

PHASE TRANSITION AND ISOTOPE-INDUCED PHONON SOFTENING IN ^{nat}B_{4.3}C BORON CARBIDE AT MODERATE TEMPERATURES

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ABSTRACT

A recent theoretical structure model of carbon-rich boron carbide (Yao et al.) assumes a continuous phase transition accompanied by loss of inversion symmetry near 790K and a first-order transition at 717 K, breaking the 3-fold rotational symmetry. We checked this model by experiment, performing DSC measurements on single crystal B_{4.3}C. A clear anomaly at 712 K, close to the theoretically predicted phase transition, has exothermic character, opposite to the endothermic one predicted. Phonon splitting between 700 and 800 K indicates structural changes. The IR-active vibration of the bending mode of the C-B-C chains between 100 and 800 K shows additional anomalies between 400 and 500 K: the distribution of isotopes on the B(3) site changes drastically, accompanied by a considerable lattice softening.

INTRODUCTION

The outstanding characteristics of boron carbide led to various applications as abrasive materials, high temperature industrial ceramics, lightweight armor, tough coatings and reinforcement of other materials, control rods in nuclear reactors or radioactive shielding. Unique electronic properties make it a promising candidate for direct thermoelectric energy conversion (for recent reviews see Refs.^{1,2,3}). First synthesis of boron carbide was achieved in the 19th century^{4,5}, an early review on industrial material was given by Lipp⁶, an actual review on properties has been published by Domnich et al.⁷, a critical review on the electronic properties was reported by Werheit⁸.

The homogeneity range, extending from B_{4.3}C at the carbon-rich to B₋₁₁C at the boron-rich limit, is characterized by a variation of the very complex structure. A well-defined unit cell that could represent the entire structure, is missing. Therefore, methods commonly used to determine crystalline structures like X-ray and neutron diffraction as well as NMR failed in this case. The structure is composed of elementary cells, which are similar in shape but differently composed. The deviations from the frequently used idealized structure models are so strong that these are unsuitable for estimating actual properties reliably. Neglecting this fact led to fundamental discrepancies between theory and experiment. For details, see for example Refs.^{9,3}.

The rhombohedral elementary cell consists of a 12-atom icosahedron at the vertex and a mostly three-atomic chain on the main diagonal. Specifically, there are B₁₂ and B₁₁C icosahedra, CBC and CBB chains and B□B (□, vacancy) arrangements. Their shares, depending on the actual chemical composition, were determined by phonon spectroscopy on isotopically highly enriched boron carbides by Werheit and Shalamberidze⁹. In the case of B_{4.3}C, there are 100 % B₁₁C

icosahedra, ~ 89% C-B-C chains, less than ~2% C-B-B chains, ~ 9 % chainless cells. Numerous fundamental questions with respect to structural details are still open.

Lezhava et al.¹⁰ reported on internal friction measurements in boron carbide. The chemical composition of their samples is undefined, but probably close to the carbon-rich limit of the homogeneity range B_{4.3}C. Using electron microscopy, the authors observed defects in the form of high concentrations of twins in the crystallites of their samples. The temperatures of internal friction maxima, listed in Table I, were obtained on arc-melted and subsequently annealed samples; thus a general validity of the obtained results is assumed. A convincing explanation of the relaxation processes which are responsible for the internal friction maxima, is missing so far. The activation energies (see Table I) suggest atomic site exchange processes as the reason.

Table I. Internal friction maxima of boron carbide (arc-melted and annealed in vacuum for 10 h at 1000 K) obtained at 1.5 Hz, (Lezhava et al. ¹⁰)				
Data from original paper ¹⁰		New fit with program ORIGIN		
T (K)	Activation energy (eV)	T(K)	strength	Half-width ΔT(K)
115	0.15	118	0.065	16
180	0.2	175	0.048	30
200	0.35	200	0,065	22
460	0.9	472	1,139	55
620	Suppressed by annealing (1 h at 770 K)	619	1,051	60
750	2.1	756	1.138	73

Recently, Yao et al.¹¹ described theoretically an idealized high-temperature boron carbide phase similar to that observed experimentally at ambient conditions. Towards lower temperatures, the inversion symmetry of this phase is lost near 790K via a continuous phase transition. Finally, below 717 K, the 3-fold rotational symmetry is broken via a first order transition, yielding monoclinic symmetry. This phase transition is caused by the site exchange of carbon atoms within the icosahedra.

