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IR Active Phonon Spectra of B–C–Al Compounds with Boron Carbide Structure

R. Schmechel, H. Werheit, and K. Robberding

Solid State Physics Laboratory, Gerhard Mercator University Duisburg, D-47048 Duisburg, Germany

and

T. Lundström and H. Bolmgren

Institute of Chemistry, Uppsala University, S 75121 Uppsala, Sweden

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The IR spectra of boron carbide containing up to about 1.5 at.% aluminum atoms are determined between 80 and 5000 cm^{-1} for temperatures between 70 and 450 K. While the essential features of the boron carbide phonon spectrum remain largely unchanged, there are several new low energy absorption bands at about 190 and 290 cm^{-1} obviously induced by the aluminum atoms. The band at 190 cm^{-1} is attributed to the bending mode of Al$_2$ chains, which are assumed to be formed in otherwise chain-free unit cells of boron-rich boron carbide. The dynamical conductivity of aluminum-doped boron carbide decreases with increasing aluminum content, while the Seebeck coefficient showing p-type behavior for all compounds increases. This makes evident that doping with aluminum atoms changes the electronic properties of boron carbide. © 1997 Academic Press

INTRODUCTION

p-Type boron carbide is the boron-rich solid with the hitherto most favorable electronic properties for high-efficiency direct thermoelectric energy conversion (1). However, its technical realization needs an n-type counterpart with otherwise similar properties. n-Type boron-rich solids are for example solid solutions of Fe and V atoms in β-rhombohedral boron with interstitially accommodated metal atoms (2, 3). Besides, a further improvement of the electronic properties of boron carbide is desired. One way to do this could be the formation of ternary compounds with boron carbide structure.

In the present paper the IR spectra of ternary B–C–Al compounds with boron carbide structure are determined. The IR phonon spectra allow conclusions on the crystalline structure. The FIR spectra yield some qualitative information on the dynamical conductivity. Besides, the Seebeck coefficient is roughly measured to check the possibility of modifying the electronic properties of boron carbide.

SAMPLE MATERIAL AND PREPARATION

The samples (see Table 1) were prepared by arc-melting pellets consisting of mixtures of B$_4$C powders (from Cerac, Inc., Milwaukee, WI) and freshly prepared filings of aluminum (from Vigelands Bruk, Norway). The hexagonal unit cell parameters of undoped B$_4$C were determined to be $a = 6.6031(3)$ Å and $c = 12.0785(10)$ Å. The purity was 99.5% for the boron carbide (Ca, Si, and Fe as main impurities) and 99.997% for the aluminum. The solidified samples were equilibrated at 1260°C for about 120 h and finally quenched in oil. Small amounts of aluminum were lost during the melting process. This was checked and corrected for by weighting the samples prior to and after melting.

The carbon content was determined by difference; i.e., it was assumed that the concentration of B + C + Al was 100% (impurities were not considered). B and Al were determined using ICP-AES (inductively coupled plasma atomic emission spectrometry). The phase indentification was performed by determining cell dimensions from Guinier–Hägg recordings. Also intensities were measured to get a rough estimation on the relative concentration of the different phases.

The aluminum content of the boron carbide phase was estimated by using the intensities of the strongest X-ray lines multiplied by weight factors according to the Al content in the compositions B$_4$C and Al$_8$B$_4$C$_7$. For the unknown phases indicated by weak lines the average weight factor of both known phases was used.

EXPERIMENTAL SETUPS

Reflectivity spectra of the samples were obtained with a Fourier transform IR spectrometer in the spectral range

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TABLE 1
B–C–Al Samples Investigated, Ordered According to the Al Content in the Boron Carbide Phase

