

## FT-Raman spectra of isotope-enriched boron carbide

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### Abstract

For some boron-rich solids, in particular boron carbide, it is proved that FT-Raman spectroscopy yields reliable spectra of the Raman-active phonons, while the conventional Raman spectra are strongly influenced by the surface properties of the samples, and hence they are less suitable to detect the bulk properties of these solids. The FT-Raman spectra of <sup>10</sup>B, <sup>11</sup>B, and <sup>13</sup>C isotope-enriched boron carbide of compositions B<sub>4,3</sub>C, B<sub>6,5</sub>C, and B<sub>10</sub>C have been measured in completion to the recently published IR-Phonon spectra of the same samples. Considering the description of movement of atoms in specific Raman-active modes determined by Shirai and Emura, the spectra are evaluated and discussed with respect to the composition-dependent concentrations of structural elements like B<sub>12</sub> and B<sub>11</sub>C icosahedra, CBC, CBB, and CCC chains within the homogeneity range. Most of the Raman bands can be attributed to specific lattice vibrations.

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### 1. Introduction

The homogeneity range of boron carbide extends from B<sub>4,3</sub>C at the carbon-rich limit to about B<sub>11</sub>C at the boron-rich limit. It is well known that the basic structure consists of an icosahedron at the vertex and a three-atomic chain on the main diagonal of the rhombohedral elementary cell, which is parallel to the crystallographic *c*-axis. However, X-ray and NMR methods have failed to determine structural details like the variation of the structural elements dependent on the actual chemical composition (see Ref. [1] and references therein). Theoretical calculations of the electronic properties yielded incorrect results (e.g., metallic instead of semiconducting behavior), because they were based on idealized structures that do not occur in reality [2–5].

The evaluation of the IR phonon spectra allowed determining some essential information on composition and concentration of the structure elements in the elementary cells. For boron carbide, we avoid the term “unit cell” because the cell is no real structural unit, but there are B<sub>12</sub> or B<sub>11</sub>C icosahedra at the vertices, CBC, CBB, B□B and, depending on the preparation, CCC arrangements on the main diagonal of the rhombohedral cell, whose relative concentrations considerably vary within the homogeneity range [1,6–9]. Using these results, it was shown that the electronic properties of boron carbide are strongly correlated with the real crystal structures characterized by the generation of defects compared with the idealized structures [6,8]. The consideration of the Raman-active phonons promises further insight into the structural details.

FT-Raman spectroscopy has been proved to yield reliable spectra of the bulk phonons of boron carbide, while the conventional Raman spectroscopy is strongly impaired by the surface properties of the samples and therefore less suitable [10]. Below, FT-Raman spectra of isotope-enriched boron carbide are presented and

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Table 1  
Lattice constants of the investigated samples

	$a_{\text{hex}}$	$c_{\text{hex}}$	$a_{\text{rh}}$	$\alpha_{\text{rh}}$
$^{10}\text{B}_{4,3}\text{C}$	5.614(7)	12.075(9)	5.168(7)	65.78
$^{10}\text{B}_{6,5}\text{C}$	5.629(8)	12.178(12)	5.199(8)	65.53
$^{10}\text{B}_{10}\text{C}$	5.649(6)	12.188(9)	5.210(6)	65.66
$^{10}\text{B}_{4,3}^{13}\text{C}$	5.616(8)	12.076(8)	5.169(8)	65.78
$^{10}\text{B}_{6,5}^{13}\text{C}$	5.626(7)	12.181(8)	5.198(7)	65.53
$^{10}\text{B}_{10}^{13}\text{C}$	5.648(7)	12.188(7)	5.210(6)	65.66
$^{11}\text{B}_{4,3}\text{C}$	5.608(8)	12.072(8)	5.165(8)	65.77
$^{11}\text{B}_{6,5}\text{C}$	5.625(5)	12.176(9)	5.198(7)	65.52
$^{11}\text{B}_{10}\text{C}$	5.647(7)	12.186(8)	5.209(8)	65.65

evaluated. These results complete the IR-Phonon spectra, which were recently measured on the same samples [11].

For the idealized  $\text{B}_{13}\text{C}_2$  structure ( $\text{B}_{12}(\text{CBC})$ ), according to group theory the lattice vibrations of boron carbide are classified as  $5A_{1g} + 2A_{1u} + 2A_{2g} + 6A_{2u} + 7E_g + 8E_u$ . Twelve of these modes are Raman active and 12 modes IR active [12]. However, as the real structure deviates from the idealized one, the number of experimentally detected vibration modes is expected to be higher than that obtained by group theory.

