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The correlation between the thermoelectric properties and stoichiometry in the boron carbide phase B_4C–$B_{10.5}C$

MICHEL BOUCHACOURT*, FRANCOIS THEVENOT
Equipes "céramiques spéciales et traitements de surface", Ecole Nationale Supérieure des Mines et Centre de Recherches Rhône Alpes de Céramiques spéciales CRRACS, 158, cours Fauriel, 42023 Saint-Etienne Cédex, France

Electrical conductivity, thermoelectrical power and thermal conductivity measurements on boron carbide samples show that the electrical conductivity follows the small polaron hopping theory and that thermal conductivity occurs by phonon diffusion. The evolution of these properties with carbon content illustrates the particular role played by the 13.3 at % C compound in the phase homogeneity range $B_{10.5}C$ to B_4C. The value of the figure of merit (0.85×10^{-3} K at 1250 K) proves that this particular boron carbide compound could be a very interesting candidate material for high-temperature thermoelectrical conversion.

1. Introduction

"Nuclear electric propulsion is under consideration in the USA for future outer planet missions. Previous results from a space craft system study showed that an optimum hot junction temperature is in the range of 1500 K for advanced nuclear reactor technology combined with thermoelectric conversion [1]". For these temperatures there is a need for new thermoelements which exhibit stable compositions and low vapour pressures over the temperature gradients. The remarkable properties of boron carbide [2] (high-temperature stability, low density, etc.) indicate that this material could be the solution for this problem. However, in spite of numerous studies, conflicting results have been obtained for the electrical and thermal properties; in particular, the value of the figure of merit of boron carbide, which governs the efficiency of thermoelectric devices, is not well known. The aim of this work is to determine the dependence of the figure of merit (via the electrical and thermal conductivities and Seebeck effect), on the temperature and the carbon content within the phase homogeneity range of boron carbide.

2. Experimental details

Boron carbide cylindrical specimens (12.5 mm diameter, 10 mm height) were prepared with different boron to carbon ratios within the homogeneity range $B_{10.4}C$ (8.8 at % C) to B_4C (20.0 at % C) [3], by hot-pressing (1800 to 2200° C, 32.5 MPa, 15 to 60 min, under argon) in boron nitride-lined graphite dies using mixtures of magnesiothermal synthetized boron and boron carbide powders [4, 5]. The samples (Table I) have been completely characterized for analysis, density and lattice parameters, as described in previous papers [5, 6].

Electrical conductivity measurements, σ, were made up to 1500° C on 1 mm thick slices cut perpendicular to the cylinder axis using the d.c. van der Pauw technique [7].

Thermoelectric power measurements, S, were carried out up to 900° C. Nickel end-caps (0.1 mm thick foil) were bonded by hot-pressing (600 to

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*Present address: Centre de recherches EDF, Les Renardières, Ecuelles, 77250 Moret/Loing, France.

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TABLE I Sample compositions

Sample no.	Composition, at % C	Apparent density ρ (g cm^{-3})	Porosity† π	Number of atoms per rhombohedral unit cell [5, 6]	Molecular formula [5, 6]
1	9.7	2.32*	0.06	15.27	$B_{13.79}C_{1.48}$
2	11.5	2.376	0.042	15.24	$B_{13.49}C_{1.75}$
3	11.6	2.325	0.062	15.24	$B_{13.47}C_{1.77}$
4	12.3	2.479	0.001	15.22	$B_{13.35}C_{1.87}$
5	12.8	2.365	0.048	15.22	$B_{13.27}C_{1.95}$
6	14.7	2.496	$\simeq 0$	15.18	$B_{12.95}C_{2.23}$
7	16.3	2.481	0.008	15.15	$B_{12.68}C_{2.47}$
8	16.6	2.39	0.045	15.13	$B_{12.62}C_{2.51}$
9	17.8	2.399	0.044	15.11	$B_{12.42}C_{2.69}$
10	20	2.52	$\simeq 0$	15.0	$B_{12.05}C_{3.02}$

*Estimated.

†$\pi = (1 - \rho/\rho_{th})$ using the relation $\rho_{th} = 2.422_4 + 0.0048_9$ (C) at % [5, 6] where ρ_{th} is the theoretical specimen density.

800° C, 10 MPa under argon) in order to facilitate attachment of thermocouple wires for the measurements [5].

The thermal diffusivity, α, was determined up to 1500° C on approximately 1 mm thick slices using the heat pulse technique (Parker's method [8, 9]).

The thermal conductivity, λ_0, can be calculated from the product:

$$\lambda_0 = \alpha \rho C_p,$$

where α is the thermal diffusivity, ρ the apparent density and C_p the specific heat: C_p (cal mol^{-1} K^{-1}) = $22.99 + 5.40 \times 10^{-3}\, T(\mathrm{K}) - 10.72 \times 10^5\, T^{-2}$ (K) for the B_4C boron carbide [10] (unfortunately no data are available for boron-rich boron carbide material). The values obtained can be corrected to eliminate the effect of inherent porosity using the formula:

$$\lambda = \lambda_0 \frac{(1 - \pi)}{(1 + 2.2\pi)},$$

where π is the porosity (formula in good agreement with many investigations [11]).

