substance: boron compounds with group IV elements: boron carbide
property: boron carbide doped with H, He, Mg, C, Si

The behavior of hydrogen, nitrogen and oxygen impurities in boron carbide (and aluminium dodecaboride) for gas sensors [91K1].
Ternary metal boron carbide systems in [99B].

H-doped boron carbide

IR studies in particular of the B-H vibration in amorphous $B_{1-x}C_x$ films in [91S].

IR study of local vibrations in hydrogenated amorphous $B_{1-x}C_x$ (and amorphous B) alloys prepared by plasma deposition; absorption due to B – H and C – H bonds in Fig. 1 [90S].

Hydrogen solubility in the temperature range 700...1000 °C, dilute model for the H solublity on the assumption that hydrogen atoms are dissolved on interstitial sites [92S].

He-implanted boron carbide

Behavior of implanted He in boron carbide in the temperature range 750 to 1720 °C [87S].

Mg-doped boron carbide

High figure of merit *z* for Mg-doped boron carbide (B_9C + 0.5 % Mg) compared with other icosahedral boron-rich solids in [91K2].

figure of merit
(*z* in K^{-1})
(B_9C + 0.5 % Mg)

z	~0.1	*T* = 450 K	obtained from diagram	91K2
	~0.3	*T* = 700 K		
	~0.5	*T* = 1000 K		
	~0.63	*T* = 1200 K		

C-doped boron carbide

Mechanical properties of C-doped boron carbide ("injection molded B_4C-C ceramics") depending on carbon content, sintering temperature and grain size in [97S].

Si-doped boron carbide

Structure, chemical bond

Phase diagram and preparation in [90T].

Incorporation of Si by liquid-solid interactions during sintering [87T2].

Thermo-mechanical synthesis and properties of ceramic boron carbide with silicon [87B].

lattice parameters

Composition	*a* [nm]	*c* [nm]	*c*/*a*	
$B_{12.00}C_{3.00}$	0.5616(1)	1.2087(2)	2.152(2)	90T
$B_{12.04}C_{2.88}Si_{0.01}$	0.5619(1)	1.2125(2)	2.158(1)	
$B_{12.33}C_{2.33}Si_{0.33}$	0.5623(2)	1.2242(2)	2.177(2)	
$B_{12.61}C_{2.01}Si_{0.38}$	0.5655(2)	1.2366(2)	2.187(1)	
$B_{12.89}C_{1.75}Si_{0.36}$	0.5654(2)	1.2350(2)	2.185(2)	
$B_{13.15}C_{1.55}Si_{0.30}$	0.5663(2)	1.2350(2)	2.181(2)	
$B_{13.54}C_{1.34}Si_{0.12}$	0.5667(2)	1.2260(2)	2.163(1)	
$B_{13.68}C_{1.32}$	0.5672(2)	1.2204(2)	2.152(2)	

The acommodation of Si atoms in the boron carbide structure causes a considerable elongation of the *c axis*, while the *a* axis remains largely unchanged. See Fig. 2 [87T1, 90T, 94K, 94W1, 94W2].

In a wide part of the homogeneity range of boron carbide, the accommodation of Si atoms can be described by the formation of Si_2 chains in unit cells, which are chainless (α-rhombohedral boron-like or with two unbounded B atoms saturating the outer bonds of the equatorial B atoms of the icosahedra) in undoped boron carbide (see Fig. 3) [94K, 94W1, 94W2].

On formation and earlier structure models see [87T1, 90T].

structure refinement of a crystal with a = 5.5841(5) Å and c = 12.3014(16) Å (assumed structure $B_{12}(CBC)_{0.949}(SiBSi)_{0.051}$ (SiBSi chains seem not consistent with more recent results, see below) [87M].

