ON MICROSTRUCTURE AND ELECTRONIC PROPERTIES OF BORON CARBIDE

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ABSTRACT

Boron carbide (homogeneity range B₄₋₁₁C) exhibits ~ 15 atoms per elementary cell and is composed of B₁₂ or B₁₁C icosahedra and linear structure elements CBC, CBB or B□B (□, vacancy), whose shares depend on the chemical composition. Their random distribution excludes x-ray diffraction and NMR from structure analysis. Phonon spectroscopy on isotopically pure boron carbide solves this problem. – Experimental investigations established semiconducting character. They contrast with theoretical band structure calculations concluding metallic behavior because of being based on incorrect idealized structures. The actual band scheme (gaps 2.09 and 2.41 eV) exhibiting high-density gap states allows consistently interpreting the experimental results. – Seebeck coefficients of ~300 μV/K up to 2000 K make it a promising candidate for thermoelectric energy conversion. Theoretical speculations on superconductivity up to 36.7 K were not confirmed.

INTRODUCTION

Outstanding characteristics of boron carbide are the high melting point (Tₘ > 2700 K), great hardness (H_K, H_V = 30 ... 38 GPa), low density (d = 2.51 g cm⁻³), high chemical stability, high neutron absorption cross section (due to the ¹⁰B content) and high Seebeck coefficient (S ~ 300 μVK⁻¹) up to at least 2000 K.

Significant applications are in the form of abrasive materials, high temperature industrial ceramics, lightweight armor, tough coatings and reinforcement of other materials, nuclear applications like control rods in nuclear reactors or radioactive shielding.

First synthesis of boron carbide was achieved in the 19th century ¹,², an early review on industrial material was given by Lipp ³, an actual review on properties has been published by

Figure 1. Boron Carbide. Rhombohedral elementary cell, , consisting of a 12 atom icosahedron and a mostly three-atomic chain parallel to the c axis. Idealized B₁₃C₂ (B₁₂ CBC) model; icosahedron: light green, polar atoms; dark green, equatorial atoms. Visualization by the program VESTA⁶.
Domnich et al. \(^4\), a critical review on the electronic properties was reported by Werheit \(^5\).

Symmetry type of the structure is \(R\overline{3}m\) (space group 166). Initially, the rhombohedral unit cell was assumed to be composed of \(B_{12}\) icosahedra at its vertices and a linear CCC chain on the main diagonal parallel to the crystallographic c-axis, leading to the chemical composition \(B_{12}C_3\). After the central chain atom was proved to be solely boron, the structure formula \((B_{12})\) CCC was modified to \((B_{11}C)\) CBC. This structure model is depicted in Fig. 1 using the program VESTA \(^6\). The apparently plausible formula \(B_4C\) is long since proved to be incorrect \(^7\), but nevertheless it has often been used as a synonym for boron carbide.

According to the present state of art, the chemical compound \(B_4C\) or \(B_{12}C_3\) does not exist, at least not, when it is prepared by the common high-temperature preparation methods melting or hot-pressing, typically exceeding 2300 K. Actual chemical compounds of boron carbide exist in the large homogeneity range extending from the carbon-rich limit \(B_{4.3}C\) \(^7\) to the boron-rich limit \(B_{10.8}C\) \(^8\). Various structure elements have been identified; their concentrations depend on the actual chemical composition, and the distribution is assumed to be statistical, as no superlattice has been identified so far:

- \(B_{12}\) icosahedra
- \(B_{11}C\) icosahedra with the C atom accommodated in one of the 6 polar sites
- CBC chains
- CBB chains
- \(B\Box B\) arrangements (\(\Box\), vacancy)

Thus, boron carbide has no real crystal structure characterized by a well defined unit cell, but exhibits at the most an elementary cell with a twelve-atom icosahedron and a mostly three-atom chain, both in varying compositions, which are randomly distributed.