3. Results

3.1. Temperature dependence of the electrical and thermal properties

The results of the electrical conductivity, thermoelectric power and thermal diffusivity measurements on the boron carbide samples are shown in Figs. 1 to 3 as a function of temperature or reciprocal temperature. Thermal conductivity values are plotted in Fig. 4. In Figs. 3 and 4 some previous values for boron carbide "B_4C" (20 at % C) [11, 12] have been included.

3.1.1. Electrical conductivity

The electrical conductivity of boron carbide increases with temperature, in agreement with the properties of this semiconductor material previously observed for "B_4C" (20 at % C) and for compounds belonging to the phase homogeneity range [13–18]. The curves presented in Fig. 1 are similar to those proposed by Wood [18]. In the temperature range examined, our results (Fig. 5) agree with the so-called theory of "small polaron hopping" which was recently developed by Wood and Emin [18, 19]: the electrical conductivity, σ, is proportional to $T^{-3/2} \exp(-E_h/kT)$, where E_h is the hopping activation energy. The calculated activation energies are plotted in Table II, and are in good agreement with those of Wood [18].

3.1.2. Thermoelectric power

Boron carbide is a p-type semiconductor; the Seebeck coefficient remains positive over the whole phase homogeneity range, increases slightly with temperature, and reaches values of 200 to 300 μV K^{-1} at 1250 K (Fig. 2). The values which we obtained are of the same order of magnitude as those presented in some earlier studies [1, 14–20].

TABLE II The hopping activation energy, E_h, of boron carbide within its homogeneity range (8.8 to 20.0 at % C)

Samples no (Table I)	Composition (at % C)	E_h (eV)
2	11.5	0.157
4	12.3	0.169
6	14.7	0.172
9	17.8	0.185
10	20.0	0.180

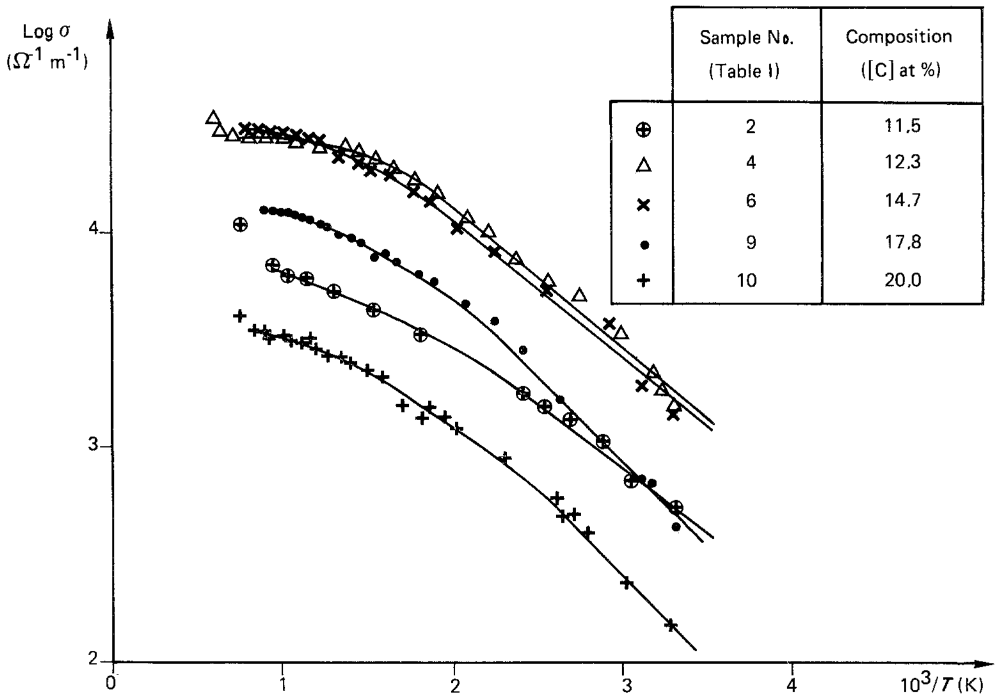

Figure 1 Dependence of the electrical conductivity on reciprocal absolute temperature.

