# Thermoelectric Properties of Boron-Rich Solids and their Possibilities of Technical Application

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#### Abstract

The thermoelectric properties of  $\beta$ -rhombohedral boron and boron carbide, the best-investigated icosahedral boronrich solids, are reviewed. Because of its high density of gap states (~10<sup>21</sup> cm<sup>-3</sup>) generated by intrinsic defects, p-type boron carbide behaves electronically extrinsic up to at least 2000 K, and therefore it exhibits excellent thermoelectric performance. This can even be considerably improved by suitable interstitial doping (Si, Al). As the possibility of n-doping of boron carbide can be largely excluded, other n-type counterparts are required for technical application. Some alkaline hexaborides (Takeda et al.) and rare-earth boron carbonitrides (Mori et al.) are shown to be promising candidates to close this gap.

### Introduction

Boron-rich solids are characterized by a large variety of complex structures essentially consisting of nearly regular polyhedra like  $B_{12}$  icosahedra,  $B_{12}$  dodecahedra,  $B_6$  octahedra and related structural elements. These are bonded directly to one another or via single boron or non-boron atoms thus forming open frameworks allowing the insertion of foreign atoms by substitution for regular B atoms or by interstitial accommodation. Moreover, intrinsic vacancies and structural defects play an essential role for the electronic properties (see [1,2,3] and references therein). Till now, only few of these materials have been sufficiently investigated to discuss their thermoelectric properties.



Fig. 1.  $\beta$ -rhombohedral boron. Seebeck coefficient of pure and doped  $\beta$ rhombohedral boron at room temperature (Slack et al. [5], for Werheit et al., Kuhlmann et al., Schmechel et al., and further examples of doped  $\beta$ rhombohedral boron, see [1] and references therein)

The suitability of materials for thermoelectric devices is to be checked on the basis of the theoretical efficiency

(1) 
$$\eta = \frac{T_{high} - T_{low}}{T_{high}} \frac{M - 1}{M + T_{high}/T_{low}}$$
$$M = \left[1 + z(T_{high} - T_{low})/2\right]^{1/2} \qquad z = S^2 \sigma/\kappa$$



Fig. 2. β-rhombohedral boron. Seebeck coefficient of doped β-rhombohedral boron vs. temperature; broken lines [5], symbols [6]. Insert, Seebeck coefficient of pure and doped boron vs. 1/T (for details and references, see [4])

To optimize the factor  $T_{high} - T_{low}/T_{high}$ , which is the theoretical efficiency of a Carnot machine, requires materials allowing application at very high temperatures. In this respect, boron-rich solids are outstanding materials because of their high melting points  $T_m$  typically exceeding 2000 K, e.g. boron carbide with  $T_m \approx 2600$  K, and metal hexaborides with  $T_m > 2500$  K.

The factor  $(M-1)/M+T_{high}/T_{low}$ ) essentially depends on z containing the transport properties, which are relevant for thermoelectrical application. In particular must be obeyed that towards high temperatures semiconductors usually become intrinsic. This means that their charge transport is essentially determined by electrons and holes, both thermally excited across the band gap. In this temperature range doping becomes ineffective, the Seebeck effects of electrons and hole largely compensate each other and hence the resulting efficiency becomes rather small. The resulting sign of S depends on the type of the more mobile carriers.

#### β-rhombohedral boron

This tendency towards intrinsic behavior determines the high-temperature thermoelectric properties of  $\beta$ -rhombohedral boron, one of the few boron-rich semiconductors investigated in some detail. Fig. 1 shows that suitable n-doping of this originally p-type semiconductor can lead to considerable negative Seebeck coefficients; however, unfortunately at lower temperatures only. As shown in Fig. 2, at higher temperatures the electronic transport approaches intrinsic behavior with a comparably low positive *S* [5,6].

Doping of  $\beta$ -rhombohedral boron with metal atoms leading to n-type conduction is limited because the number of suitable interstitial sites and there possible occupancies are restricted. For this reason, there seems to be no chance to accommodate n-doping elements in sufficient concentration to pin the Fermi level near the conduction band at high temperatures. Therefore,  $\beta$ -rhombohedral boron must be largely excluded as a candidate for high-efficiency thermoelectric application.