Therefore, the most prominent methods of structure analysis, x-ray as well as neutron scattering and NMR, fail in determining the actual microstructure of boron carbide, indeed for different reasons. X-ray and neutron diffraction, averaging a large volume with differently

![Figure 2. Lattice parameters of boron carbide vs. C content; characteristic compositions marked at the upper rim. Small circles (black) and small upward trinangles (red)\(^9\). Large circles (black) and downward triangles (red)\(^11\), stars, high quality single crystal\(^10\), \(B_{12.88}C_{1.99}\) \(^12\), diamond (black).](image-url)
composed elementary cells, yield the atomic sites correctly, but are unable to determine their individual occupancies. Moreover, these methods are decisively impeded by the difficulty of distinguishing B and C atoms because of their very similar scattering cross section.

NMR spectra of boron carbide contain the overlapping resonances of $^{11}$B and $^{13}$C isotopes respectively, whose local environments vary in the volume analyzed. This aggravates decisively the general problem of NMR, whose interpretation is unambiguous at most in neat structures. Otherwise, it depends on the more or less arbitrarily chosen structure models used for fitting the spectra. In the case of boron carbide, the random mixture of differently composed cells and structure elements makes a reliable analysis of the spectra nearly impossible.

In Figure 2 the lattice parameters of boron carbides with carbon contents between 8.8 and 24.5 % obtained by Gosset and Colin are displayed. The parameters of a high quality single crystal and of the isotope enriched samples discussed below agree quite well. The parameters reported by Sologub et al. on $B_{12.88}C_{1.99}$ deviate considerably, in particular with respect to the rhombohedral angle $\alpha$. Apparently, $\alpha$ in the rhombohedral or $c$ in the hexagonal description depend sensitively on small amounts of impurities or other structural modifications.

Schwetz and Karduck determined $B_{4.3}C$ to be the carbon-rich limit of the homogeneity range. Excess carbon atoms are not incorporated in the structure but precipitated in the form of graphitic carbon layers. This is consistent with the electronic transport properties shown in Figure 3. At carbon contents below $B_{4.3}C$ boron carbide is semiconducting, while higher carbon contents induce a superimposed metallic conduction. Initially assuming the carbon-rich limit to be $B_4C$, then this behavior was misinterpreted as a metal-semiconductor transition.

In particular close to the carbon-rich limit of the homogeneity range, a reliable chemical analysis of boron carbides requires separately determining free and bound carbon (a suitable wet-chemical method was described by Schwetz and Hassler). Sometimes, boron carbides with carbon contents of 25 at % or even more have been obtained, hence considerably exceeding the carbon-rich limit $B_{4.3}C$ with 18.87 at %. Konovalikhin and Ponomarev report on a boron carbide single crystal $B_{11.4}C_{3.6}$ with 24 at % carbon. The structure parameters (hexagonal, $a = 5.594(2)$ Å, $c = 11.977(7)$ Å; rhombohedral, $a = 5.13514$, $\alpha = 66.0054$) are far outside the limits of figure 2. This suggest a deviating structure possibly induced by the preparation method SHS (self-propagating high-temperature synthesis).
STRUCTURE DETERMINATION BY MEANS OF PHONON SPECTRA

Determining the relative occurrence of structure elements by analyzing the phonon spectra of boron carbide is based on the relative intensities of specific phonons. Boron and carbon atoms are distinguished according to their different masses or bonding forces; both induce a shift of the phonon frequency. In boron carbides with natural isotope contents (19.9% $^{10}\text{B}$, 80.1% $^{11}\text{B}$) this analysis is complicated by the not randomly distributed isotopes. Hence isotope-enriched boron carbides are required. The influence of the different carbon isotopes on the phonon spectra is negligible, as natural carbon contains 98.9% $^{12}\text{C}$.

Chain-free elementary cells

A peculiarity in the boron carbide structure is the existence of chain-free cells or, differently expressed, vacancies of the central B site in the elementary cell. This has been consistently determined by different experimental methods, (i) phonon spectroscopy, (ii) neutron powder diffraction, (iii) accommodation of Si atoms, (iv) x-ray scattering. The results are shown in Figure 4.