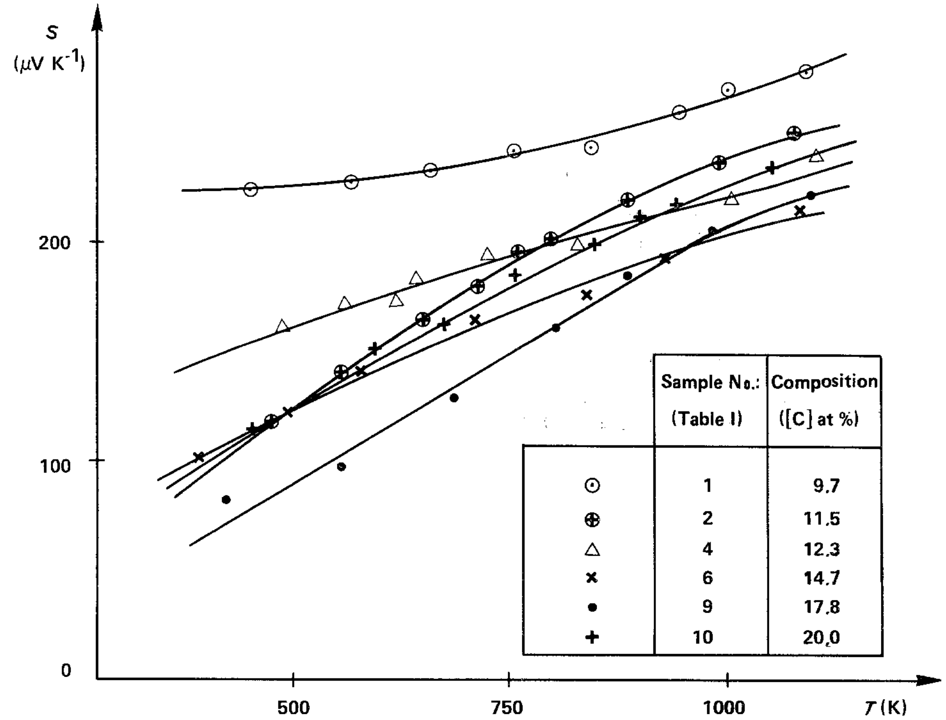

Figure 2 Temperature dependence of the thermoelectric power, S.

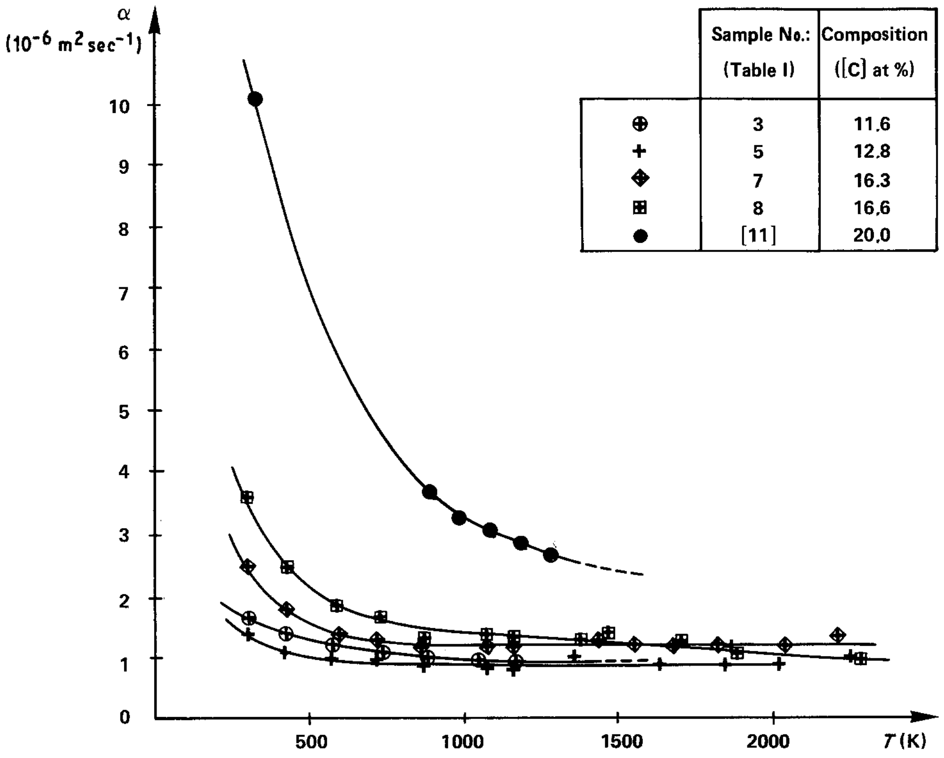

Figure 3 Temperature dependence of the thermal diffusivity, α, (● results from Gilchrist and Preston [11]).

3.1.3. Thermal diffusivity and thermal conductivity

The thermal diffusivity decreases as the temperature increases (Fig. 3). In the temperature range considered, the thermal conductivity varies slightly (Fig. 4) [15], being proportional to reciprocal temperature (Fig. 6); this proves that the heat conduction mechanism in this material occurs by phonon diffusion, in agreement with some earlier results [21–23].