In order to check this theoretical model by experiment, we measured the temperature-dependent specific heat of a high-quality B_{4.3}C single crystal between ~265 and ~770 K. Moreover, we analyzed the temperature-dependent behavior of the phonon near 420 cm⁻¹, representing essentially the bending vibration of the central B atom in the C-B-C chain of boron carbide perpendicular to the crystallographic c-axis.

EXPERIMENTAL

Specific Heat

We utilized high-quality single-crystalline B_{4.3}C boron carbide prepared by Tanaka and Leithe-Jasper^{12,13}). The specific heat has been examined in the temperature range between ~265 and ~770 K using power compensated differential scanning calorimetry (DSC, Perkin-Elmer DSC 8500). The result displayed in Figure 1 was obtained at increasing temperatures by the following method. First, an empty aluminum crucible with lid was measured, then a disk of corundum was inserted into the crucible and measured with the same program. Finally, a piece of boron carbide with a flat face was employed. The evaluation of the three measurements was done by the supplied procedure included in the software package of the equipment.

A clear effect occurs between 620 K and 770 K with maximum at 712 K. The half-width is 82 K. The fluctuations of the specific heat at lower temperatures might be due to experimental uncertainties.

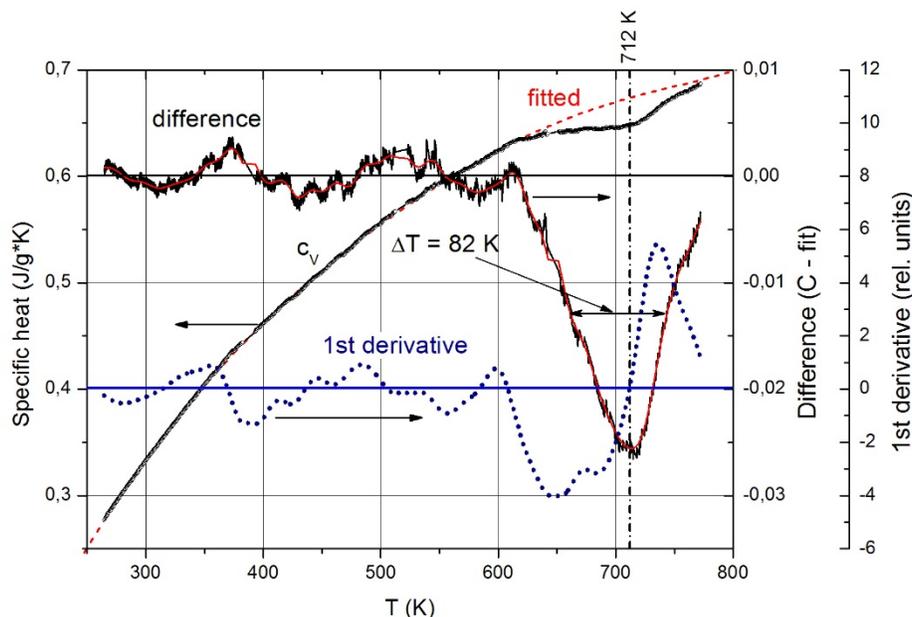


Figure 1. Specific heat of $B_{4.3}C$ boron carbide vs. T . Open circles, measured; red dashed line, polynomial fit to the results at lower T ; black line, difference between measured data and fit; dotted line, 1st derivative.

Phonon (C-B-C Bending Mode)

Phonon spectra are sensitive tools for verifying structural changes. In the case of $^{nat}B_{4.3}C$ boron carbide the phonon near 400 cm^{-1} is the only one so far, which has been measured up to 800 K (see Werheit and Gerlach¹⁴). As outlined by Werheit and Shalamberidze⁹, considering theoretical calculations by Shirai et al^{15,16} and Vast et al.^{17,18}, this phonon represents preferably the bending vibration of the C-B-C chains. It is essentially determined by the central boron atom in the three-atomic chain B(3) vibrating perpendicular to the chain axis^{19,20}. The end atoms of the chain hardly contribute to this vibration, as their position is fixed by their strong bonds to equatorial atoms of the three neighboring icosahedra. This phonon exhibits a strong isotope effect (Werheit et al.^{21,22}).

Applying the Kramers-Kronig transformation on the reflectivity spectra in the range of this phonon¹⁴, the absorption spectra in Figure 2 were obtained. They are only slightly affected by the superimposed tail of the heavily damped plasma edge of the free carriers¹⁴. The reduction of the oscillator strength with temperature increasing might be essentially due to shielding effects of the free carriers¹⁴.