Phonons of isotopically pure boron carbides

In Figure 5 typical spectra of the IR-active phonons of boron carbide are displayed. Systematic experimental investigations and theoretical calculations by Shirai et al. and Vast et al. allow attributing some of the phonon modes to specific movements of atoms. Stretching and bending modes of the three-atomic chain are shown in Fig. 6a and 6b respectively. The main peak of the stretching mode is attributed to CBC and the smaller one to CBB shifted to lower frequencies in consequence of the weaker bond strength. In isotopically pure $\text{B}_{4.3}\text{C}$ CBB is missing. In the case of mixed carbon isotopes, there is a weak peak at lower frequencies probably due to the 20% share of the heavier $^{13}\text{C}$ isotope.
In the bending mode, the missing influence of carbon isotopes confirms that the central site is occupied by boron only. Again, there are two components of different intensity due to CBC and CBB chains respectively.

As noted in Figure 5, the strong mode near 1100 cm\(^{-1}\) belongs to the inter-icosahedral vibrations of the polar atoms of the icosahedra. There are 2 x 3 polar atoms; in \(\text{B}_{11}\text{C}\) icosahedra one of the six sites is randomly occupied by a C atom. Compared with B, the C atom is shifted

![Figure 5. IR phonon spectra of some \(^{10}\text{B}\) enriched boron carbides. Attribution of IR-active phonons of boron carbide to movement patterns of specific atoms; arrows indicate moving direction of the central B atom in the particular vibration.](image)

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![Figure 6. Chain-related vibrations of boron carbide\(^8\); a, stretching mode; b, bending mode.](image)
towards the center of the icosahedron; thus inducing a distortion. In regular $B_{12}$ icosahedra, the three adjacent polar atoms move simultaneously.

![Image of phonon modes and wave numbers.](image)

Figure 7. Inter-icosahedral vibrations of the polar atoms in boron carbide$^8$; B-B vibration attributed to the main component; B-C vibration attributed to the component shifted to lower frequencies.

Distortions of structural elements induce splitting of the phonon modes related. As shown in Figure 7, the concerning mode in boron carbide is threefold split. We attribute the strongest component to B-B vibrations and the weaker one shifted to lower frequencies to B-C vibrations. The third component is not identified so far, it might be caused by further distortions of the icosahedra, possibly by the Jahn-Teller effect.

For a more detailed description of the numerical evaluation of the different phonon modes of boron carbide, the reader is referred to ref. $^8$.

**COMPOSITION OF THE ELEMENTARY CELLS**

The relative contributions of CBC and CBB chains to the phonon modes in Figure 6 refer to the concerning cells only. Therefore, at first the fraction of chain-free cells must be considered; it is obtained from the average of the experimental data in Figure 4. The remaining portion contains CBC and CBB chains respectively. Their relative share is obtained from Figure 6, using the relation of the particular components of the stretching and bending mode each. The results are shown in Figure 8a, where the data of isotopically pure boron carbides are connected by lines. C atoms are obviously not remarkably involved in these vibrations, as the results of $B_x^{12}C_{0.2}^{13}C_{0.8}$ are exactly the same.

The accordingly obtained data of some $^{nat}\text{B}_x\text{C}$ samples$^8$ are displayed additionally. At higher carbon contents ($> 0.13$), these data agree very well with the isotopically pure boron carbides, while deviation considerably in the case of boron-rich boron carbides. Obviously, these deviations are due to less well defined stretching vibrations of the CBB chains in $^{nat}\text{B}_x\text{C}$ ($x >$
Different quality of sample preparation can be excluded, as some of these samples are more costly prepared (synthesized by melting or melted after hot-pressing) compared with the isotope-enriched ones. Apparently, there occurs a complicated interaction between isotope distribution and structural details.

Impurity atoms accommodated in the boron carbide structure affect the shares of structural components considerably. This is demonstrated in Figure 8 by means of a boron carbide containing 2% Si atoms. They meet exactly the share of chain-free cells in concerning undoped boron carbide. Moreover, CBB chains are missing, as no concerning vibrations are discernible in the spectrum.

After the attribution to the chains, the remaining amount of boron and carbon atoms is attributed to $B_{12}$ and $B_{11}C$ icosahedra and yields the results shown in figure 8b. Their content depends almost linearly on the C content, of course contrary to each other. Again, the data of carbon-rich compounds fit well, while boron-rich $^{nat}B_xC$ deviate significantly, in particular at low carbon contents. The data of $B_{10.37}C$ are even unrealistic. A fit using higher concentrations of chain-free unit cells failed because of missing compatibility with the concentrations of CBC and CBB chains. The reason for the deviating results of boron-rich $^{nat}B$ boron carbide remains open; an effect of non-random isotope distribution seems possible.