Atom	*x*	*z*	U_{11}	U_{33}	U_{12}
B(1)	0.16260(7)	0.35815(8)	40(2)	54(3)	20(2)
B(2)	0.10850(7)	0.11317(5)	47(2)	43(3)	23(2)
B(3)	0	0.5	128(5)	91(7)	64(2)
C	0	0.38429(8)	29(2)	46(2)	15(1)
Si	0.0962(2)	0.5			

Si: fixed U = 0.005; occupancy factor = 0.030

$y = -x$; $U_{22} = U_{11}$, U_{ij} ($\cdot 10^{-4}$) Å^2

relative force-field constant ($k_{Si–Si}$ / $k_{B–B}$ (intericosahedral))

$k_{Si–Si}$ / $k_{B–B}$	0.72	T = 300 K	estimated from Raman spectrum for Si doped boron carbide	94W2

electronic properties

According to the sign of the thermoelectric power, Si-doped boron carbide is p-type independently of the degree of doping. The thermoelectric power exceeds that of undoped boron carbide considerably (see Fig. 4).

thermoelectric power

S	355 μV K^{-1}	T = 300 K	$B_{69}C_{11}Si$	94W2, 94W2, 95W

optical properties

Absorption edge of Si-doped boron carbide in Fig. 5 [94W2, 94W1].

IR phonon spectrum of Si-doped boron carbide Fig. 6 [94W2, 94W1].

Raman spectrum of Si-doped boron carbide in Fig. 7 [94W2, 94W1].

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Fig. 1.

Amorphous boron carbide. Absorption coefficient vs. wavenumber; **(a)** absorption due to the B-H bonds for various C contents in the gas phase (x_g = 0, 24, 50 and 70 %C), **(b)** absorption due to the C-H bond for x_g = 40 and 70 % C [90S].