Sample no.	Composition as analyzed	Al content (at.%)		Phases present		
		Total	**“B_4C”**	“B_4C”	$Al_8B_4C_7$	Weak
G 2801	$(B_{4.3}C)_{99}Al_1$	0.2	**0.2**	1000		
G 2901	$(B_4C)_{96}Al_4$	0.75	**0.57**	1000	60	90
G 3401	$(B_{3.8}C)_{96}Al_4$	0.94	**0.83**	1000	40	20
G 3001	$(B_{4.2}C)_{94}Al_6$	1.19	**0.99**	1000	50	40
G 3201	$(B_{4.2}C)_{92}Al_8$	1.68	**1.12**	1000	100	140
G 3101	$(B_{4.2}C)_{93}Al_7$	1.95	**1.19**	1000	130	180
G 2101	$(B_{5.6}C)_{91}Al_9$	1.43	**1.43**	1000 + 720		

Note “B_4C” denotes phases indexed with a boron carbide hexagonal cell. In G2101 there are thus two such phases with different unit cell dimensions.The notation “weak” means that there are some weak lines that do not belong to any of the phases indicated. The concentration of the different phases is roughly indicated by the relative intensities of the strongest lines.

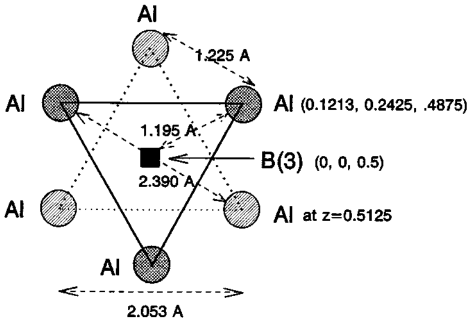

FIG. 1. Al sites in the boron carbide unit cell together with the position of the central B(3) site.

between 80 and 5000 cm^{-1} with a resolution of 2 cm^{-1}. By use of the Kramers–Kronig relation (KKR) the absorption spectra were calculated. Toward high frequencies the prerequisite for KKR was fulfilled, because the measurements were extended to the approximately dispersion-free range between absorption edge and lattice vibrations. Toward low frequencies there is no dispersion-free range in boron carbide because of the dynamical conductivity. However, using a suitable extrapolation, which takes this behavior into account, the prerequisite for the allowable application of the KKR could be realized.

The Seebeck coefficient was estimated by a hot-spot method using a temperature-stabilized soldering iron. The temperatures of the hot spot were varied between 100 and 300°C. In the case of pure boron carbide this method has been proven to yield reliable results.

STRUCTURE

The only structure investigation on ternary compounds of boron, carbon, and aluminum with boron carbide structure has been performed by Neidhard *et al.* (4). They attribute the aluminum atoms to the position Al(1) (Z(1) in Neidhard's notation) with the hexagonal coordinates $x = 0.4546$, $y = -0.4546$, $z = 0.1542$. In the idealized structure of boron carbide this is an interstitial site. It is convenient to consider for a moment the Al atoms (equivalents of the Al atom at (0.4546, 0.4546, 0.1542)) situated outside the B(3) atom at (0, 0, 0.5) (B(*m*) in Neidhard's notation). There are six such sites possible at (0.1213, 0.2425, 0.4875) and two equivalents in the *z* plane 0.5125 (Fig. 1). The interatomic distances B(3)–6Al(1) and Al(1)–2Al(1) are 1.195 and 1.221 Å, respectively. Accordingly Al(1) and B(3) cannot simultaneously occupy these positions in the same unit cell, as already stated by Neidhard *et al.* (4). However, this is no problem since they found the occupancy to be only 5.7% for Al(1) and 61% for B(3). When an Al atom occupies the Al(1) position it is bonded to 9 atoms, namely 1C at 1.76 Å, 1B(1) at 1.96 Å, 2 B(2) at 1.98 Å, 1C at 2.00 Å, 2B(1) at 2.15 Å, and 2B(2) at 2.20 Å. However, such a hole would also be available if the three-atomic chain is missing altogether. Furthermore this possiblity is preferable as an alternative, since in such a case we would not have the very short Al(1)–C distances at 1.76 and 2.00 Å, respectively. In summary the B(3) atoms have no Al neighbors in the same unit cell. However, contrary to Neidhard *et al.*, we have come to the conclusion that, when no B(3) occurs in the unit cell, one or two Al atoms can be accommodated in the strongly compressed 6 Al(1) octahedron surrounding the empty B(3) position (Fig. 1). From the viewpoint of these structural considerations the complete absence of three-atomic chains combined in principle with one or two Al atoms seems to be probable structure models for the accommodation of Al atoms in the boron carbide structure. The existance of two-atomic chains (Al_2) like those known, e.g., for $B_{12}O_2$, $B_{12}P_2$, and $B_{12}As_2$ (5) cannot be excluded. However, in contrast to these compounds the Al_2 chain would be arranged almost perpendicular to the *c* axis (only 7.2° inclination)