**HOMOGENEITY RANGE**

As mentioned, the carbon-rich limit of the homogeneity range of boron carbide is $B_{4.3}C$. From the optical spectra it is evident that – apart from $B_{11}C$ icosahedra and chain-free cells – this compound contains C-B-C chains only. Then the actual chemical composition requires a certain share $x$ of chain-free elementary cells. Considering C atoms in the different kinds of elementary cells, the share is $x = 0.094$ resulting from

$$C - \text{content}(B_{4.3}C) = \frac{1}{5.3} = \frac{3(1-x)}{15(1-x)+14x}$$

(total C-content = share of C atoms / sum of atoms in ($B_{11}C$) CBC and ($B_{11}C$) $B\Box B$ cells).
The boron-rich limit of the homogeneity range is accordingly obtained. The relation \( \frac{CBC}{CBB} \sim 0.78/0.22 \) results from the phonon components and the share of chain-free cells 0.28 is estimated extrapolating the averaged data in Fig. 2 to the carbon content 0.082 of the most boron-rich boron carbide so far prepared by Gosset and Colin\(^9\). Of course, a stable structure of boron-rich boron carbide needs one icosahedron per elementary cell. Accordingly, the C content at the boron-rich limit of the homogeneity range, based on 57% B\(_{12}\)CBC, 15% B\(_{12}\)CBB and 28% B\(_{12}\)□B, estimated from Fig. 2, is

\[
\begin{align*}
C_{\text{B-rich limit}} &= \left( \frac{C}{B + C} \right)_{\text{B-rich limit}} \\
&= \frac{0.57 \cdot 2 + 0.15 \cdot 1}{(0.57 + 0.15) \cdot 15 + 0.28 \cdot 14} = 0.088
\end{align*}
\]

**ELECTRONIC PROPERTIES**

For many years, the discussion on the electronic properties of boron carbide was significantly determined by the discrepancy between experimental realities and theoretical calculations. Experimentally, the semiconducting character of boron carbide had been definitely proved\(^{31,32,33,34,35}\). In contrast, theoretical calculations yielded metallic behaviour, in which the Fermi level was positioned within the valence band, and electron deficiencies in the order of 10\(^{21}\) cm\(^{-3}\) were assumed\(^{3,30,36,37,38,39}\). The resultant problem of explaining the low electrical conductivity was approached by the hypothesis of bipolaronic hopping\(^{40,41,42}\), thereby ignoring numerous conflicting experimental results (in detail discussed in Ref.\(^43\)). The real reason for the deficiency of the theoretical calculations, namely that they were based on hypothetical structures (B\(_{11}\)C)CBC or (B\(_{12}\)CBC deviating considerably from the real ones, was not recognized.

An according discrepancy between experimental and theoretical results is known in the case of \(\beta\)-rhombohedral boron, another icosahedral boron-rich solid, as well\(^{44}\). Apparently, a general feature of such structures seems to be that idealized structures exhibit electron deficiencies and incompletely filled valence bands respectively, accordingly yielding metallic character, while the real structures are semiconductors.

Based on \(\alpha\)-rhombohedral boron, \(\beta\)-rhombohedral boron and boron carbide, Schmechel and Werheit\(^{44}\) showed that, when applicable, such electron deficiencies are exactly compensated by intrinsic structural defects. In the electronic structures related, the respective electronic states are split from the valence band and form unoccupied localized electronic states in the band gap and leave the remaining valence band completely filled with electrons.

Recently, Shirai and Uemura\(^{45}\) discussed this behaviour theoretically on crystalline solids with large unit cells in general. They stated in such structures an increasing degree of internal freedom evoking a rising chance for atoms to meet other minima of energy in the atomic configuration. In the case of boron-rich crystals, they assigned this behaviour to a breaking of stoichiometry.