3.2. The dependence of the thermal and electrical properties of boron carbide on the carbon content

Table III summarizes results from the literature, and illustrates their contradictions. Our results are presented in Figs. 7 to 9; for each property, we observe a break in the slope at the composition corresponding to the compound with 13.3 at % C. This observation corroborates the particular role played by this compound in the

TABLE III Influence of the carbon content on the thermal and electrical properties in the boron carbide phase range (from literature data)

Properties	Evolution with carbon content (C)	Origin of samples	Reference
Electrical conductivity:	decreases when C increases	hot pressing, CVD . . .	[20]
	increases when C increases	hot pressing	[24]
	maximim value for 13.3 at % C	hot pressing, (unshielded graphite mould)	[17]
	is no monotonical function of (C)	arc melting (samples are single and two phased)	[16]
Thermoelectrical power:	decreases when C increases	arc melting (samples are single and two-phased)	[16]
	increases when C increases	hot pressing, CVD . . .	[20]
		hot pressing, (unshielded graphite mould)	[17]
Thermal conductivity:	increases when C increases	hot pressing	[23]

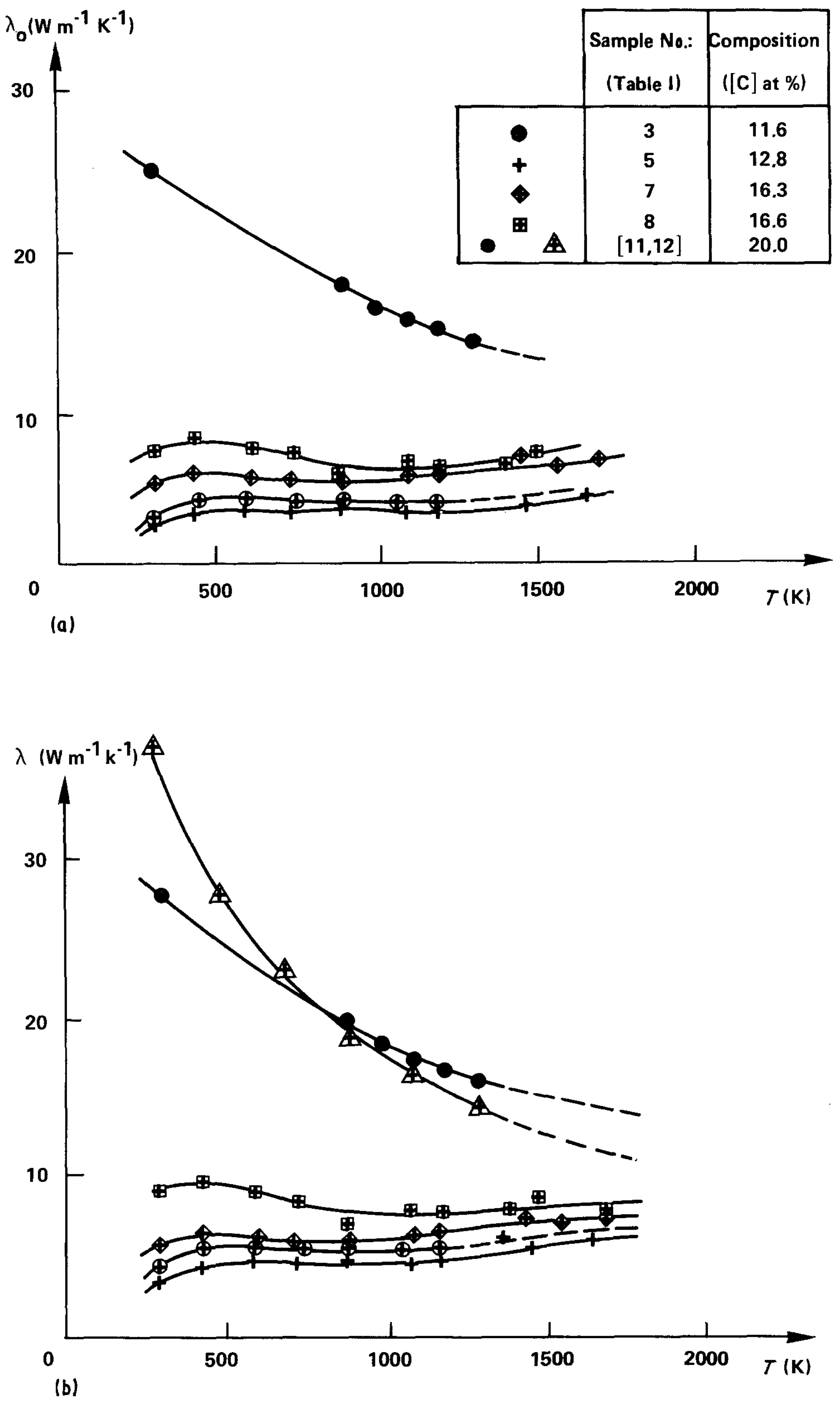

Figure 4 Temperature dependence of the thermal conductivity, λ. (a) Calculated values: $\lambda_0 = \alpha\rho C_p$; (b) corrected values: $\lambda = \lambda_0\ (1 - \pi)/(1 - 2.2\pi)$. (● results from Gilchrist and Preston [11] and Murgatroyd and Kelly [12]).