With respect to these considerations on the structure of the investigated B–C–Al compounds the structure of solid solutions of silicon in boron carbide seems to be important. Based on phonon spectroscopy (6) it was proved that the concentration of silicon dissolved in boron carbide could be quantitatively explained by the attribution of Si_2 chains to the otherwise chainfree unit cells in pure boron-rich boron carbide. This supports the assumption that, contrary to the argumentation by Neidhard *et al.*, in the investigated samples the aluminum atoms could exist in the form of two-atomic chains as well. Moreover, till now in no case had a structure like that proposed by Neidhard *et al.* been found with one foreign atom asymmetrically accommodated relating to the center of the unit cell (5). In the same way a two-atomic chain arranged almost perpendicular to the *c* axis would be unique for the α-rhombohedral boron structure group. Therefore a reexamination of the structure seems useful.

EXPERIMENTAL RESULTS

a. Phonon Spectra

The IR spectra were measured at 80, 300, and 400 K each. The reflectivity and absorption spectra of the different samples at 300 K are shown as examples in Fig. 2. The phonon frequencies of pure boron carbide remain largely unchanged in the Al-doped materials. As typical for phonons the resonance frequencies decrease slightly with increasing temperature while the damping constants increase.

In some of the spectra there are weak absorption bands between 300 and 700 cm^{-1} (315, 358, 505, 519, 570, 655, and 685 cm^{-1}). They occur only in samples containing phases additional to the boron carbide phase, however not, e.g., in the spectrum of sample G2101 having the highest Al content but beeing free from additional phases. Hence it is obvious that these bands belong to phonons of the additional phases, and therefore they will not be further considered.

Two additional absorption bands obviously induced by Al atoms in the boron carbide phase are found at lower frequencies (at about 190 and 293 cm^{-1}). Their resonance frequencies decrease slightly with increasing temperature like those of the boron carbide phonons.

The oscillator strengths of all IR absorption processes are plotted in Fig. 3 versus the Al content. For the 190- and 293-cm^{-1} absorption bands the temperature dependences of the oscillator strengths and damping constants are shown in detail in Fig. 4. To get these data the absorption bands were at first separated from the measured total absorption by subtracting the background obtained by interpolation between ranges outside the specific band.

b. Seebeck Coefficient

Figure 5 shows the Seebeck coefficient of the B–C–Al compounds depending on the Al content of the prevailing boron carbide phase. Each point is the average of five independently measured values. Within the accuracy of measurement the Seebeck coefficient increases linearly with the Al content.

DISCUSSION

The IR spectra of the investigated B–C–Al compounds exhibit all the phonons, which are characteristic for boron carbide. This confirms the main scheme of the structure of these ternary compounds as proposed by Neidhard *et al.* (4).

These authors assume that one Al atom maximum is accommodated per unit cell, which atom adopts the bonding function of the central atom of the three-atomic chain B(3). Ignoring for a rough estimation the shift of the Al atom in the Al(1) site from the B(3) position, one expects according to

$$\frac{\omega_{\mathrm{Al}}}{\omega_{\mathrm{B}}} = \sqrt{\frac{m_{\mathrm{B}}}{m_{\mathrm{Al}}}} = \sqrt{\frac{10.82}{26.98}} = 0.63$$