In order to determine the concentration of actual defects in boron carbide, we take the energetically most probable structure formula (B\(_{12}\)CBC)\(^{37}\) for reference. Then, according to Schmechel and Werheit\(^{44}\), the actual defects in boron carbide are

- B\(_{11}\)C icosahedra, exhibiting one excess electron compared with B\(_{12}\) icosahedra, accordingly generating one donor in the electronic structure,
- CBB chains. Compared with CBC, they have a deficiency of one electron and yield accordingly one acceptor,
- □B arrangements. Compared with CBC, they have a deficiency of four electrons and yield four acceptors each.
Based on the structural elements of boron carbide in Figure 8, the concentrations of the concerning electronic states in the band gap were calculated; they are shown in Figure 9. The number of these kinds of gap states clarifies the discrepancy between theory and experiment. However, the question of defects and their electronic states in boron carbide is not finally solved. In particular, the actual energetical positions in the electronic band scheme are not known. Moreover, additional electronic gap states evoked by further intrinsic structural defects or impurities might be efficient as well. Such defects are the deformation of $\text{B}_{11}\text{C}$ compared with $\text{B}_{12}$ icosahedra\textsuperscript{46} and the non-random distribution of boron isotopes in $\text{natB}$ boron carbides\textsuperscript{8,19}.

As theoretical results on this topic are missing so far, at present we depend on suitable experimental investigations for establishing the band scheme\textsuperscript{47} shown in Figure 10. There, the directions of electronic transition, depending on the type of experiment, are indicated by arrows. Most important in this context are various optical and electrical experiments, which need to be consistently interpreted.

Figure 9. Defect states in boron carbide vs. carbon content. Full symbols, isotopically pure boron carbide; open symbols, $\text{natB}_x\text{C}$ samples. The B\textsuperscript{□}\textsuperscript{B} acceptors (full line) correspond to the averaging line in Figure 4.

Figure 10. Actual band scheme of boron carbide\textsuperscript{47}. 
Some of the most important experimental results are shown below. In Figure 11, the absorption edge in the optical spectrum is displayed. Its steep rise towards high photon energies is essentially determined by the interband transitions \(^{48,10,49}\). Theoretical model calculations were used for the evaluation; they attribute specific dependences of the absorption coefficient on photon energy to particular kinds of electronic transitions. This way, at ambient temperature the indirect band gaps 2.09 and 2.41 eV were obtained.

![Figure 11. Absorption edge of boron carbide\(^{48,10,49}\) depending on temperature (polycrystalline samples). Single crystal at ambient temperature.](image)

At about 1.5 eV, the spectra at lower temperatures contain a significant peak, whose intensity decreases with T increasing. This has been identified by the luminescence spectrum \(^{49,50}\) shown in Figure 12. In connection with X-ray Raman scattering (XRS) and site-specific ab-initio

![Figure 12. Luminescence spectrum of boron carbide\(^{49,50}\). Points, measured; thin lines, averaged results, initial ones and those after detracting the fitted main peak; bold lines, fitting by theory (see \(^{50}\)).](image)
calculations by Feng et al.\textsuperscript{51}, the emission peak is attributed to a p-type exciton associated to the central B atom in the elementary cell. The luminescence peak consists of two components, whose intensity relation is 4.1. This corresponds quite well with the relation $^{11}\text{B}/^{10}\text{B} = 4.03$ in nat$^4\text{B}_3\text{C}$, if random isotope distribution in this site is assumed in contrast to the results in Ref.\textsuperscript{8} indicating a non-random distribution of isotopes. According to Figure 8, C-B-C chains are the only ones containing a central B atom in $^4\text{B}_3\text{C}$, thus allowing for improving initial assumptions\textsuperscript{50}. The stability of excitons decreases with the temperature increasing, thus the accordingly decreasing absorption in Figure 11 can be easily explained.

The exciton absorption might be the essential reason for the absorption of the single crystal shown in Figure 11, which exceeds that of polycrystalline boron carbide considerably. It is well known that the probability of exciton formation decreases with defect concentrations increasing, and this might be the case in polycrystalline compared with single crystal boron carbide. (Remark: The very high fundamental absorption exceeding $\alpha = 6000 \text{ cm}^{-1}$ is important with respect to the controversially discussed Raman spectra of boron carbide. The energy of typical lasers in commercial Raman spectrometers exceeds 2 eV. Because of the high absorption coefficient in this range, the penetration depth of the exciting radiation is very small, and Raman scattering takes place essentially in surface region of the sample. Hence, such Raman spectra are largely determined by surface phonons; for details, see e.g.\textsuperscript{52}).