## 2. Sample material

$^{10}\text{B}$ ,  $^{11}\text{B}$  and  $^{10}\text{B}$ – $^{13}\text{C}$  enriched boron carbides of the compositions  $\text{B}_{4,3}\text{C}$ ,  $\text{B}_{6,5}\text{C}$  and  $\text{B}_{10}\text{C}$  were investigated. The sample material was prepared by hot pressing at 40 MPa for 30 min at 2000–2050°C from powder obtained by a direct total synthesis of the elements (1950°C, 2 h). The isotope enrichment was 98.4 at%  $^{10}\text{B}$ , 99.4(2) at%  $^{11}\text{B}$ , and 80.1(2) at%  $^{13}\text{C}$ . The samples on which the Raman investigations were performed are the same, on which the IR-phonon spectra were reported in Ref. [11]. The lattice parameters (Table 1) satisfactorily agree with those known from literature [13]. The lattice constants of  $^{10}\text{B}$  enriched boron carbide are slightly larger than those of  $^{11}\text{B}$  enriched material as expected according to the higher zero-point energy. For more details of sample properties see Ref. [11].

## 3. Results

The FT-Raman spectra were measured with a Bruker FT-Raman spectrometer (Type FRA 106/IFS 66v). To reduce noise, averaged interferograms of up to  $10 \times 1000$  scans were Fourier-transformed into the real spectra. The resolution of the spectra is about  $2 \text{ cm}^{-1}$ . The spectra are displayed in Fig. 1. The Raman frequencies are listed in Table 2.

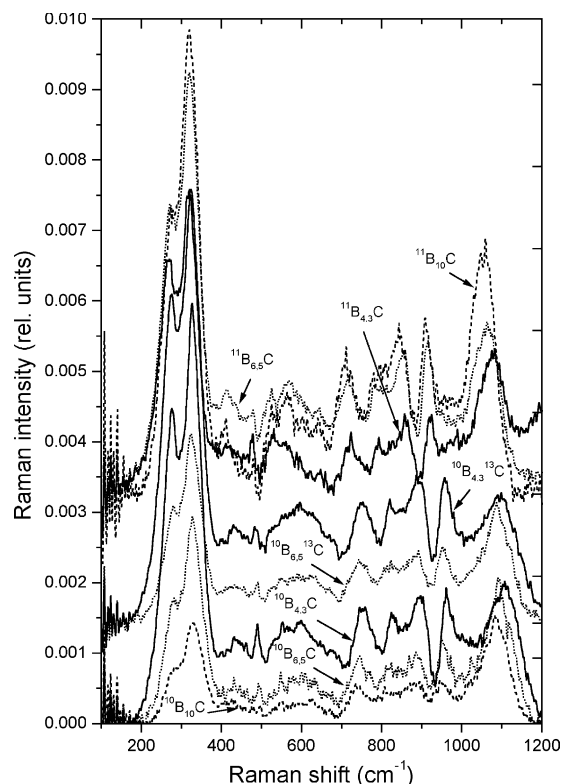


Fig. 1. FT-Raman spectra of the boron carbide compounds  $\text{B}_{4,3}\text{C}$ ,  $\text{B}_{6,5}\text{C}$ ,  $\text{B}_{10}\text{C}$ , enriched with the isotopes  $^{10}\text{B}$ ,  $^{11}\text{B}$ , and  $^{10}\text{B} + ^{13}\text{C}$ , respectively.

## 4. Discussion

The aim of the present investigation is to attribute Raman bands of boron carbide to specific vibrations by analyzing the influence of isotopes. In spite of their qualitative similarity, the intensity of the Raman spectra depends on the specific properties of the different samples. Therefore, from the spectra only the frequencies of the Raman modes can be immediately obtained. For other parameters like broadness or damping it is necessary to derive secondary criteria by eliminating the individual intensities of the spectra. Obviously single Raman lines were analyzed by single, broad bands by multiple Lorentzian fits.