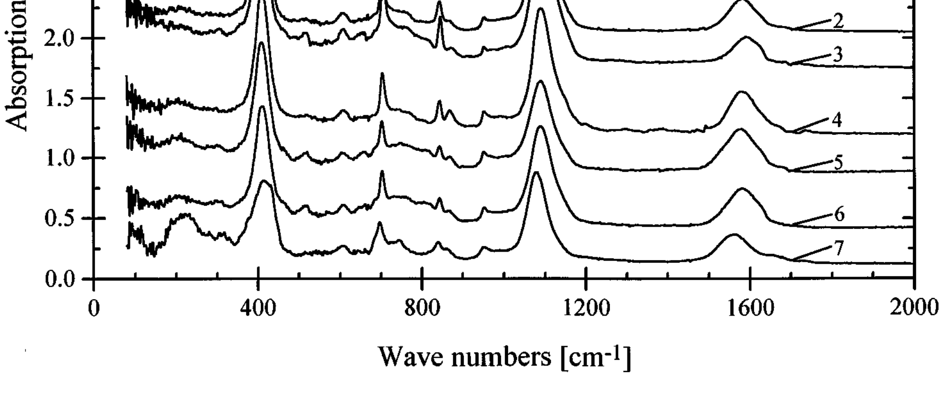

FIG. 2. Absorption spectra of the B–C–Al compounds with boron carbide structure at 300 K.

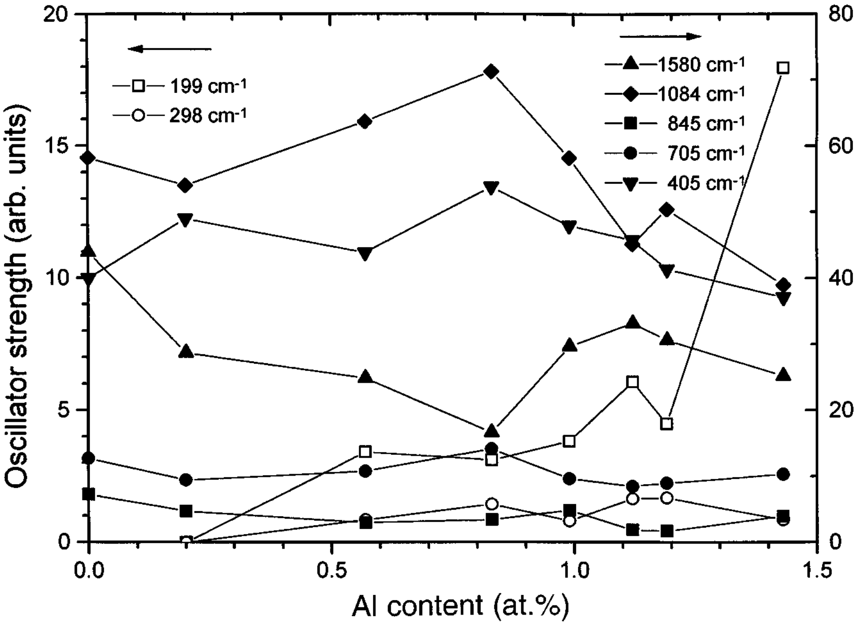

FIG. 3. Oscillator strengths of the phonons of the B–C–Al compounds with boron carbide structure versus Al content.

the resonance frequency of the stretching mode of the three-atomic chain in pure boron carbide to be shifted from 1580 cm^{-1} to about 1000 cm^{-1} in Al-doped material. However, the weak phonon at that frequency is much stronger in the spectrum of undoped boron carbide, and already for this reason it cannot be attributed to three-atomic chains with central (or slightly shifted) Al atoms. Moreover, based on the assumption of Neidhard *et al.* for an Al content of about 1.5 at.%, in about 23% of the unit cells CBC or CBB chains would be replaced by corresponding chains with quasi-central Al atoms, and the oscillator strength of the related phonon would be correspondingly high. But obviously there is no phonon in the spectrum, which could be taken as a confirmation of this assumption of Neidhard *et al.* that single Al atoms substitute for the central boron atoms B(3) in the chains.