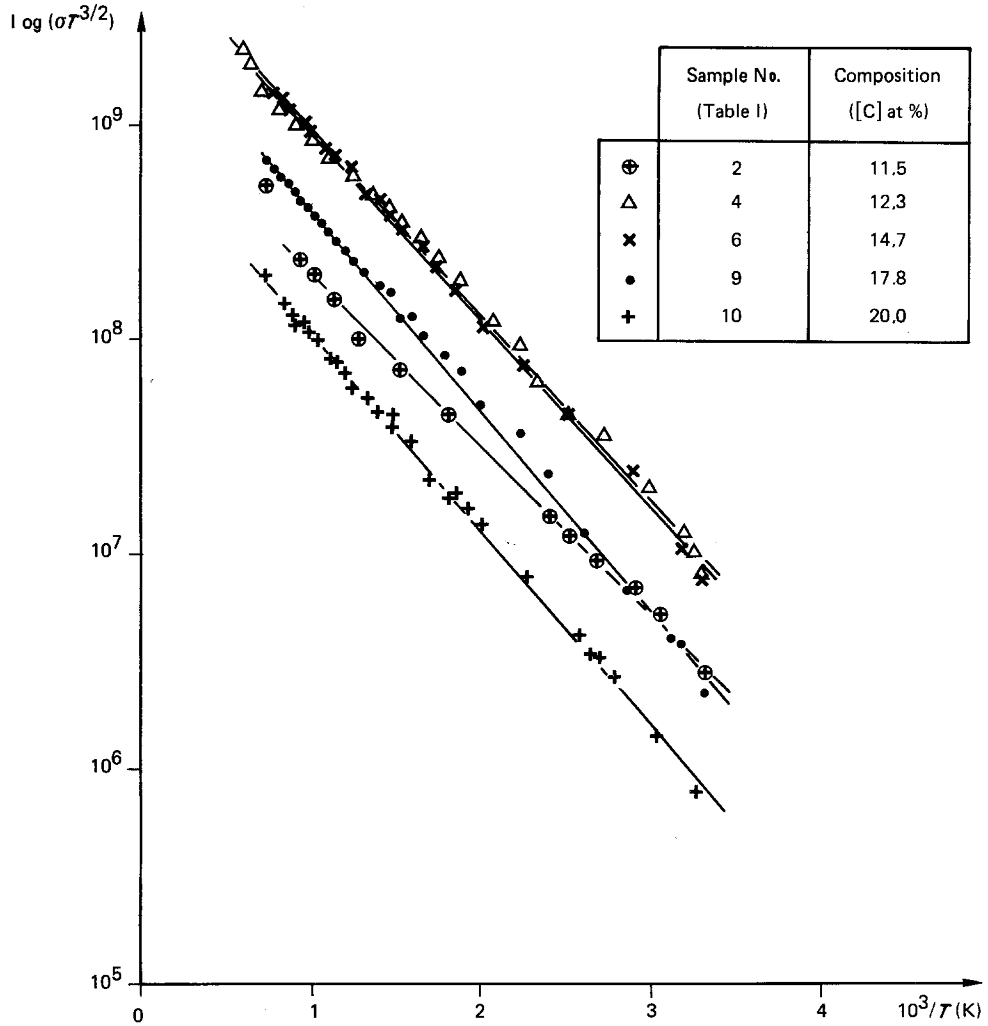

Figure 5 Dependence of log $(\sigma T^{3/2})$ on reciprocal absolute temperature.

phase homogeneity range as already observed, from crystallographic data [5, 6].

Fig. 10 shows that the hopping activation energy, E_h, of boron carbide increases slightly when the carbon content increases (there is perhaps a break in the slope for the 13.3 at% C composition). The evolution was not observed by Wood [18]; it could be related to the occupation of sites in the crystal lattice: the activation energy increases as the number of filled crystallographic sites decreases, starting from 15.33 atoms per unit cell for the boron-rich limit compound ($B_{10.5}C$) to 15 atoms per unit cell for the carbon-rich limit compound ($B_{4.0}C$) [6]. (We have already shown that the 13.3 at% C "compound" contains 15.21 atoms per unit cell [6].)

The scatter of the previous results stems, in our opinion, from the origin of the samples. We have already shown that melted samples are generally inhomogeneous [5, 25], and that materials which are hot pressed without an efficient chemical barrier are highly contaminated by graphite from the mould and plungers [4, 5]. For this reason we do not recommend the use of integrally bonded graphite electrical contacts previously employed by Reynolds and Elsner [17] and Wood [18] which involve an important interdiffusion of boron and carbon at high temperature; this fact has two consequences:

1. all the boron-rich compounds are pushed towards "B_4C" type stoichiometry, and
2. there is a rapid decrease of the thermoelectrical characteristics.