![Figure 13. High-temperature electrical conductivity of boron carbide\textsuperscript{34,53,54,55}.](image)

The Arrhenius plot of the electrical conductivity in semiconductors yields the thermal activation energy of the charge carriers. At sufficiently high temperatures, where the contribution of doping becomes negligible, this activation energy yields the band gap between valence and conduction band.

In boron carbide, this does not apply. The extremely high density of acceptor-like gap states prevents intrinsic conductivity up to very high temperatures. As shown in Figure 13, up to temperatures considerably exceeding 2000 K, the electrical conductivity is determined by several distinct activation energies, which are restricted to a limited range of temperature, each\textsuperscript{53,54,34,55}. In the results of Wood\textsuperscript{54}, the kink at 2300 K indicates that even at such high temperatures the Fermi level is pinned by high-density gap states, and that apparently even close to the melting point intrinsic electrical conductivity is not established in boron carbide.

The gap state determined electronic transport at these high temperatures is confirmed by the Seebeck coefficient exemplarily shown in Fig. 14\textsuperscript{55,56}. In the range of intrinsic conductivity of typical semiconductors, the Seebeck coefficient is small, as the number of electrons and holes is nearly equal and hence their contributions compensate largely each other. However, in boron
carbide the effect of holes remains prevalent and yields a high Seebeck coefficient up to very high temperatures. This makes boron carbide a promising candidate for thermoelectric energy conversion.

These results explain easily why all attempts have failed to obtain n-type boron carbide by interstitial or substitutional doping with foreign elements. Sufficient concentrations of excess electrons allowing for compensating $10^{21}$ to $10^{22}$ cm$^{-3}$ acceptors require such high concentration of foreign atoms, that they would be incommensurate with the boron carbide structure. On the other hand, some foreign elements generate additional acceptors, thus considerably increasing the Seebeck coefficient of boron carbide$^{56}$. Any way, the realisation of Seebeck elements with boron carbide requires other semiconducting n-type counterparts.

During the efforts in realizing superconductivity of icosahedral boron-rich solids, Calandra et al.$^{30,39}$ predicted superconductivity of metallic boron carbide up to 36.7 K. We checked this experimentally at 30 K by far-infrared optical absorption measurements$^{47}$. Confirming the above results, the absorption spectrum in Figure 15a excludes definitely boron carbide to be metallic or superconducting could occur at this temperature. There is no indication

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**Figure 14.** Seebeck coefficient of boron carbide, selected results after Aselage et al.$^{55}$ and Werheit et al.$^{56}$.

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**Figure 15.**

**a**, low photon energy absorption index of B$_{4.3}$C at 30 K; insert, fitting of the numbered peaks to a Lyman series$^{47}$.

**b**, attempt of attribution of the peak positions to a level, 45 meV above the valence band edge.
of different behavior towards lower temperatures. High electrical conductivity is indicated by optical absorption, strongly increasing with energy decreasing ($\alpha \sim \omega^{-2}$ in the case of Drude-type carriers).

The FIR spectrum contains several distinct narrow absorption bands. According to the insert of Fig. 15a they fit a Lyman-type series of excitations. This suggests attributing to a gap state with excitation levels near to the valence band edge, like proposed in Figure 15b.

**CHARGE TRANSPORT**

The band scheme shown in Figure 10 and the positive sign of the Seebeck coefficient up to high temperatures suggest that the charge transport in boron carbide takes place in the valence band or in the adhered high-density gap states. The theoretical band structure calculations\(^{36,37,38}\) yield flat bands; hence large effective masses of free carriers, and accordingly low mobilities. As the Fermi level is positioned in the band gap, probably pinned in high-density gap states, the following types of charge transport are expected:

- Hopping between localized gap sites. According to Mott, the electrical conductivity in the case of variable-range hopping varies as $\sigma \sim T^{-1/4}$.
- Band-type conductivity in the valence band. Electrons thermally excited from the valence band into gap states, leave free holes, whose movement is possibly affected by multiple trapping and thermal re-excitation like in $\beta$-rhombohedral boron\(^{57,58}\).