The decreasing oscillator strength of the stretching mode of the three-atomic chain (1580 cm^{-1}) (Fig. 2) in Al-doped

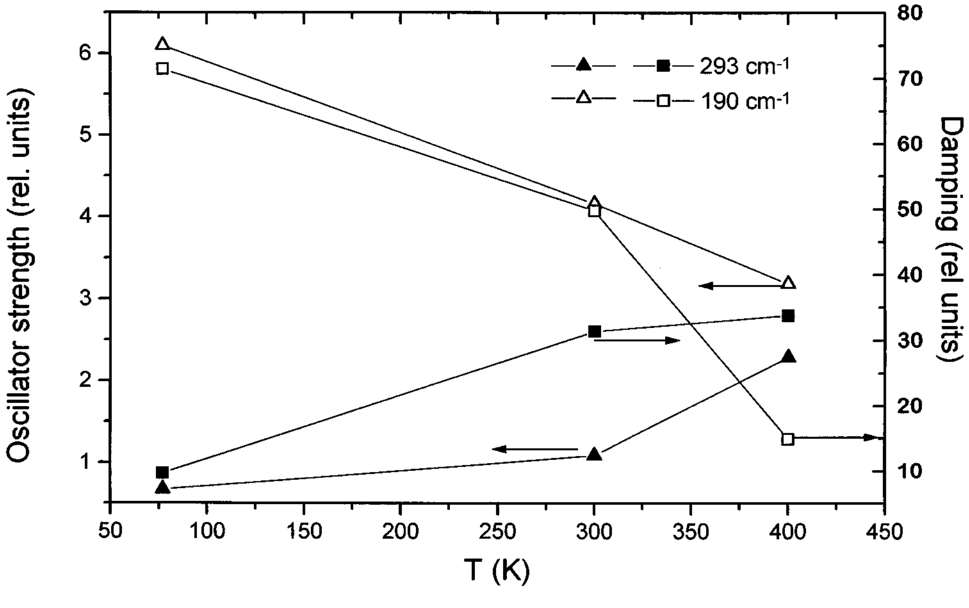

FIG. 4. Oscillator strength and damping of the 190- and 293-cm^{-1} phonons.

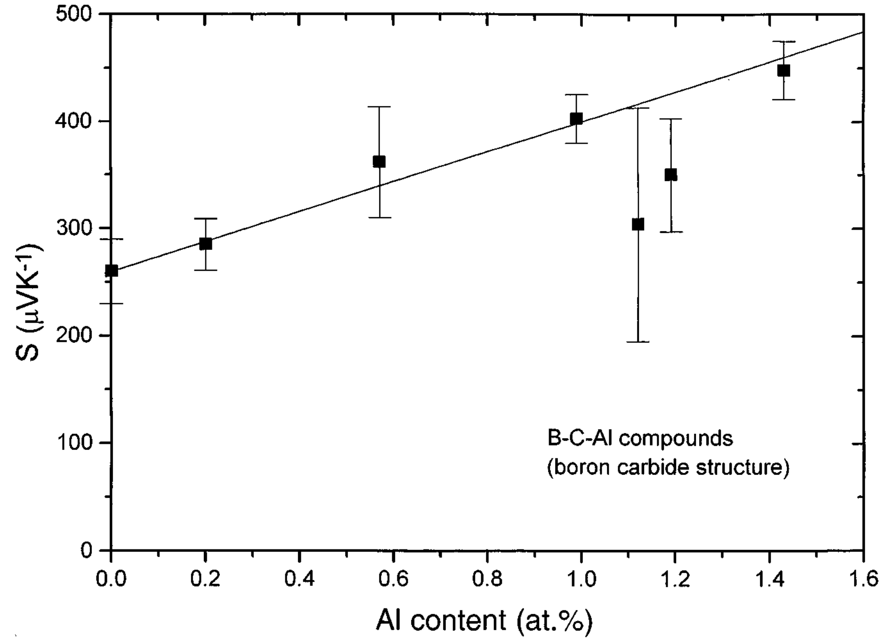

FIG. 5. Seebeck coefficient of the B–C–Al compounds versus Al content in the boron carbide structure.

samples is comparable with that in pure boron carbide, when the chemical composition deviates from that at the carbon-rich limit of the homogeneity range $B_{4.3}C$ (7). Therefore, in agreement with the structural considerations, it can be largely excluded that Al_2 chains displace the normal three-atomic chains in the unit cells of boron carbide.