The phonon spectra were evaluated using the program ORIGIN, after having been separated from the absorption background by subtracting a suitably adapted linear baseline. Up to 700 K two components each were sufficient to fit the absorption peaks. As the relation of the frequencies is close to $(10/11)^{1/2}$ their attribution to ^{10}B and ^{11}B isotopes is obvious. Between 700 and 800 K both components split into two parts each.

The shares of isotopes, obtained from the oscillator strengths of the components, are shown in Figure 4. For comparison, the corresponding resonance frequencies of isotopically highly enriched

$B_{4,3}C$ are marked. The deviations of the ^{10}B and ^{11}B resonance frequencies in monocrystalline $^{nat}B_{4,3}C$ indicate that the isotope distribution on the central B(3) site of the chain depends sensitively on the actual feature of the structure.

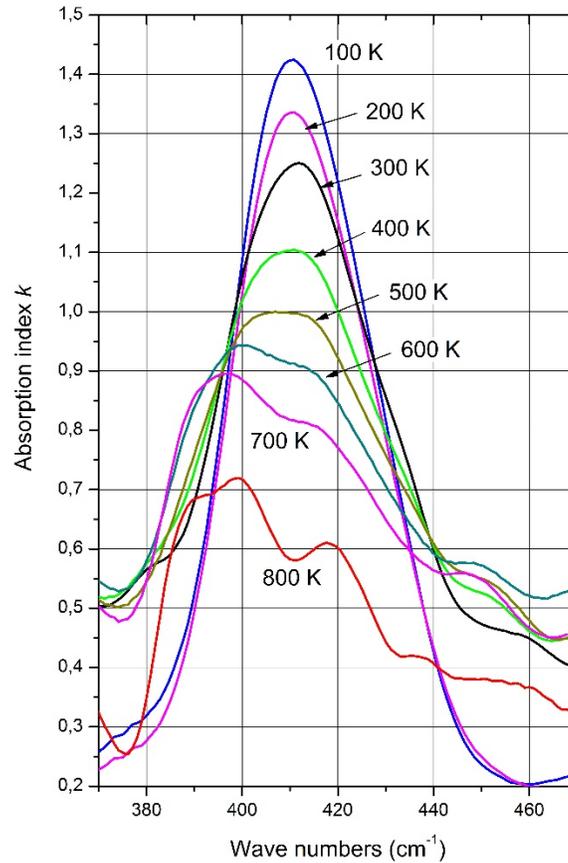


Figure 2. Phonon absorption of $B_{4,3}C$ boron carbide in the spectral range of the bending mode of the C-B-C chain between 100 and 800 K. The spectra have been vertically shifted for reducing overlapping.

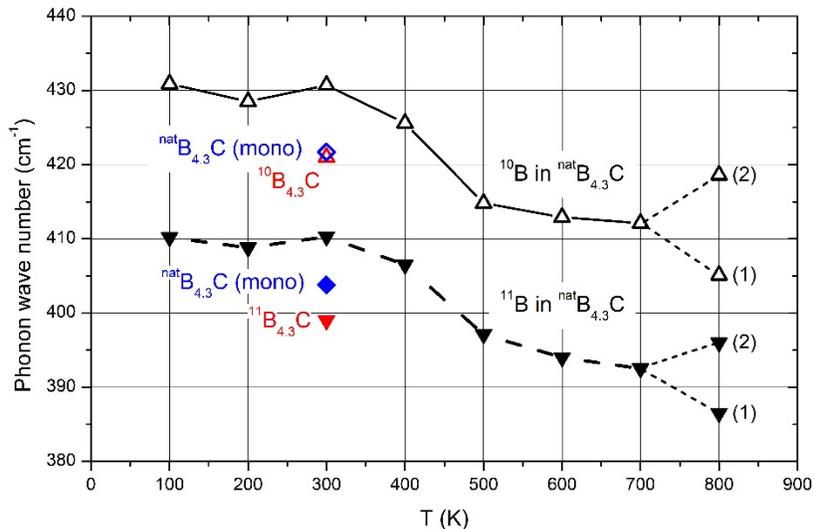


Figure 3. Frequencies of the ^{10}B and ^{11}B components of the phonon near 420 cm^{-1} in boron carbide vs. T . The frequencies at ambient conditions obtained on isotopically nearly pure samples and a high-quality single crystal are shown for comparison.

At temperatures below $\sim 400\text{ K}$, the concentrations of ^{10}B and ^{11}B isotopes on the B(3) site in the $\text{B}_{4.3}\text{C}$ sample investigated correspond satisfactorily to the contents in natB . However, between 400 and 500 K a drastic change takes place: the occupancy of ^{10}B isotopes increases considerably, exceeding the value statistically expected from natB by far. At higher temperatures the shares of the isotopes on the B(3) site approach each other and become nearly equal at 800 K , still far away from their shares in natB .