## 5. Analysis of the Raman peaks in the sequence of increasing frequencies

Shirai and Emura [14,15] predict two librational modes in the Raman spectrum of boron carbide, the rotation of the icosahedron expected at  $172 \text{ cm}^{-1}$  and the rotation of the three-atom chain expected at  $330 \text{ cm}^{-1}$ . The attribution of a Raman peak at  $168 \text{ cm}^{-1}$  found in conventionally measured Raman spectra to the former one has become invalid, since the

Table 2  
Raman frequencies of isotope-enriched boron carbide

No.	<sup>11</sup> B <sub>4,3</sub> C	<sup>10</sup> B <sub>4,3</sub> C	<sup>11</sup> B <sub>6,5</sub> C	<sup>10</sup> B <sub>6,5</sub> C	<sup>10</sup> B <sub>6,5</sub> <sup>13</sup> C	<sup>11</sup> B <sub>10</sub> C	<sup>10</sup> B <sub>10</sub> C	<sup>10</sup> B <sub>10</sub> <sup>13</sup> C	Exp. symmetry type [1,9]	Calc. frequency [14,15]	Theor. symmetry type [14,15]	Structure movements [14,15]
1	267(1)	276.5(1)	268(1)	279.5(1)	277.1(2)	270.4(1)	280.5(1)	—	A <sub>1g</sub>	172	E <sub>g</sub>	Rotating icosahedron
2	319(1)	326.5(1)	319.2(1)	328.6(1)	327.6(2)	321(1)	330.4(1)	328(2)	A <sub>1g</sub>	335	E <sub>g</sub>	Rotating CBC chain and wagging icos. Rotating CBB chain and wagging icos.
3	414(2)	433(2)	412(2)	431(2)	427(3)	410(2)	425(2)	—	A <sub>1g</sub>	—	—	—
4	477(2)	489(2)	478(2)	494(3)	489(3)	480(3)	495(3)	—	E <sub>g</sub>	—	—	—
5	526(3)	552(3)	526(4)	550(3)	546(3)	524(3)	549(3)	—	(E <sub>g</sub> )	546/51	A <sub>1g</sub> /E <sub>g</sub>	No chain
6	566(3)	600(3)	570(3)	587(4)	585(3)	561(3)	584(3)	—	(E <sub>g</sub> )	589	A <sub>1g</sub>	—
7	646(3)	644(3)	641(4)	622(20)	—	633(3)	625(3)	—	E <sub>g</sub>	655	E <sub>g</sub>	—
8	720(2)	753(2)	715(2)	746(2)	744(3)	710(3)	736(3)	—	E <sub>g</sub>	692	E <sub>g</sub>	—
9	790(2)	822(1)	789(1)	815(3)	817(3)	786(4)	801(6)	—	A <sub>1g</sub>	828	A <sub>1g</sub>	—
10	862(2)	899(2)	854(2)	881(2)	887(2)	851(2)	890(2)	—	A <sub>1g</sub>	—	—	—
11	923(2)	960(2)	916(2)	954(2)	951(2)	912(2)	951(2)	—	A <sub>1g</sub>	964	A <sub>1g</sub>	Symmetrically stretching chain
12	1040(3)	1072(3)	1037(3)	1026(3)	1021(4)	1035(3)	1048(3)	—	A <sub>1g</sub>	1004	E <sub>g</sub>	Rotating chain and stretching icos.
13	1078(2)	1116(2)	1073(2)	1093(3)	1080(4)	1067(2)	1090(2)	1050(6)	A <sub>1g</sub>	1016	E <sub>g</sub>	Breathing B <sub>12</sub> icosahedron Breathing B <sub>11</sub> C icosahedron

Note. Symmetry type in brackets means uncertain assignment.

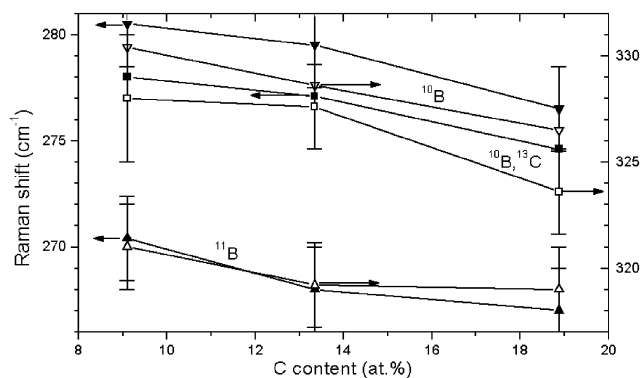


Fig. 2. Peaks 1 and 2. Raman shift of the chain librational modes vs. C content for <sup>10</sup>B, <sup>11</sup>B and <sup>10</sup>B-<sup>13</sup>C isotope-enriched boron carbide.