## **Boron carbide**

Boron carbide exhibits a large homogeneity range extending from  $B_{4,3}C$  at the carbon-rich to about  $B_{11}C$  at the boron-rich limit. There is no well-defined unit cell representing the whole structure but only rhombohedral elementary cells composed of twelve-atomic icosahedra at the vertex, and mostly three-atomic chains on the main diagonal, both in different statistically distributed compositions. There are  $B_{12}$  and  $B_{11}C$  icosahedra, and linear CBC, CBB,  $B\Box B$  and sometimes CCC arrangements, whose concentrations depend on the actual chemical composition (see [2], [7,8]). Compared with the idealized, according to theoretical calculations energetically most favorable hypothetic structure  $B_{13}C_2$ (structure formula  $B_{12}(CBC)$  [9,10], metallic character), the real semiconducting structures of boron carbide contain high concentrations of vacancies and antisite defects. These are quantitatively correlated with the high concentration of gap states  $(\sim 10^{21} \text{ cm}^{-3})$ , split off from the valence band and responsible for the semiconducting character of real boron carbide [11,12], and in particular for the outstanding thermoelectric properties as well.



**Fig. 3.** Boron carbide. Preliminary band scheme based on optical absorption, luminescence, photoabsorption, and transport properties. The maximum total density of defect-generated gap states is of the order 1 per unit cell, i.e. 3 10<sup>21</sup> cm<sup>-3</sup> [2,11,12,13,14,16]. The experimentally determined transitions are indicated by arrows. An additionally predicted donor level [11,12], which has not yet been experimentally verified, is not marked.

A preliminary band scheme of boron carbide is displayed in Fig. 3. It is based on results of optical absorption, luminescence, photoabsorption, electrical conductivity [2,13,14,15,16].



**Fig. 4.** Boron carbide. Selected Seebeck results (Wood [18,19], Aselage et al. [20,21]; others by Werheit et al, see [2] and references therein). Insert, *S* vs. carbon concentration, solid symbol [20], open symbols [17]

Some selected results of temperature and composition dependent Seebeck effect measurements on boron carbide are displayed in Fig. 4 [2,18,19,20.21]. The essential result is that *S* weakly varies within the homogeneity range; minimum close to  $B_{13}C_2$ , and monotonously increases up to at least 2000 K. There is no remarkable indication of intrinsic behavior in this range. Reason is the extraordinary high concentration of gap states generated by structural defects [11] and pinning the Fermi level up to very high temperatures.



**Fig. 5.** Boron carbide. Electrical conductivity plotted vs. T<sup>-1/4</sup> according to Mott's theory of variable-range hopping [2,3]. Insert, plot vs. T<sup>-1</sup> showing thermally activated processes at high temperatures [22].

Fig. 5 shows the electrical conductivity of boron carbide plotted according to Mott's law of variable range hopping,

which law is obviously satisfied in a large range of temperature. This transport obviously takes place within the high-density gap states. At high temperatures, thermally activated carriers remarkably contribute to the charge transport (see insert of Fig. 5). This superposition of hopping and band conduction was separately proved at lower temperatures by analyzing the dynamical transport of boron carbide determining the FIR spectra [23,24].

In the whole homogeneity range the thermal conductivity (Fig. 6) is very low, and it remains low up to the limit of the hitherto available measurements at about 1100 K [25,26,27,3]. Its magnitude and behavior is similar to that of glasses. This is not surprising, when the enormous density of structural defects is taken into account.



Fig. 6 Boron carbide, carbon-doped boron. Thermal conductivity vs. carbon content [25,26,3]. Insert, Temperature dependence of the thermal conductivity of boron carbide [27].

The total effect of the thermoelectric properties is represented by the figure of merit z or by the dimensionless value zT (Fig. 7) essentially determining the efficiency  $\eta$  in equation (1). Obviously boron carbide is a very promising candidate for thermoelectric energy conversion.



Fig. 7. Boron carbide. Figure of merit z and zT vs. temperature. Data below 1200 K were calculated using the average experimental thermal conductivity; for higher T it is linearly extrapolated.

However, for thermoelectric devices with the high efficiency according to equation (1) a corresponding n-type counterpart is required. In classical semiconductors this problem is usually solved by suitable doping.

