

# The role of non-hydrostatic stresses in phase transitions in boron carbide



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## ABSTRACT

The structural changes in boron carbide  $B_4C$  under non-hydrostatic stresses were studied by quantum molecular dynamics simulation. Three different structural changes were observed: abrupt and continuous bending of three-atomic chain and the disordering of the structure. The differences between them are discussed in terms of crystal symmetry. The existence of special deformation direction could activate abrupt bending above 40 GPa, while at quasi-hydrostatic loading structure remains stable up to 70 GPa. Crystal defects can reduce threshold value of stress therefore explain possible structural transitions observed in some experiments.

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## 1. Introduction

In the last years boron carbide remains an attractive object of study, both for experiment and modeling. This ceramic combines a number of remarkable properties [1,2], which makes it a promising material for ballistic armor [3], abrasives and cutting tools [4], thermoelectrics [5,6] and neutron detectors [6].

When one discusses the problem of using boron carbide as a structural material, probably the central question is structural transitions under stress. This question is still open, likely because of the complex structure of boron carbide. This complexity may lead to a complex picture of phase transitions. The second reason is difficulties in structural analysis due to nearly identical cross-sections for neutrons and electrons of boron and carbon. The recent progress in this area [7,8], however, should be noted.

We will briefly summarize known experimental facts about structural changes under pressure in boron carbide. The results of shock-wave (SW) experiments suggest, but don't provide clear evidence, that in the range between 30 and 50 GPa boron carbide undergoes a series of structural changes (see [9–11]). The mechanism of these changes is not clear. Besides, under dynamical loading above Hugoniot elastic limit (HEL) the abrupt loss of shear strength occurs [9]. The latter effect is often connected with the formation of narrow amorphous bands, which were observed in ballistic experiments [3] by subsequent STEM-analyses. This transition and amorphous bands were also observed in indentation experiments [12,13,7] and during unloading from critical stress in diamond anvil cells (DAC) [14], when non-hydrostatic loading

regime was realized. However during quasi-hydrostatic loading structural changes were not observed [14,15].

One of the consequences from the mentioned results is that non-hydrostatic stress is crucial in the activation of structural transition. This point was examined by first-principles modeling by several groups [16,14,17,18]. As their analysis show, significant deformation along three-atomic chain or shear deformation leads to disordering of the structure. At the same time at hydrostatic loading of ideal structure such effect is absent. It was also shown that at hydrostatic loading structural transition is possible in the structure with boron vacancy in the chain [19].

It should be stressed out, that mentioned works are basically focused on, probably, the most intriguing feature of boron carbide - anomalous loss of shear strength above HEL, because it limits its applicability as a structural material. The clarity in this question is still absent. One of the reasons is difficulties in modeling of such process as amorphization due to its large spatial scale.

Quantum molecular dynamics (QMD) simulation of boron carbide with different structures and stoichiometry was also performed by Taylor et al. [20,21]. Again, it was shown, that uniaxial loading and shear stress are crucial for mechanical stability of boron carbide. Moreover, stoichiometry and exact atomic arrangement of boron and carbon were found to be of great importance. Shock Hugoniot was also obtained via QMD + "Hugoniosat" method [21]. It was found, that if structure of boron carbide differs from  $(B_{11}C^p)$  CBC, than structural transition occurs above 40 GPa, in reasonable agreement with results of shock-wave experiments. Corresponded structural change is abrupt bending of three-atomic chain, leading to discontinuous volume change.

However, there are still open questions. What is the role of non-hydrostatic stress in structural transitions? Why three-atomic

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chain bends? In order to answer these questions the study of boron carbide behavior under non-hydrostatic stress was carried out from atomistic point of view.

This paper is organized as follows. Computational details are given in Section 2. Section 3 contains the results: stress state diagrams discussion (Section 3.1), the analysis of structural transitions (Section 3.2), and the discussion and comparison with the results of other groups and experiment (Section 3.3). Section 4 are devoted to conclusions.

## 2. Computational details

First of all, we will describe the considered structure. The structure of boron carbide (ideal stoichiometry  $B_4C$ ) contains two characteristic units: (1) 12-atomic icosahedra, located at the vertexes of the rhombohedral unit cell and (2) three-atomic chains, lying at the main diagonals of rhombohedra. The elementary unit cell contains 15 atoms. The sites of the icosahedron can be divided into polar and equatorial, depending on whether corresponding atoms form bonds with other icosahedron or chain, respectively.

The paper deals with the polar form of boron carbide ( $B_{11}C^p$ ) CBC, as the most energetically favorable one, according to the results of total energy calculation. In this form one carbon atom replaces boron in polar site of icosahedron, the chain contains two carbon atoms and remaining boron atom in the middle. It should be noted that the exact structure of boron carbide is still the subject of study, due to the mentioned above difficulties. Briefly, X-ray diffraction [22,23], nuclear magnetic resonance (NMR) [24], neutron diffraction [25], the study of Raman scattering [26,27] and absorption [28] of the X-rays shows that the structure of the chain is CBC. The remaining carbon atom is located in the polar site, according to the calculations of the Gibbs energy [29] and potential energy [30] as well as to the simulation of vibration spectra [31] and NMR spectra [32]. It should be noted, that experimentally observed  $R\bar{3}m$  symmetry group is, perhaps, due to the disorder in the arrangement of carbon atoms between the polar sites [33].