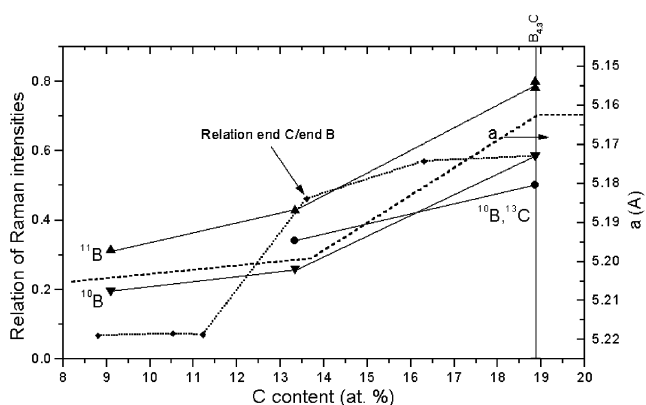


Fig. 3. Peaks 1 and 2. Relation of the peak intensities of the librational mode of the chains in boron carbide (peak 1, CBC chain; peak 2, CBB chain), compared with the relation between the chain end C atoms and the chain end B atoms (obtained from Refs. [3,7]) and with the lattice constant *a* (see Ref. [5] and references therein).

conventional Raman spectroscopy was proved to be largely unsuitable for boron carbide [10]. In the FT-Raman spectra there is no Raman peak reliably discernible in this frequency range.

The strongest Raman peaks (Nos. 1 and 2 in Table 1), close to 270 and 320 cm<sup>-1</sup> respectively, obviously represent the librational mode of the three-atomic chain in boron carbide as described by Shirai and Emura [14,15]. The two Raman frequencies (Fig. 2) are due to the predominant CBB and CBC chains. Since the frequency of this mode is essentially determined by the chain end atoms bonded to equatorial atoms of the icosahedra, in Fig. 3 the relation of the Raman intensities of both peaks is compared with the C/B relation of the chain end atom concentrations obtained from Refs. [8,11]. There is a rough correlation. However, it must be considered that the lattice parameters, that are expected to influence the Raman intensity, vary within the homogeneity range of boron carbide, and in Fig. 3 is seen that the lattice constant *a* is apparently

better correlated with the intensity relation between both Raman bands. The local lattice polarizability, which is responsible for the Raman intensity, strongly depends on the immediate surrounding of the active center and the related specific conditions. This is confirmed in Fig. 3 showing that the intensity relation clearly depends on the isotope mass.

The Raman frequencies increase with decreasing C content of the samples, which is related to an increasing lattice constant (see Fig. 3). This behavior is opposite to those found in most of the other Raman bands in the spectrum. The dilation of the lattice by an increasing lattice constant  $a$  is analogous to that induced by the reduction of an outer pressure. In the dilatated lattice, the librational mode is less impeded. Following Vast et al. [16], who investigated the pressure dependence of the Raman spectrum of  $\alpha$ -rhombohedral boron, we take this behavior as an evidence for librational modes.

A weak peak (No. 3) occurs between about 410 and 435  $\text{cm}^{-1}$ . As it is rather broad, one can assume that the icosahedra essentially contribute to this vibration. No concrete description of the actual movement of atoms in this mode has become known.

A further exception from the typical behavior is the Raman mode (No. 4) between about 476 and 495  $\text{cm}^{-1}$ : Its shift (Fig. 4) increases with the carbon content decreasing similar to that of the librational modes (Nos. 1 and 2). The exceptionally large spectral shift due to the transition from the  $^{12}\text{C}$  to the  $^{13}\text{C}$  isotope indicates that C atoms are considerably involved. Possibly, this band is the same as the unusually narrow band at 485  $\text{cm}^{-1}$  in conventional Raman spectra [1,14,17–19]. However, the strong dependence of its frequency on B and C isotopes suggests that it may be a phonon of the boron carbide structure and not of molecules adhered to the surface. On one hand, the comparison with the very sharp Raman peak in  $\alpha$ -rhombohedral boron at 525  $\text{cm}^{-1}$  and with the peaks 1 and 2 of boron carbide suggests some