For boron carbide attempts of doping were reported for numerous elements (for H, He, Mg, C, Si, N, P, O, Al, Cr, Fe, see [2] and references therein; for Fe, V, P see [28]). Some of the doping elements hitherto investigated increase *S* considerably. Si [29,30] (for *S* of nominal  $B_{69}C_{11}Si$ , see Fig. 4) and Al [31] are accommodated in the chain-free (B $\square$ B) elementary cells of boron carbide, only, and therefore their maximum concentration is limited. For Al, the concentrationdependent *S* is shown in Fig. 8.

Till now, n-type boron carbide has not been realized. Taking the high concentration of gap states of up to about  $3 \cdot 10^{21}$  cm<sup>-3</sup> (see Fig. 3) into account, this is not surprising, because a corresponding overcompensation is required by substitutional or interstitial accommodation of foreign atoms. Such a high concentration of foreign atoms would probably destroy the boron carbide structure. However, Hwang et al. [32] report on n-type nickel-doped boron carbide thin films, but their result has not been confirmed by other authors.



Fig. 8. Seebeck coefficient of Al-doped boron carbide [31]

## n-type boron-rich solids

For  $\beta$ -rhombohedral boron, the p-type behaviour is due to split-off valence states in the gap generated in consequence of structural defects [11,12] like in boron carbide. It was shown that, at least in particular cases, where the concentration of gap states is sufficiently low, p-type icosahedral boron-rich solids can be transferred to n-type by suitable interstitial doping (see above). In  $\beta$ -rhombohedral boron, interstitial doping is limited by the restricted number of possible interstitial sites for the accommodation of metal atoms. As the electronic band structure of  $\beta$ -rhombohedral boron is essentially determined by the B<sub>12</sub> icosahedra of the structure, it seems to be useful to try other structure families containing B<sub>12</sub> icosahedra as determining structural elements as well, but at least partly allowing much higher metal contents. In this connection are to be mentioned the

- tetragonal boron structure groups,
- orthorhombic γ-AlB<sub>12</sub> structure group,
- REB<sub>50</sub> type borides
- $AlB_{10}/C_4AlB_{24}$  structure group

- MgAlB<sub>14</sub> type borides
- YB<sub>25</sub> structure group
- YB<sub>66</sub> type borides

Unfortunately, till now for all these structure groups measurements of thermoelectric properties have been performed in single cases at most, but never in systematic investigations (see [2]). Negative Seebeck coefficients were reported for MgAlB<sub>14</sub>, Al<sub>8</sub>B<sub>4</sub>C<sub>7</sub>, YbB<sub>6</sub> and ErAlB<sub>14</sub> (see [2] and references therein).

Indeed, recently some very promising thermoelectric investigations on some other n-type boron-rich solids have been performed:

Takeda et al. [33,34,35] have proved that alkaline hexaborides (CaB<sub>6</sub>, SrB<sub>6</sub>, and BaB<sub>6</sub>) exhibit considerable negative Seebeck coefficients monotonously increasing up to at least 1100 K, and with other promising thermoelectric properties up to very high temperatures as well.

Mori and Nishimura [36,37] investigated  $HoB_{17}CN$ ,  $REB_{22}C_2N$  (RE=Y, Er, Lu), and  $YB_{28.5}C_4$  containing  $B_6$  octahedra,  $B_{12}$  icosahedra and C-B-C chains as structural elements. Seebeck coefficients of the rare earth boron carbonitrides have a negative sign, and increase monotonously up to the limit of previous measurements at about 1100 K and other rather favorable thermoelectric properties.

## Conclusions

Because of their outstanding general properties like high melting points, extreme hardness and strong resistance against chemical attack, boron-rich solids are excellent materials for application under extreme external conditions, which are not accessible for many other materials. In particular, this holds in the case of devices for thermoelectric energy conversion, which require a high efficiency for their economic use, as well. As shown, for the realization of this goal, besides of favourable thermoelectric properties, the utilisation of highest possible temperatures is a necessary prerequisite.

Though n-type doping of boron carbide has proved to be impossible, the construction of devices for high-efficiency thermoelectric energy conversion can be realized, when the ptype boron carbide is combined with n-type alkaline hexaborides or n-type RE boron carbonitrides respectively.

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