Both mechanisms are expected to occur simultaneously\(^{59}\); indeed, one of them might prevail depending on the actual temperature. According to Figure 13, at temperatures exceeding $\sim 400$ K band-type conductivity is decisive. In Figure 16, the electrical conductivity of several boron carbides\(^{34}\) is plotted for checking the application of Mott’s law. Within the homogeneity range, the influence of the chemical composition is weak. In the range from $\sim 15$ to $\sim 200$ K, the slope is linear indicating that variable–range hopping is prevailing. Below 10 K, the mechanism is not clear. However, the accuracy of measurement at such low conductivities is limited and requires additional confirmation.

Further information on charge transport is obtained from the density of carriers. Figure 17 shows the results of different experimental methods. Chauvet et al.\(^{60}\) measured ESR spin densities from 4 to 1200 K; other results\(^{61,62,63}\) are more or less compatible. Contrary to the authors, we attribute the spins to localized electrons in the gap states shown in Figure 10.

Below 100 K, the spin density of $\sim 10^{19}$ cm\(^{-3}\) is largely independent of temperature. With

![Figure 16. Electric conductivity of boron carbide, plotted according to Mott’s law of variable-range hopping $\sigma \sim T^{-1/4}$\(^{34}\).](image-url)
temperature increasing, valence electrons are thermally excited from the valence band and occupy further gap states. Their density, shown in Figure 17, was obtained by subtracting the low temperature spin level. The excited valence electrons leave free holes in the valence band allowing for band-type transport; their concentrations in Figure 17 stem from Hall effect\textsuperscript{34,54,64}, magnetoresistivity (Shubnikov-de Haas oscillations)\textsuperscript{53,64} and dynamical conductivity\textsuperscript{65,66}.

The quantity of free holes should correlate with the thermally excited share of spins in the localized gap states. As shown in Figure 17, the agreement is quite satisfactory, in particular concerning the thermal activation energies. At higher temperatures, this is $\Delta E = 0.18$ eV. At lower temperatures, the error margins are large only allowing for roughly estimating an activation energy of the order $0.05$ eV. According to Figures 10 and 15b such levels exist.

CONCLUSION

The homogeneity range of boron carbide extends from B$_{4.3}$C at the carbon-rich to B$_{-10.3}$C at the boron-rich limit. Randomly distributed B$_{12}$ and B$_{11}$C icosahedra combined with CBC, CBB and BCB linear arrangements form the particular structures. Their concentrations depend on the actual chemical composition. The chemical compound B$_4$C, still often incorrectly used as a synonym for boron carbide, does not exist. This holds at least in the case of boron carbides, which are typically synthesized at temperatures exceeding 2000 to 2300 K.

B$_{4.3}$C has the less distorted structure in the homogeneity range and is the only composition allowing for preparing single crystals from the melt. Nevertheless, even this compound contains considerable amounts of intrinsic defects in the form of nearly 10 % chain-free elementary cells. This high concentration of structural defects even in such a tightly bonded structure is possibly due to the very high preparation temperatures. The associated high thermal energy could be sufficient for generating the defects, which are subsequently quenched, when cooled down. For checking, boron carbides produced by low-temperature syntheses, for example in metallic solutions, should be examined.

In the whole homogeneity range, boron carbide is a p-type semiconductor, largely independent of the actual chemical composition. Its electronic properties can be consistently described in the usual way with valence and conduction band separated by a well-defined band gap. Typical for boron carbide are high concentrations of acceptor-like states of the order of $10^{21}$
cm$^{-3}$. These are generated by structural defects, determined as deviations from the energetically most favorable idealized structure (B$_{12}$)CBC.

This is the reason, why n-type boron carbide is obviously precluded. The boron carbide structure is apparently not compatible with the accommodation of sufficiently high concentration of electron-donating foreign atoms, which would be required for compensating the acceptor-like intrinsic gap states.

The high Seebeck coefficient exceeding 300 $\mu$VK$^{-1}$ up to at least 2000 K makes boron carbide a promising candidate for direct thermoelectric energy conversion. However, an n-type counterpart of otherwise similar properties is required for suitable Seebeck elements$^{56}$.

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