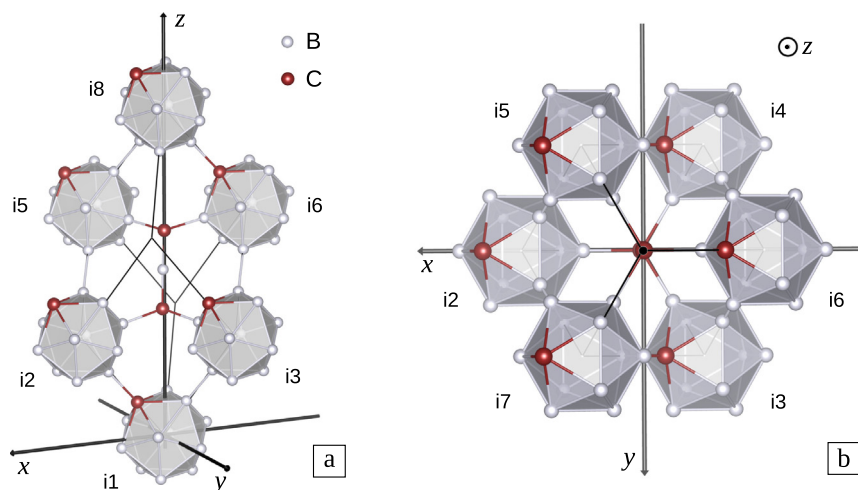
For modeling  $2 \times 2 \times 2$  supercell of 120 atoms was used. Some of the results were tested at  $3 \times 3 \times 3$  (405 atoms) supercell in order to exclude possible depending on the cells size. To simulate non-hydrostatic compression supercell was compressed along the axis of the Cartesian coordinate system, shown in Fig. 1. This coordinate system has several advantages, though it does not coincident with the translations vectors.

Firstly, it reflects the characteristic directions in the cell. The main diagonal of the rhombohedral cell, containing three-atomic chain, is coincide with  $z$  axis. The existence of carbon in polar sites of the icosahedra lowers symmetry from rhombohedral to the monoclinic one.  $x$  axis was chosen so that the edge of the unit cell containing carbon atom lays in the  $(x, z)$  plane. Secondly, the chosen coordinate system allows to trace more clearly the changes in the structure during deformation. Indeed, the compression along  $z$  axis, which is mainly studied in simulations by other groups, corresponds to compression along the chain. The main effect of the compression along the  $x$  axis is that three-atomic chain (remaining undeformed) approaching to the icosahedra  $i2$  and  $i6$  (Fig. 1b). When one compress along  $y$ , pairs of icosahedra  $i4, i5$  and  $i3, i7$  became closer to the chain. One can expect that the presence of carbon in the polar site will lead to qualitatively different results for different icosahedra, approaching to the chain. This assumption was justified by our results.

To study the behavior of boron carbide at non-hydrostatic loading the following technique was used. Deformation was carried out along two axes of the coordinate system, shown in Fig. 1. First, the ratio  $\varepsilon_{ii}/\varepsilon_{jj}$  between the relative deformations along these directions was fixed. Here,  $i, j = x, y, z$ . Next,  $\varepsilon_{ii}$  and  $\varepsilon_{jj}$  were varied in a certain range so that ratio remained constant. In each of these stressed states QMD was performed, and after thermal equilibrium was established, the average values of diagonal stress tensor components  $\sigma_{ii}$  were determined.

QMD was performed using PAW code VASP [34], with the exchange–correlation in the PBE form [35].  $2 \times 2 \times 2$  gamma-centered  $k$ -point grid (8  $k$ -points in the irreducible Brillouin zone) and the cut-off energy of the basis of plane waves of 450 eV were used. The convergence achieved was 1 meV/atom for total energy and 0.5 GPa for pressure. Both NVE and NVT ensembles at 500 K were used for QMD with 1 fs time-step and 3 ps total simulation time. The ionic relaxation also was carried out with the same  $k$ -point grid and cut-off energy. The convergence criteria were total energy difference of  $10^{-6}$  eV for electronic iterations and  $10^{-5}$  eV for total energy of optimized structures.

Finally, we will note the reasons why in this work QMD was used, not ionic relaxation at zero temperature. The excitation of the system due to thermal motion of ions can reveal the energy minimum, which is not possible to find at zero temperature due to the finite energy barrier. As shown in our previous work [36], this effect does occur.



**Fig. 1.** (a) The structure of polar form of boron carbide ( $B_{11}C^p$ ) CBC and the Cartesian coordinate system, used in the work. (b) The same, but along  $z$  axis. Icosahedra are numbered by  $i1$ – $i8$ . Two of the icosahedra are not shown in both cases.

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