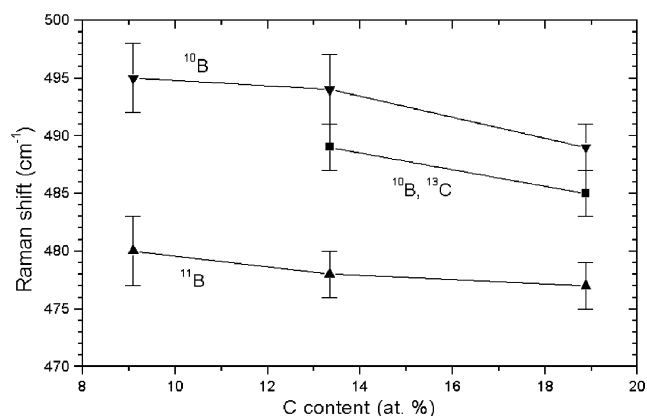


Fig. 4. Peak 4. Shift of the Raman mode between about 477 and 495  $\text{cm}^{-1}$  vs. carbon content.

similarity with librational modes according to Vast et al. [16]. Otherwise, the high frequency excludes the attribution to the missing librational mode of the icosahedron. Taking the strong influence of the carbon isotope on frequency into account, this band may be an additional mode of the chains and their end atoms. The strengths of this band decreasing with concentration of CBC chains [1,6,8], together with the large shift caused by the C isotopes, suggest to attribute the band to the CBC chains or to C atoms in the end positions of the chains.

If this assumption is correct, there should be a corresponding mode of CBB chains or, more generally, of B atoms in end positions of the chains. Because of the smaller mass, this is expected at higher frequencies. In the adjacent range between about 500 and 700  $\text{cm}^{-1}$  the spectra exhibit broad bands essentially consisting of three modes (Nos. 5–7). Multiple Lorentzian fits allow to determine the three Raman frequencies. However, because of the spectral noise the other parameters could not reliably be determined. The data of the Raman modes between about 525 and 552  $\text{cm}^{-1}$  (No. 5) are plotted in Fig. 5. The error margins are rather large. Nevertheless, the data for  $^{11}\text{B}$  exhibit the increase of the Raman frequency that is expected for a librational mode. The frequency decrease for  $^{10}\text{B}$  and  $^{10}\text{B}$ - $^{13}\text{C}$  enriched boron carbide is within the error margin and much smaller than for CBC. The shift due to the  $^{13}\text{C}$  isotope is larger than for icosahedral vibrations but smaller than for the CBC chain, corresponding to a lower carbon contribution. Raman data ( $^{10}\text{B}_{4,3}\text{C}$ , 551  $\text{cm}^{-1}$ ;  $^{\text{nat}}\text{B}_{4,3}\text{C}$ , 532  $\text{cm}^{-1}$  [9];  $\text{B}_{7,91}\text{C}$  537  $\text{cm}^{-1}$  [20]), obtained with very large numbers of scans, are available in the expected spectral range and confirm the dependence on the composition as it is expected for a librational mode.

Recently, the Albuquerque group has obtained some conventionally measured Raman spectra of boron

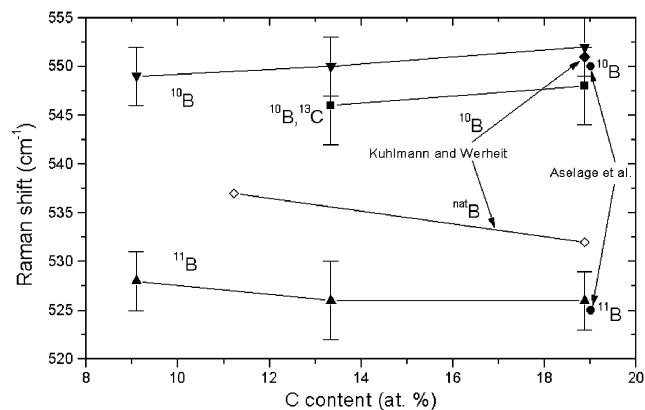


Fig. 5. Peak 5. Shift of the Raman mode between about 525 and 552  $\text{cm}^{-1}$  vs. C content. Additional results obtained by Kuhlmann and Werheit [9], Kuhlmann [19], and Aselage et al. [18] are included for comparison.

carbide that are similar to the FT-Raman spectra and hence more reliable than their previous spectra [19]. The narrow bands at about 525 and 550  $\text{cm}^{-1}$  taken from Fig. 5 in Ref. [19] agree with our results.