Furthermore, hot pressing under vacuum [18]

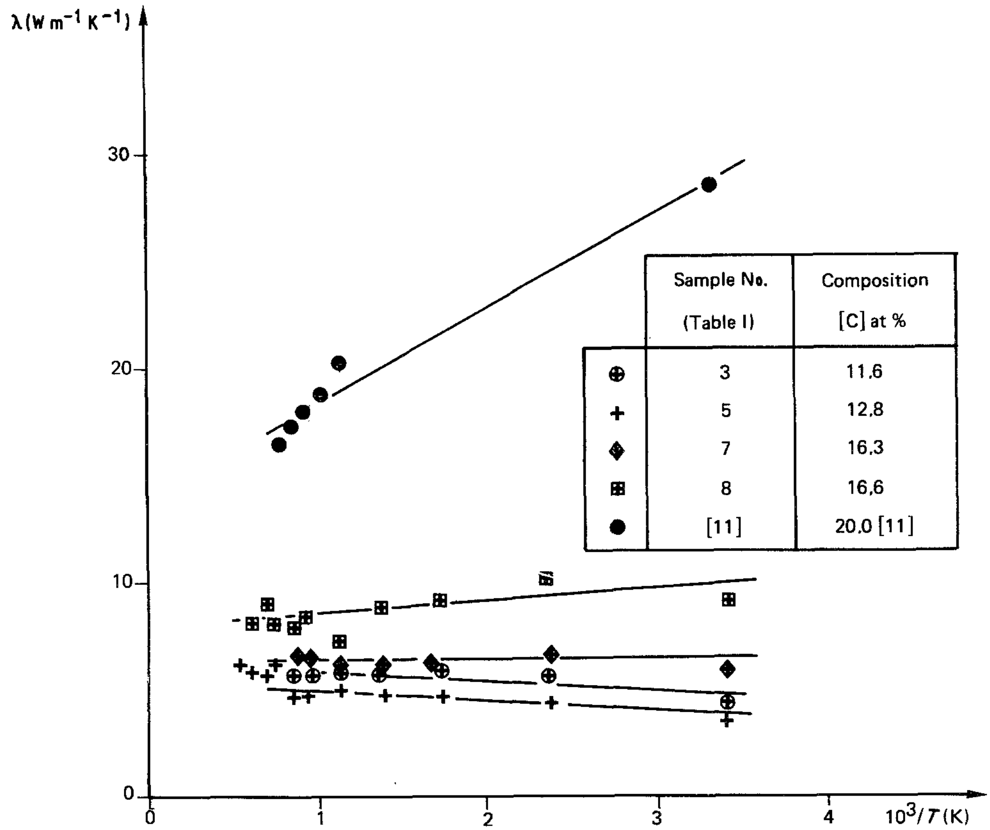

Figure 6 Dependence of the thermal conductivity on reciprocal absolute temperature.

could involve a rapid volatilisation of the starting elements (boron and carbon).

3.3. Thermoelectric figure of merit

Fig. 11 presents the values of the coefficients of merit $Z = S^2\sigma/\lambda$, calculated from the measurements of the electrical, σ, and thermal, λ, conductivities, and the Seebeck effect, S, on our samples. These results show that the figures of merit increase with temperature. Furthermore, for a given temperature, the 13.3 at % C composition possesses the highest S value: $0.85 \times 10^{-3}\,K^{-1}$ at 1250 K. This value underlines the promise of carbon carbide for use in high-temperature thermoelectric generators.

4. Conclusion

The electrical and thermal properties of hot-pressed boron carbide samples have been studied in the phase homogeneity range: 8.8 to 20.0 at % C. The results concerning electrical conductivity measurements confirm the theory of small polaron hopping. The thermal conductivity results prove that heat transfer through the material occurs by phonon diffusion.

The evolution of the different physical properties of boron carbide with carbon content shows the particular role played by the 13.3 at % C composition ($B_{13}C_2$); the high value of its figure of merit ($0.85 \times 10^3\,K^{-1}$ at 1250 K) suggests its use for high-temperature thermoelectrical conversion (P thermocouple branch). Highest values could be probably obtained by increasing the sample purity. The determination of the figure of merit of samples doped with such elements as aluminium, silicon [1], phosphorus, arsenic or sulphur . . . which are able to substitute for boron, or carbon, in the boron carbide lattice [5, 26–29], could also be explored to increase the thermoelectrical conversion yield. Small metallic atoms (magnesium, beryllium) which can insert in the lattice, have been added to B_9C; there is a net loss of power output [30].

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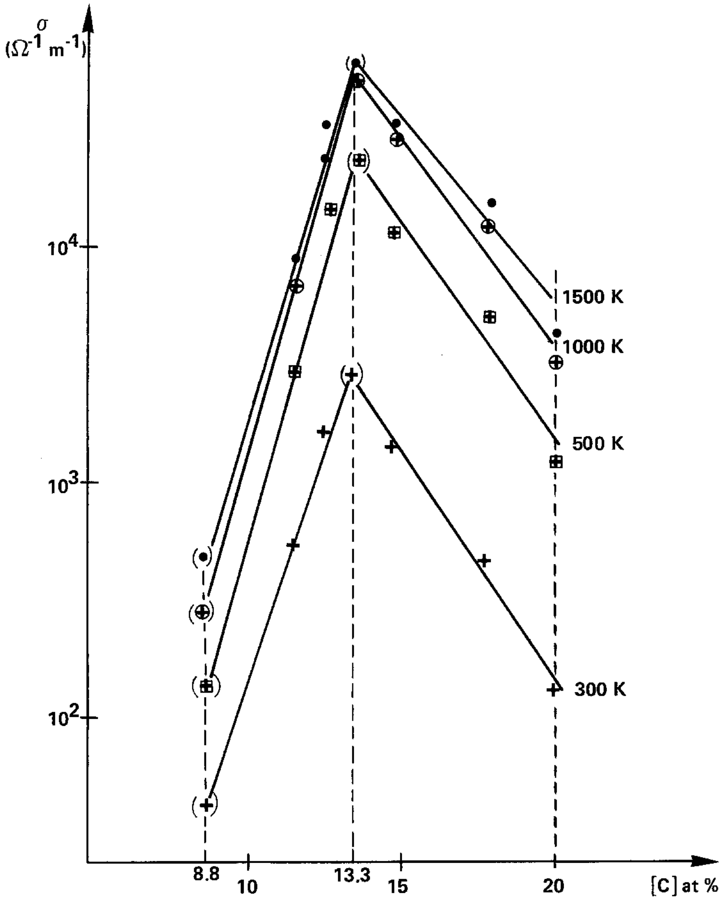

