

**COMMENT ON: “IS LINEAR GROUP X–Y–Z IN BORON CARBIDE
THE WEAKEST LINK IN THE STRUCTURE?” BY S. V.
KONOVALIKHIN AND V. I. PONOMAREV (RUSSIAN JOURNAL OF
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Abstract – The characterization of the boron carbide investigated in the above-mentioned paper and some of the conclusions made on it by the authors are critically appraised with regard to reliable results obtained earlier by other scientists.

The homogeneity range of boron carbide comprises chemical compositions between $B_{4.3}C$ and $B_{-10.36}C$ (see [1] and references therein). The carbon-rich limit $B_{4.3}C$ was proven by Schwetz and Karduck [2] for the first time and has been subsequently confirmed by several other groups. The structure is composed of rhombohedral elementary cells containing a twelve-atom icosahedron at the vertex and a preferably three-atom chain on the main diagonal, parallel to the crystallographic c -axis. Concentrations of B_{12} and $B_{11}C$ icosahedra and linear C-B-C, C-B-B and $B\Box B$ (\Box , vacancy) arrangements vary depending on the actual chemical composition (see [3,4] and references therein). If existing at all, other kinds of structural elements as considered by Konovalikhin and Ponomarev are below the current experimental detection limit.

The boron carbide investigated by Konovalikhin and Ponomarev was obtained by SHS (self-propagating high-temperature synthesis), that is an untypical preparation method for boron carbide. The carbon content of 24 % exceeds that of the carbon-rich limit of the homogeneity range (18.86 %) considerably. In contrast, the structure parameters (hexagonal, $a = 5.594(2) \text{ \AA}$, $c = 11.977(7) \text{ \AA}$; rhombohedral, $a = 5.13514 \text{ \AA}$, $\alpha = 66.0054^\circ$) reported by the authors [5] are close to those of high-purity, high-quality floating-zone grown $B_{4.3}C$ single crystals ($a = 5.6060(14) \text{ \AA}$, $c = 12.0851(78) \text{ \AA}$) [6,7].

The authors estimated the composition $B_{11.4}C_{3.6}$ (18.86 % C) implying linear relation between lattice parameters and carbon content and extrapolating lattice parameters obtained from literature to those determined on their compound. However, that relation is not linear in the surrounding of the carbon-rich limit of the homogeneity range but exhibits a significant kink near $B_{4.3}C$ (see for example Gosset and Colin [8] or [1]).

It is well known that carbon, exceeding the concentration of bound carbon in $B_{4.3}C$, forms graphitic layers of free carbon in the structure (see [9,10,4]). Hence, determining the actual chemical composition of the share of boron carbide in a sample presupposes that the concentrations of bound and free carbon are identified separately, for example using the method described by Schwetz and Hassler [11]. As this is missing in the paper under discussion, the composition $B_{11.4}C_{3.6}$ claimed by the authors is highly questionable. The good agreement of the structure parameters with those of single crystal $B_{4.3}C$ suggests that the sample might contain a considerable amount of free carbon, while the remaining share of crystalline boron carbide has the actual composition $B_{4.3}C$. In this case the structure comprises 100 % $B_{11}C$ icosahedra, ~ 91 % C-B-C, < 2 % C-B-B and ~ 9 % $B\Box B$ (\Box , vacancy) or alternatively B(3) vacancies (B(3), central chain atom) [3].

Within the entire homogeneity range, any structure of boron carbide consists of such differently composed elementary cells (see [3,4]). This holds even for the compound $B_{4.3}C$, the only composition that allows the preparation of macroscopic boron carbide single crystals [6,7]. The distribution of the differently composed cells might be statistical, as supercells in boron carbide structures have not been verified so far. Accordingly, X-ray or neutron diffraction are unsuitable methods for determining the fine structure of boron carbide reliably, as they average the properties of different cells in an extended inhomogeneous volume (for details, see [4]). This holds for the atomic positions, and in particular for the thermal vibration amplitudes U_{eq} discussed in the paper under discussion as well. Accordingly, the latter parameter discussed by the authors is not at all the actual thermal effect, but it is essentially determined by the superimposed statistical uncertainty of the geometrical position of the respective atomic site in the inhomogeneous structure of boron carbide.

In the discussion of links in the structure of boron carbide, the consideration of the IR- and Raman-active phonons (see [4,7,12] and references therein) is missing. They yield immediate information on the various bond strengths between the structural elements.

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