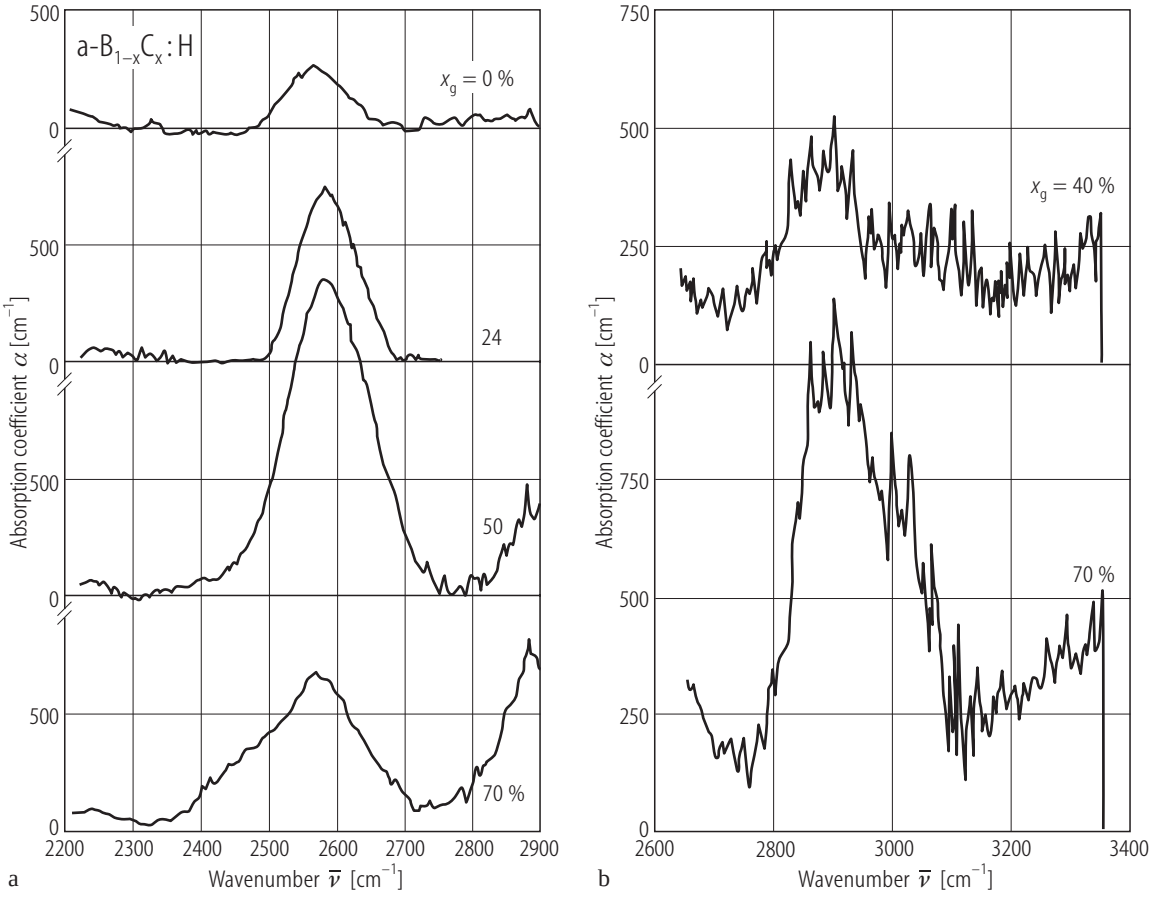

Fig. 2.

Boron carbide :Si. Lattice parameters vs. carbon content, compared with undoped boron carbide. As indicated by arrows, the results reported for "B_4C" should be shifted to the carbon-rich limit of the homogeneity range $B_{4.3}C$ [90T, 94W1, 94W2], diamonds, [74K, 75B]; open squares, [66L]; open circles, [85L].

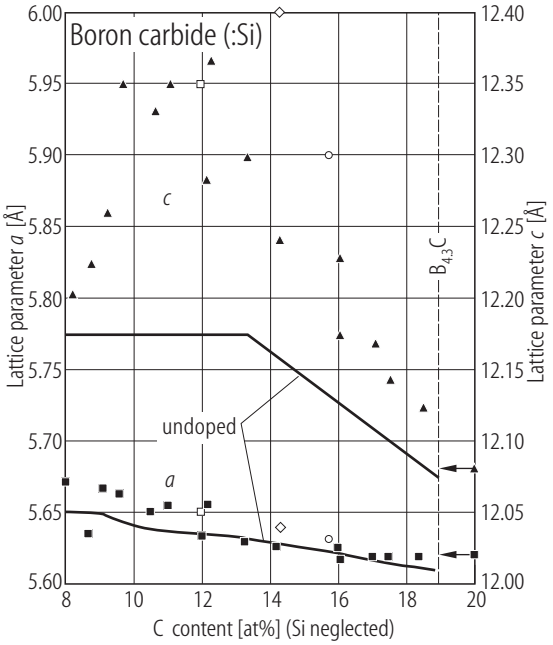

Fig. 3.

Boron carbide:Si. Si content (right ordinate) compared with Si sites in chainless unit cells (two possible sites per chainless unit cell assumed) vs. carbon content [94K, 94W1, 94W2]..

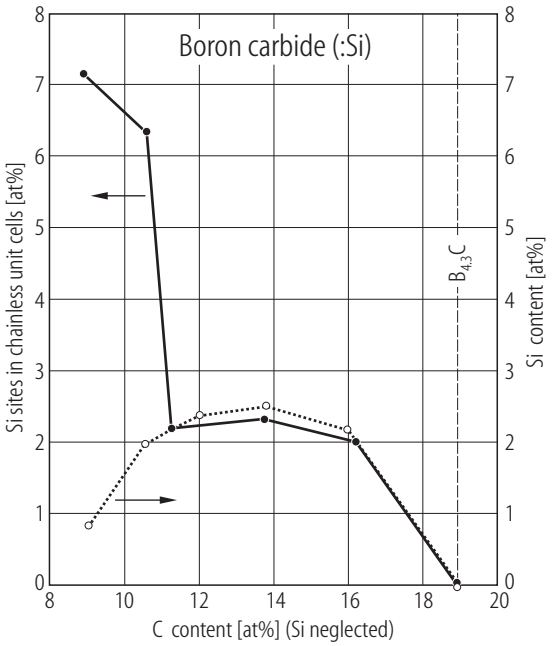

Fig. 4.