Figure 7 Carbon content dependence of the electrical conductivity (samples: 2, 4, 6, 9 and 10, Table I) (   ) characteristic extrapolated values.

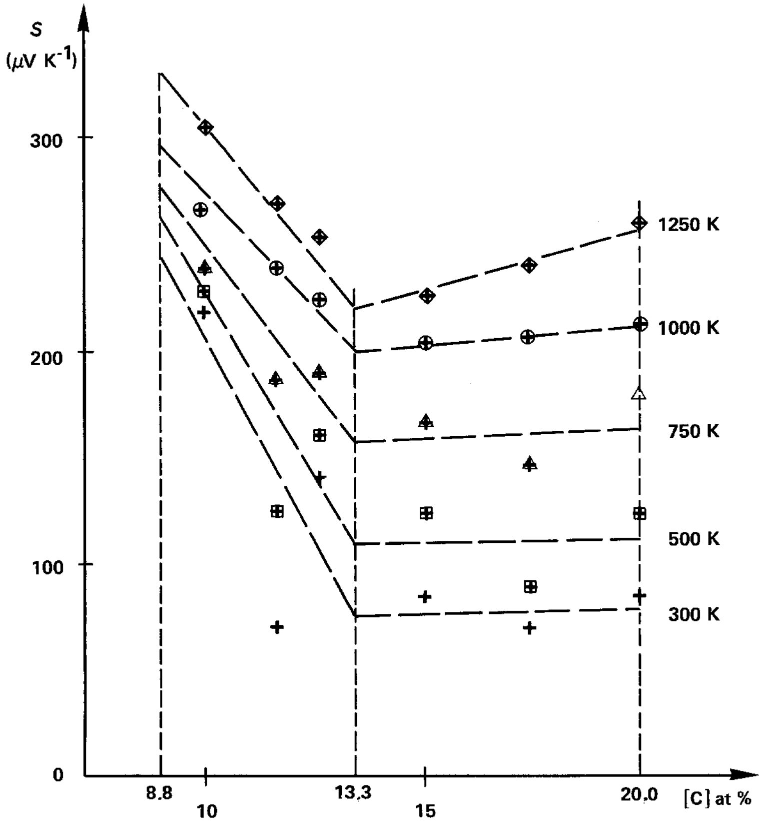

Figure 8 Carbon content dependence of the thermoelectric power (samples: 1, 2, 4, 6, 9 and 10, Table I).