For the pair of modes 476–495 and 525–552 the tendency of librational modes seems at least largely proved. The strong influence of the C isotope on frequency shows that this vibration is due to a rather small atomic arrangement like the chain or the chain end atoms bonded to the equatorial atoms of the icosahedra.

The calculated Raman frequencies 546 and 551  $\text{cm}^{-1}$  [14,15] result from very complicated vibrations of the icosahedra without contributions of the chain. Accordingly, the arguments with respect to the breathing mode of the icosahedra (see below) hold here as well, and rather broad Raman bands are expected, which are hardly separated because of their close position in the spectrum. They can be possibly attributed to the two remaining modes 6 and 7 in the spectrum. As shown, this broad band can be well described by three Lorentzian bands (Nos. 5–7) with rather well-defined central frequencies (see Table 1). However, the damping is not sufficiently well determined for quantitative evaluations.

For the modes at about 550–600 (No. 6) and at about 620–650  $\text{cm}^{-1}$  (No. 7) with comparably large error margins there are no models of atomic movements available. The last one can possibly be attributed to the calculated mode at 655  $\text{cm}^{-1}$  [14,15].

Characteristic of the Raman mode between about 710 and 755  $\text{cm}^{-1}$  (No. 8) is the very small frequency shift by the  $^{13}\text{C}$  isotope. The band is too broad to be attributed to a chain vibration. Accordingly, it must be a vibration of the icosahedron, in which the carbon atoms are only weakly involved. Carbon atoms are preferably accommodated in the polar sites of the icosahedra [22]. Hence, this vibration must essentially involve equatorial atoms of the icosahedra only. Such a vibration is the  $\nu_1$  vibration of the free icosahedron described by Beckel and Vaughan [21] at 860.5  $\text{cm}^{-1}$  for the free icosahedron. However, this vibration of the free icosahedron has  $G_u$  symmetry and is not Raman active.

The band 785–820 (No. 9) is the shoulder of the distinctly stronger band at higher energies. Therefore, the data have been determined with less accuracy, and hence the small shift due to the carbon isotope seems not definitely proved in this case. The broadness of the band suggests that the icosahedra are essentially involved in this vibration. A description of the movement of atoms is not available. The stronger band between about 850 and 900  $\text{cm}^{-1}$  (No. 10) shows the typical frequency shifts depending on the isotope masses. Here again the essential contribution of the icosahedra is assumed. A description of the movement of atoms is not available.

A mode whose properties are expected to remarkably depend on the isotope enrichment is the symmetrical

stretching mode of the three-atomic chain with calculated frequency 964  $\text{cm}^{-1}$  [1,14,15]. The frequencies of the according modes in the Raman spectra ( $^{10}\text{B}$ , 951–960  $\text{cm}^{-1}$ ;  $^{11}\text{B}$ , 912–923  $\text{cm}^{-1}$ ) (No. 11) exhibit a comparably small frequency shift for the C isotopes suggesting that the central B atom of the three-atomic chains CBC and CBB essentially moves in this mode. Accordingly, the vibration is well defined and the damping is small.

Following Shirai and Emura [14,15], the frequency of the Raman-active breathing mode of the  $\text{B}_{12}$  icosahedron is 1078  $\text{cm}^{-1}$ . In the real structure of natural boron carbide, the icosahedron contains different boron isotopes  $^{10}\text{B}$  and  $^{11}\text{B}$ , which are statistically distributed according to their occurrence of 18.83% and 81.17%, respectively. Moreover, depending on the actual composition, there are  $\text{B}_{12}$  and  $\text{B}_{11}\text{C}$  icosahedra with different relations: 0:100% for  $\text{B}_{4.3}\text{C}$ , about 50:50% for  $\text{B}_8\text{C}$ , and about 65:35% for  $\text{B}_{11}\text{C}$  [8]. The C atoms are statistically accommodated preferably in the six polar sites of the icosahedra [22]. The  $\text{B}_{11}\text{C}$  icosahedron is remarkably distorted compared with the  $\text{B}_{12}$  icosahedron [22]. An additional distortion of the icosahedron is expected depending on the actual composition-dependent chain arrangement in the specific elementary cell (CBC, CBB,  $\text{B}\square\text{B}$ , CCC). Accordingly, the Raman band representing the breathing mode of the icosahedra is not expected to be well defined.