Boron carbide. Overview of typical results of the thermoelectric power as a function of temperature for various chemical compositions ($B_{4.1}C$, $B_{4.3}C$, $B_{6.2}C$, $B_{6.9}C$ [91W], $B_{4.3}C$ ($\|c$ and $\perp c$) [86W2, 86W3], see also [95W], B_4C, B_9C [86W1, 86W4], $B_{69}C_{11}Si$ [94W2]; 10 % P-doped boron carbide [94A]. „Conventional method“ means that thermocouples are used to determine the temperatures at both ends of the sample. If the thermocouples are not put into a sufficiently deep hole in the sample; the measurement can be considerably influenced by the heat flow through the wires of the thermocouple. In the „new method“ this source of error is avoided by deriving the temperatures from the electrical conductivity, that is separately measured with high accuracy.

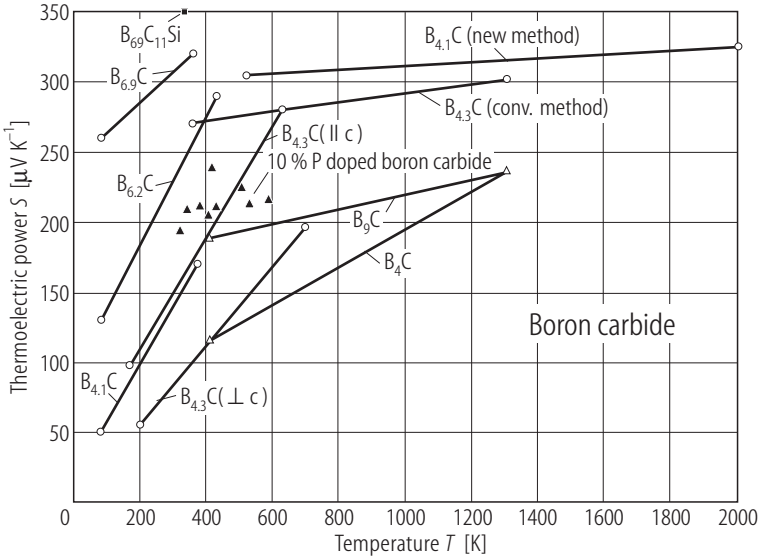

Fig. 5.

Boron carbide:Si. Absorption coefficient vs. photon energy in the absorption edge range of Si-doped boron carbide [94W2, 94W1] compared with high quality undoped boron carbide of composition $B_{4.3}C$ [92W]. The weak structure near 1.4 eV is not real but caused by the low sensitivity of the used spectrometer in this range.

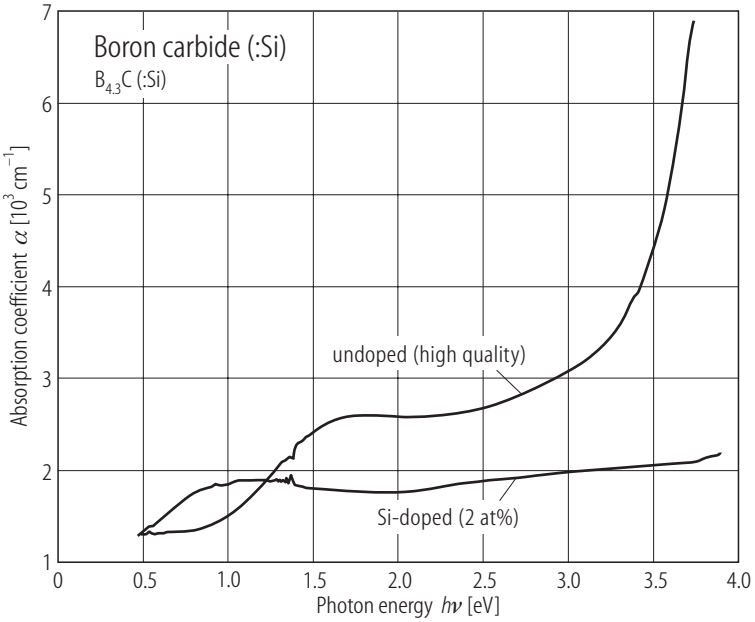

Fig. 6.