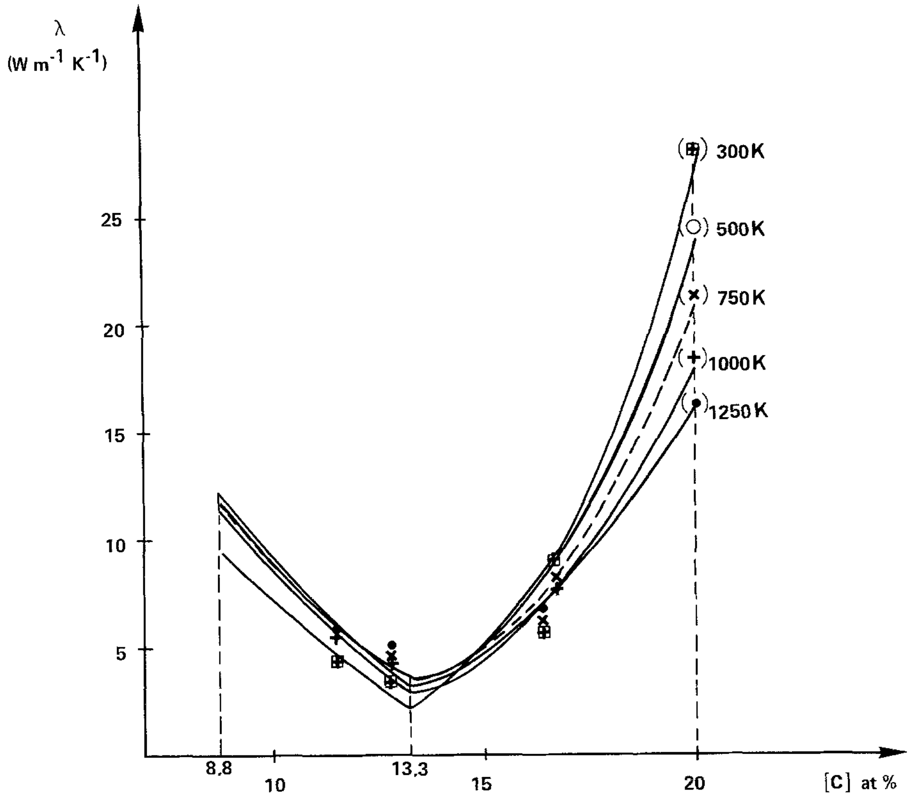

Figure 9 Carbon content dependence of the thermal conductivity (samples: 3, 5, 7 and 8, Table I). ( ) results from Gilchrist and Preston [11].

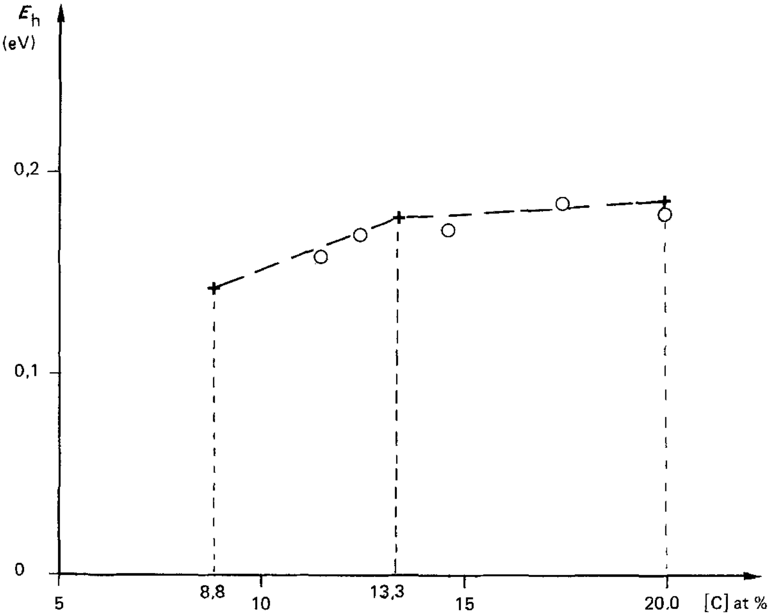

Figure 10 Hopping activation energy, E_h, of boron carbide within its range of homogeneity (8.8 to 20.0 at% C), Table II. +, calculated values starting from Fig. 7 for the limits corresponding to (1) the boron side (8.8 at% C), (2) the carbon side (20.0 at% C) and (3) the 13.3 at% C compound.

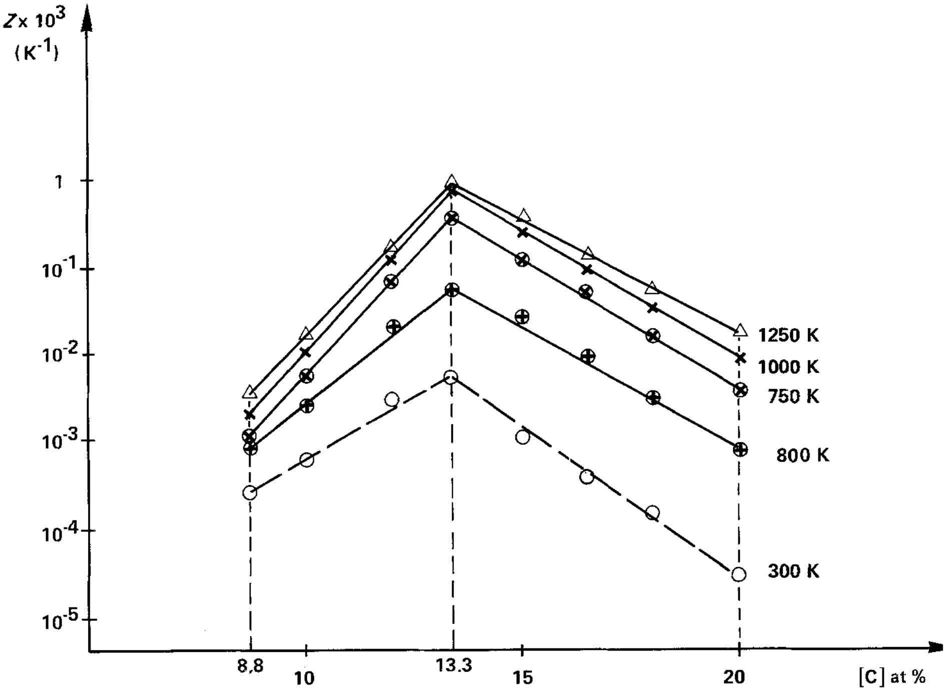

Figure 11 Carbon content dependence of the figure of merit.

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