Meaningful is the above discussed assumption that Al_2 chains are accommodated in otherwise chain-free unit cells of boron-rich boron carbide. If both Al atoms are situated symmetrically to the center on the main diagonal of the unit cell, their stretching vibration is not IR active and should therefore not occur in the IR phonon spectrum in agreement with the obtained results. However, this conclusion must be modified if, according to the proposal by Neidhard *et al.*, the Al atoms would be arranged outside the main cell diagonal. In this case IR activity of their stretching mode would be expected because the symmetry is reduced. The reason coresponding phonons are missing in the spectrum could be explained if the symmetry selection rules are only weakly violated. This would hold if the stretching mode of the Al_2 chain is only weakly influenced by bonds to other atoms. Such a condition was found to be the case in undoped boron carbide, where the bonds of the end atoms of the three-atomic chain to the equatorial atoms of the icosahedra are directed almost perpendicular to the crystallographic *c* axis coinciding with the vibration axis of the stretching mode of the three-atomic chain. Hence their influence on the stretching vibration is weak because they are stressed only by bending (7). Otherwise, with respect to assuming Al(1) sites outside the main diagonal of the unit cell, the structure model of Neidhard *et al.* must be put in question. Unfortunately, only polycrystalline samples were at our disposal for the optical measurements, and therefore polarization-dependent measurements, which could yield the orientation of the chain, were not possible.

The oscillator strength of the boron carbide phonon at 405 cm^{-1} decreases with increasing Al content. This band is assumed to be composed of a specific vibration mode of the icosahedron and the bending mode of the three-atomic chain, which are accidentally degenerated (8). Accordingly one expects a decreasing oscillator strength of the 405-cm^{-1} band with increasing density of chainless unit cells as proved by Kuhlmann (9) for pure boron carbide. Contrary to the stretching mode, the bending mode of the two-atomic chain is IR active. Because of the bigger mass of the Al atom and the probably lower bonding force, the resonance frequency of the corresponding bending mode is expected at lower frequencies. Therefore we attribute the absorption band at 190 cm^{-1} to the IR active bending mode of the Al_2 chains, whose oscillator strengths increase with increasing Al content as that of the 405-cm^{-1} phonon decreases. Unexplained in this interpretation are that the oscillator strength and the damping constant of the 190-cm^{-1} band decrease with increasing temperature. This tendency is beyond the experimental error.

The oscillator strengths of the other low frequency absorption bands due to the Al content at 293 cm^{-1} increases only slightly with increasing Al content, possibly approaching a low saturation value at higher Al contents. It is striking that the oscillator strength of this band varies opposite to that of the boron carbide phonon at 845 cm^{-1}. This phonon is attributed to a very complex threefold degenerated vibration of the icosahedron, which can be described by two groups of tetrahedrally arranged atoms on opposite sides of the icosahedron moving against one another (10). At present an explanation for the correlation is not possible. Nevertheless, it can be largely excluded that the band at 293 cm^{-1} can be attributed to a phonon due to the insertion of Al atoms in icosahedral sites, because in this case the other vibrations of the icosahedra must have corresponding counterparts as well, in contrast to the experimental result.

In the spectral range $< 400\ \mathrm{cm}^{-1}$ of undoped boron-rich boron carbide there are some weak absorption bands as well, however at other frequencies (about 75, 147, 184, and 270 cm^{-1}) (6). Probably they are due to accidental doping.

In the FIR spectra of boron carbide the dynamical conductivity, which is composed of contributions of band-type and hopping conductivity, causes a steep increase of reflectivity and absorption toward very low frequencies (11). This dynamical conductivity is considerably reduced by the insertion of Al atoms in the boron carbide structure. This behavior is distinctly different from the influence of the chemical composition of boron carbide, when it is changed within the homogeneity range. This demonstrates, in particular together with the measured Seebeck coefficient, that the insertion of aluminum atoms affects the electronic properties of boron carbide considerably. For details additional investigations are necessary.

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