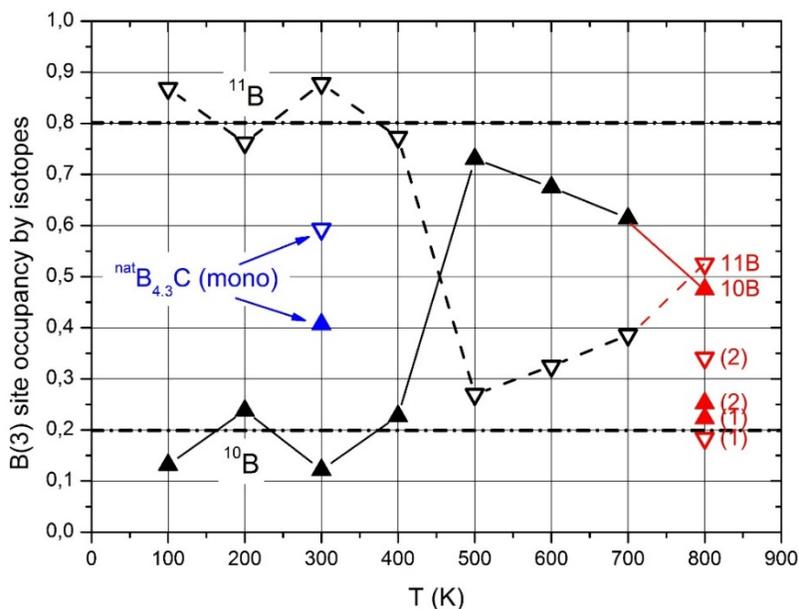


Figure 4. Shares of ^{10}B and ^{11}B isotopes on the central site B(3) of the C-B-C chain in $\text{B}_{4.3}\text{C}$ boron carbide depending on temperature. The data obtained on a high-quality single crystal at 300 K are shown for comparison. Dash-dotted lines, contents of ^{10}B and ^{11}B isotopes in natB .

It is noteworthy that the optical spectra are largely obtained in thermal equilibrium. This holds for the internal friction measurements¹⁰ mentioned above as well. Both experimental methods require a certain period for adjusting the equipment at the specific measuring temperature each. This procedure is essentially different from the specific heat measurement, where the temperature varies continuously. Therefore, depending on the relaxation time of the specific process, the indicated characteristic temperature can depend more or less significantly on the method applied.

DISCUSSION

Partially in agreement with the internal friction measurements by Lezhava et al.¹⁰, our temperature-dependent specific heat measurements and the optical absorption in the spectral range of a specific phonon as well indicate structural changes and phase transitions respectively in boron carbide at moderate temperatures. According to the restricted strength of the effects it appears reasonable to attribute them to site exchange processes of atoms in the structure elements. Regarding the specific heat this assumption is checked in Figure 4. Within the given accuracy, a rough estimation of the activation energy yields ~ 0.65 to ~ 0.96 eV, thus supporting this assumption.

The temperature dependent specific heat of boron carbide indicates a phase transition at 712 K in satisfactory correlation with the internal friction maximum at ~ 750 K. The frequencies of ^{10}B and ^{11}B isotopes in the bending mode of the B(3) site split significantly between 700 and 800 K, thus confirming a certain change in the structure of boron carbide in this temperature region. Indeed, according to the weak effect in the specific heat, this might be limited to a small change within structural components only.