The results obtained for the broad Raman band occurring between about 1055 and 1105  $\text{cm}^{-1}$  (Nos. 12 and 13) fulfil these expectations. The central frequencies are highest for  $^{10}\text{B}$ , lowest for  $^{11}\text{B}$  and medium für  $^{10}\text{B}$ ,  $^{13}\text{C}$ . The damping (halfwidth/peak height) displayed in Fig. 6 is highest for  $\text{B}_{4.3}\text{C}$ , where only  $\text{B}_{11}\text{C}$  icosahedra occur, and decreases towards the boron-rich limit of the homogeneity range, where the concentration of  $\text{B}_{11}\text{C}$  icosahedra is lower. With respect to the isotope enrichment, the damping is lowest for  $^{11}\text{B}$  and  $^{12}\text{C}$ ,

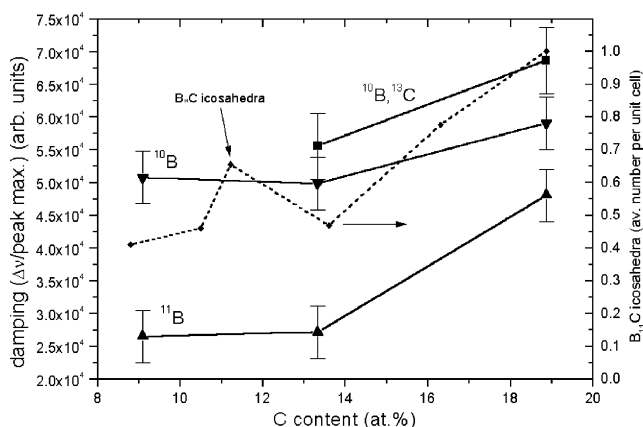


Fig. 6. Peaks 12 and 13. Damping (half-width/peak height) vs. carbon content. Concentration of  $\text{B}_{11}\text{C}$  icosahedra [1,11] for comparison.

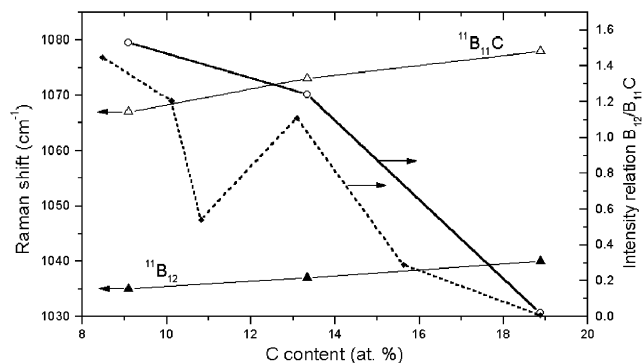


Fig. 7. Peaks 12 and 13. Raman shift of the peak components of  $^{11}\text{B}$  enriched boron carbide (open triangles,  $^{11}\text{B}_{11}\text{C}$ ; full triangles,  $^{11}\text{B}_{12}$ ). Open circles, intensity relation of the peak components (relation of the component areas of the Lorentzian fits), Full diamonds, relation  $\text{B}_{12}/\text{B}_{11}\text{C}$  from Refs. [1,11].

because their atom masses are close together, and accordingly highest for  $^{10}\text{B}$ ,  $^{13}\text{C}$ . Hence, this Raman band can be attributed to the breathing mode of the icosahedra in boron carbide.

The attempt to decompose this band by a multiple-Lorentzian fit is shown for  $^{11}\text{B}$  enriched boron carbide in Fig. 7. For  $\text{B}_{4.3}\text{C}$  a single Lorentzian fit is best and corresponds to the 100%  $\text{B}_{11}\text{C}$  icosahedra of this compound [1,7,11]. For lower carbon contents an additional band occurs at slightly lower frequencies, which can be attributed to the concentration of  $\text{B}_{12}$  icosahedra increasing with decreasing C content of boron carbide. Surprisingly, the Raman frequency of  $\text{B}_{11}\text{C}$  is about 3.6% higher than that of  $\text{B}_{12}$ , in spite of the 0.75% higher mass. Obviously, the bonding forces in  $\text{B}_{11}\text{C}$  are stronger than in  $\text{B}_{12}$ . The relation of the  $\text{B}_{12}/\text{B}_{11}\text{C}$  concentration derived from the Lorentzian fit agrees with that derived from the concentrations of icosahedra quite well, which were determined according to electronic requirements indeed by the structural defects, if CCC chains (<10% in the whole homogeneity range) are assumed to exist [1,11]. For our samples this is the case [11].

