure transmitting medium at ambient temperature. No signatures of structural phase transitions were observed on compression. Crystal structure refinements indicate that the icosahedral units are less compressible (13% volume reduction at 60 GPa) than the unit cell volume (18% volume reduction at 60 GPa), contrary to expectations based on the inverse molecular behavior hypothesis, but consistent with spectroscopic evidence and first principles calculations. The high-pressure crystallographic refinements reveal that the nature of the chemical bonds (two, versus three centered character) has marginal effect on the bond compressibility and the compression of the crystal is mainly governed by the force transfer between the rigid icosahedral structural units.

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1. Introduction

Icosahedral boron compounds (IBCs) form a fascinating family of crystalline solids with diverse and unique physical properties. Their numerous technological applications range from nuclear engineering, through armor ceramics and abrasives, to semiconductor and thermoelectric industries [1]. Boron carbide exists as a solid solution over a range of chemical compositions from $B_4C_{0.32}$ to $B_4C_{0.96}$ [2], though only compositions with carbon content up to $B_4C_{0.8}$ are considered homogenous [3]. It is known for its extreme hardness, extensive thermodynamic stability and chemical inertness [4].

The principal building block of an ideal icosahedral boron solid is a B_{12} icosahedron, which is held together by electron deficient B–B bonds, generally assumed to be of three-center nature (Δ bond) [1]. While in elemental boron phases the icosahedra are connected directly with each other, in the boron carbide family, in addition to the direct inter-icosahedral bonding, an additional triatomic linker unit is introduced, which bonds to six neighboring icosahedra, as shown in Fig. 1.

Ideal B_4C crystallizes in rhombohedral $R\bar{3}m$ space group (#166). All crystallographic discussion within this paper refers to

a hexagonal obverse setting of this space group, with 45 atoms in the unit cell, as shown in Fig. 1. Experimental challenges in pinpointing the exact location of the C atoms in the crystal structure fueled a long debate [5–16], with two models, $(B_{11}C)CBC$ and $(B_{12})CCC$, being generally favored. The latest density functional theory calculations [5,14,16] seem to converge on the conclusion that the terminal atoms of the triatomic chain are carbons and that the remaining carbon atom is most likely disordered among the polar $B2$ sites. In this model, which is also assumed in our analysis, two atomic sites $B3$ (Wyckoff position 3b) and $C1$ (Wyckoff position 6c) form a linear triatomic C–B–C chain unit. The two symmetry independent atoms that form the icosahedron are located at 18h Wyckoff positions: $B1$ (e =equatorial) and $B2$ (p =polar). $B2$ atoms are involved in the direct intericosahedral bonding ($B2$ – $B2$), whereas the $B1$ atoms are connected with the linear triatomic chains.

Because of the unique electron density distribution of the Δ bonds, with the maximum located at the center of the triangle, instead of in-between each pair of the bonded atoms, the IBCs have been described as inverted molecular solids [1]. An X-ray diffraction study of α -boron combined with maximum entropy analysis (MEM) [17] revealed important details about the electron density distribution at ambient conditions, and shed new light on the bonding character within the B_{12} icosahedra. In contradiction to the common understanding [1], the MEM results suggest that not all the icosahedral Δ bonds are equivalent. While the p – p bonds exhibit a typical three-centered character, with maximum

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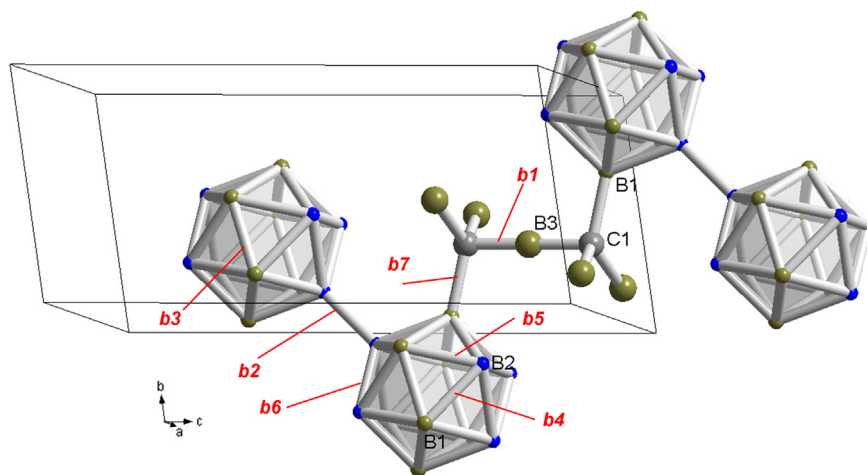


Fig. 1. Crystal structure of B_4C described in hexagonal obverse $R\bar{3}m$ unit cell with symbols **b1–b7** defining different kinds of interatomic bonds.

of the electron density located at the center of the triangle, the remaining bonds, *i.e.*, p – p – e and p – e – e have a clear two-centered character. The true Δ bond is slightly shorter than the remaining two center bonds and has a markedly higher population of bonding electrons. This interpretation, however, has not yet been confirmed by other experiments or calculations.