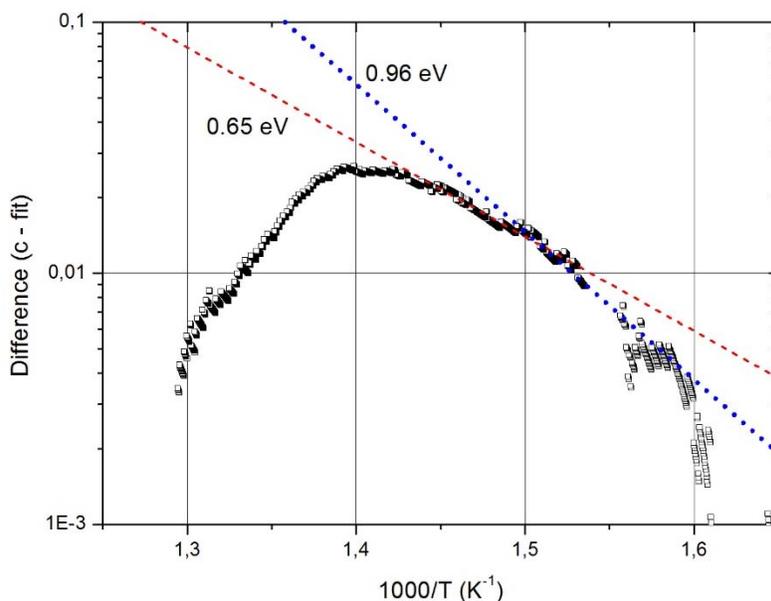


Figure 4. Anomaly of the specific heat of $\text{B}_{4.3}\text{C}$ boron carbide vs. reciprocal T. Red dashed line and blue dotted line indicate activation energies of 0.65 eV and 0.96 eV respectively.

This experimentally proved phase transition at 717 K. is close to 712 K, where Yao et al.¹¹ expect a phase transition in their theoretical structure model. However, the latter assumes endothermic behavior in agreement with the normally expected situation, that the energy of a high-T state exceeds that of a low-T state. In contrast, the experimentally determined specific heat indicates

exothermic character. Hence, both results are not compatible with one another. Moreover, the phonon spectrum rather contradicts the theoretical model, which assumes the high-T structure of boron carbide to correspond with that one experimentally determined at ambient conditions. The phonon splitting between 700 and 800 K towards higher temperatures suggests that the high-T phase of boron carbide deviates from the low-T phase.

A further peculiarity in the boron carbide structure is the drastic change of the occupancy of the B(3) site by the boron isotopes between 400 and 500 K obtained from the phonon near 420 cm⁻¹. This is correlated with the strongest maximum of internal friction¹⁰ (see Table I) thus suggesting that this internal friction maximum is evoked by the rearranging of boron isotopes by diffusion and site hopping processes respectively. It is necessary to note that the preference of ¹⁰B isotopes in the B(3) of the three-atomic chain at temperatures exceeding 500 K implies a preference of ¹¹B isotopes in the B(1) and B(2) sites of the icosahedra. Apparently, the specific heat is not measurably affected by this process, at least not within the resolution of our measurement. The rearrangement of isotopes is accompanied by a considerable lattice softening. According to $\omega = \sqrt{\gamma/\mu}$ (γ , force parameter; μ , reduced mass), the frequency shift in Figure 3 yields a reduction of the force parameter γ by $\sim 7\%$.

Boron carbide is a further example for non-random distribution of boron isotopes in boron-rich solids deviating considerably from the statistical distribution expected from ^{nat}B (80.1% ¹¹B and 19.9% ¹⁰B). This has already been generally concluded from the phonon spectra of boron carbide at room temperature⁹. The present results show that the isotope distribution depends sensitively on structural features. Moreover, the occupancies vary considerably depending on temperature.

Other examples are β -rhombohedral boron, whose intra-icosahedral B-B bonds are preferably based on ¹⁰B–¹⁰B pairs. In contrast, the inter-icosahedral B-B bonds suggest odd isotopes to be preferred²³. Also in LaB₆ it is evident that the isotopes are not randomly distributed in the structure. In this case, associations of ¹⁰B isotopes are favored compared with those of ¹¹B isotopes²⁴.

Different isotopes of the same element on the same site within the structure have the same electronic configuration and are distinguished by not more than a single neutron in the atomic nucleus accompanied by a small difference in zero point energy. Therefore the considerable deviations from random distributions are noteworthy. Further investigations are required for better understanding the mechanisms of site exchanges by isotopes.

In the case of boron carbide, series of consecutive cycles of specific heat measurements with increasing and decreasing temperatures are required for better understanding the relaxation processes involved; for example, are they reversible or do they establish a new more stable structure? Complete phonon spectra measured up to high temperatures and accordingly evaluated might give better insight in the structure of boron carbide and its variations depending on temperature.

CONCLUSION

The exothermic phase transition in B_{4.3}C boron carbide, proved by DSC measurements at 712 K, is probably related to the internal friction maximum at 750 K. The bending vibration of the central B(3) atom in the C-B-C chain splits at this temperature, thus indicating a structural change in boron carbide. However, this phase transition, which is essentially related to the three-atomic chain, is incompatible with the theoretically predicted phase transition at 717 K, which is preferably based on a reordering of the C atom in the B₁₁C icosahedron.

Between 400 and 500 K, the isotope distribution on the B(3) site changes significantly from the nearly random distribution at lower temperatures to a ^{10}B preference. This site exchange of isotopes, which is accompanied by a distinct softening of the structure, explains the strong internal friction maximum at ~ 470 K.

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