Boron carbide :Si. IR phonon spectrum; **(a)** reflectivity vs. wavenumber; insert: low frequency range compared with undoped boron carbide; **(b)** absorption index vs. wavenumber (compared with undoped boron carbide) [94W1, 94W2]. The broad absorption with maximum at about 1850 cm^{-1} is probably caused by the reflection from the rear of the thin sample.

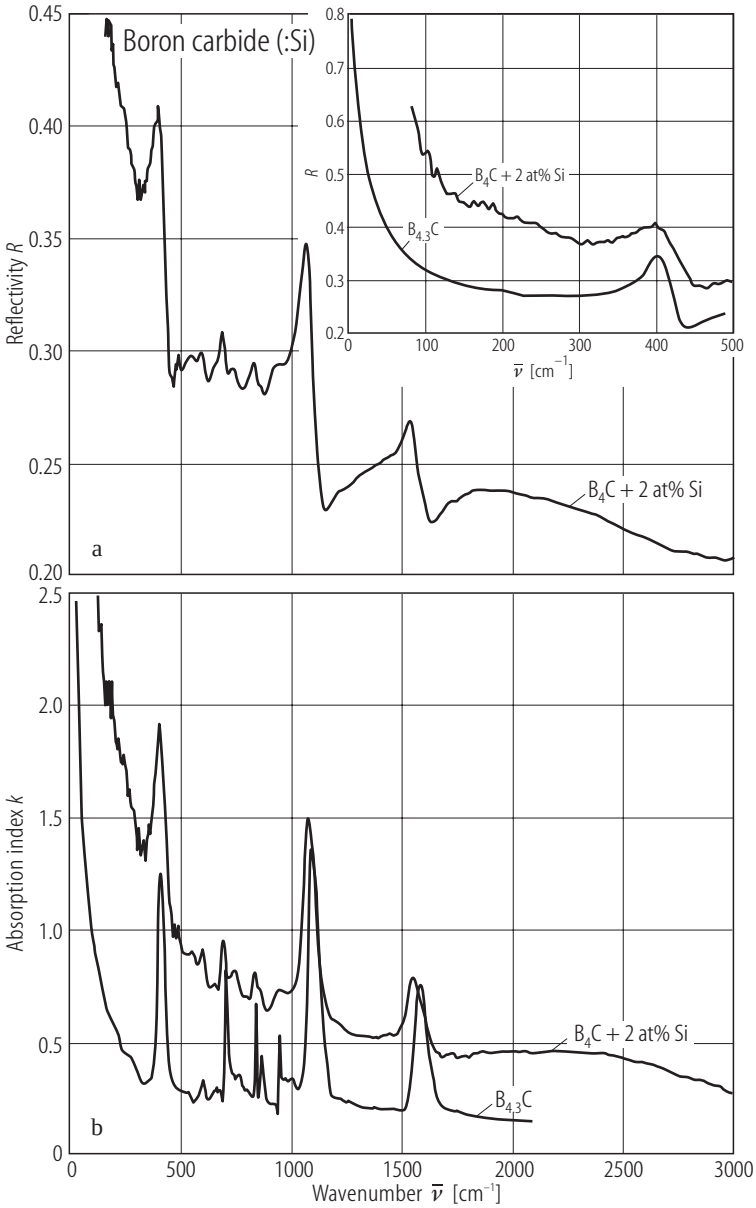

Fig. 7.

Boron carbide:Si. FT-Raman spectrum of 2 at.% Si-doped boron carbide in the Stokes and the anti-Stokes range. Inset: enlarged range of the Raman-active lattice vibrations. The narrow peaks at 1500 and 3000 cm^{-1} are caused by the exciting Nd:YAG laser [94W1, 94W2].