Inverse molecular character carries an expectation that the intericosahedral interactions should be stronger than the intraicosahedral bonds. Indeed, early classical force-field lattice dynamics calculations [18], as well as more recent *ab initio* phonon calculations [19] predict that the force constants of the intericosahedral bonds are noticeably higher than the intraicosahedral bonds.

It can usually be assumed that during isothermal hydrostatic compression of crystalline solid the bonding distances corresponding to weaker interatomic interactions should decrease more rapidly than those that correspond to the stronger bonds. Indeed, early high-pressure neutron diffraction study to 10 GPa [20] indicated that the icosahedral units in the B_4C structure are 25% more compressible than the unit cell volume. However, the bond length changes in the lower pressure regime (below 10 GPa) are very small, and comparable with the standard uncertainties, making determination of reliable bond compression trends very challenging. This conclusion about the high compressibility of the icosahedra has later been debated, based on results of subsequent spectroscopic studies and density functional theory (DFT) calculations [13,21]. It should be noted that the force constant and bulk modulus offer a different perspective on the bond strength. The former is a second derivative of the total energy with respect to the interatomic distance, at the equilibrium distance, while the latter is a first derivative of the total energy with respect to volume. In general, force constant and compressibility are expected to be related by a simple power law [22], however, since the order of the derivatives is different, in more complex cases, particularly ones that may involve charge transfer and bonding electron density changes [23], high force constant and high compressibility are not necessarily contradictory.

Recent powder diffraction diamond anvil cell study [24] demonstrated that the ambient, rhombohedral phase of boron carbide remains stable on quasi-hydrostatic compression to pressure of at least 126 GPa, however, no information was determined about the changes in bonding and molecular geometry. The very low atomic X-ray scattering factors, as well as the very small amount of the sample restricted by diamond anvil cell geometry make diffraction experiments with B_4C at ultrahigh pressures challenging. In a carefully planned and well executed powder diffraction experiments with IBC it is usually possible to determine the variations in unit cell parameters as a function of pressure, but

due to problems with achieving sufficient signal to noise ratio and inevitable peak overlaps, obtaining reliable structure factor amplitudes, required for determination of the compression mechanism is difficult. Because of these reasons we chose single-crystal X-ray diffraction (SXD) approach to study the compression mechanism of B_4C . While a little more challenging technically than powder diffraction, SXD offers a unique possibility to spatially resolve diffraction peaks and obtain three dimensional information, as well as precise values of structure factor amplitudes. Motivated to resolve the controversy of the inverse molecular behavior of boron carbide at high pressure we decided to apply the synchrotron monochromatic SXD technique to determine the exact compression mechanism over a range of pressure wide enough to make a clear judgments about the evolution of different interatomic interactions within the structure.

2. Experimental

In this study we used a sample of B_4C synthesized at the Dow Chemical Co., Michigan, with manufactured-determined ambient density $\rho_0 = 2.527 \text{ g/cm}^3$. The ambient unit cell volume determined by means of single crystal diffraction was $330.59(5) \text{ \AA}^3$, corresponding to a density of 2.547 g/cm^3 , consistent with close to stoichiometric composition. No twinning was observed in either of the studied specimens [25].

Two independent high-pressure experiments were performed. In each experiment two microcrystals of B_4C with different orientations and approximate sizes of $0.015 \times 0.015 \times 0.005 \text{ mm}^3$ were loaded into a diamond anvil cell (DAC), as shown in Fig. 2a and b. In each experiment the two sample crystals were oriented with $[-2\ 2\ 1]$ and $[1\ 0\ -3]$ directions along the DAC axis, respectively (small fragments of two larger very thin, platelet-shaped specimens). In order to increase both the coverage and redundancy of the data for the purpose of unit cell parameter and structure refinement, the data sets from both crystals were merged together using isotropic scaling feature of XPREP program [26].

Diamond anvils with 0.300 mm (experiment 1) and 0.250 mm (experiment 2) culet size and Re gasket preindented to a thickness of $\sim 0.035 \text{ mm}$ were used. In experiment 1 we utilized a combination of cubic boron nitride cBN (upstream) and tungsten carbide WC (downstream) backing plates. The angular access to the sample through the WC seat in experiment 1 was only $\pm 13^\circ$. Therefore, in experiment 2, in order to increase the accessible range without compromising the seat stability we used a WC plate with a set of four 0.5 mm deep grooves, electro-drilled in the sides

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