Otherwise, unlike with IR spectra [11], no direct evidence of CCC chains is found in the Raman spectra. The reason may be the comparably low concentration of these chains or the noise of the spectra. This holds for the  $\text{B}\square\text{B}$  arrangements as well.

## 6. Conclusion

Like the recently presented spectra of IR active phonons the FT Raman spectra of  $^{10}\text{B}$ ,  $^{11}\text{B}$ , and  $^{13}\text{C}$  isotope-enriched boron carbide of the compositions  $\text{B}_{4.3}\text{C}$ ,  $\text{B}_{6.5}\text{C}$ , and  $\text{B}_{10}\text{C}$  have been analyzed according to the description of the movement of atoms determined by Shirai and Emura. The spectra are evaluated and discussed with respect to the composition-dependent concentrations of structural elements like  $\text{B}_{12}$  and  $\text{B}_{11}\text{C}$  icosahedra, CBC, CBB, and CCC chains within the homogeneity range. Most of the Raman bands were attributed to specific lattice vibrations.

## References

- [1] H. Werheit, Boron compounds, in: O. Madelung, U. Rössler, M. Schulz (Eds.), Landolt-Börnstein Numerical Data and Functional Relationships in Science and Technology III, Vol. 41D, Springer, Berlin, 2000, pp. 1–491.
- [2] D.R. Armstrong, J. Bolland, P.G. Perkins, G. Will, A. Kirfel, Acta Crystallogr. Sect. B. 39 (1982) 324.
- [3] D.M. Bylander, L. Kleinman, S. Lee, Phys. Rev. B 42 (1990) 1394.
- [4] D.M. Bylander, L. Kleinman, Phys. Rev. B 43 (1991) 1487.
- [5] L. Kleinman, AIP Conference Proceedings Vol. 231, New York, 1991, p. 13.
- [6] U. Kuhlmann, H. Werheit, Solid State Comm. 83 (1992) 849.
- [7] R. Schmechel, H. Werheit, J. Phys.: Condens. Matter 11 (1999) 6803.
- [8] R. Schmechel, H. Werheit, J. Solid State Chem. 154 (2000) 61.
- [9] U. Kuhlmann, H. Werheit, Phys. Stat. Sol. (b) 175 (1993) 85.
- [10] H. Werheit, R. Schmechel, U. Kuhlmann, T.U. Kampen, W. Mönch, A. Rau, J. Alloys Compd. 291 (1999) 28.
- [11] H. Werheit, T. Au, R. Schmechel, S.O. Shalamberidze, G.I. Kalandadze, A.M. Eristavi, J. Solid State Chem. 154 (2000) 79.
- [12] H. Binnenbruck, H. Werheit, Z. Naturforsch. 34a (1979) 787.
- [13] D. Gosset, M. Colin, J. Nucl. Mater. 183 (1991) 161.
- [14] K. Shirai, S. Emura, J. Phys.: Condens. Matter 8 (1996) 10919.
- [15] K. Shirai, S. Emura, J. Solid State Chem. 133 (1997) 93.
- [16] N. Vast, S. Baroni, G. Zerah, J.M. Besson, A. Olian, M. Grimsditch, J.C. Chervin, Phys. Rev. Lett. 78 (1997) 693.
- [17] D.R. Tallant, T.L. Aselage, D. Emin, AIP Conference Proceedings No. 231, New York, 1991, p. 301.
- [18] D.R. Tallant, T.L. Aselage, A.N. Campbell, D. Emin, Phys. Rev. B 40 (1989) 5649.
- [19] T.L. Aselage, D.R. Tallant, D. Emin, Phys. Rev. B 56 (1997) 3122.
- [20] U. Kuhlmann, Thesis, University of Duisburg, 1994.
- [21] C.L. Beckel, J.P. Vaughan, Vibration of the regular boron icosahedra, in boron-rich solids, AIP Conference Proceedings Vol. 140, New York, 1986, p. 305.
- [22] H. Werheit, U. Kuhlmann, T. Lundström, J. Alloys Compd. 204 (1994) 197.