

Large Enhancement of Boron Carbides' Seebeck Coefficients through Vibrational Softening

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We report measurements of the Seebeck coefficients of boron carbides having compositions $B_{12+x}C_{3-x}$, $0.15 < x < 1.7$, from 6 to 900 K. These Seebeck coefficients are large, $\approx 200 \mu\text{V/K}$ at 300 K, despite boron carbides having high carrier densities, $\approx 10^{21} \text{ cm}^{-3}$. The Seebeck coefficients also have unusual temperature dependencies and depend only weakly on carrier density. These exceptional properties can arise from boron carbides' bipolaronic holes substantially softening the vibrational modes with which they interact. [S0031-9007(98)07091-4]

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Boron carbides, $B_{12+x}C_{3-x}$ with $0.15 < x < 1.7$, are refractory, p -type semiconductors having potential as high-temperature thermoelectrics. For this reason, their high-temperature electronic transport properties have been widely studied [1–5]. Both the temperature dependence of boron carbides' conductivities and their thermally activated Hall mobilities show that conduction proceeds via small-polaron hopping [2]. The density of holes implied by boron carbides' carbon content and the magnitudes of their conductivities' prefactors both indicate large carrier densities, $\approx 10^{21} \text{ cm}^{-3}$. Solids having such high carrier densities generally have small Seebeck coefficients, $\alpha \approx 10 \mu\text{V/K}$. Nonetheless, measurements of boron carbides' Seebeck coefficients typically find large values, $\alpha \approx 200 \mu\text{V/K}$ at 300 K. Because a material's thermoelectric efficiency is proportional to the square of its Seebeck coefficient and its carrier density, boron carbides are unexpectedly efficient thermoelectrics. This proportionality is expressed by a thermoelectric's figure of merit, $Z \approx \alpha^2 \sigma / \kappa_{\text{th}}$, where σ is the electrical conductivity and κ_{th} is the thermal conductivity.

Irreproducibility of measurements [1–5], associated with samples' inhomogeneities and uncontrolled compositions, has heretofore precluded an understanding of the origin of boron carbides' large Seebeck coefficients. In this Letter, we describe reproducible measurements of the Seebeck coefficients over an unusually wide temperature range, 6 to 900 K, of well-characterized samples that transcend boron carbides' wide single-phase regime, 9 to 19 at. % carbon. We find that the anomalously large Seebeck coefficients depend only weakly on carbon concentration and possess a distinctive temperature dependence. We attribute this novel Seebeck effect to boron carbides' charge carriers being molecular bipolarons that result from these solids' unusual structure and bonding. In particular, the predominant contribution to the Seebeck coefficient is associated with softening of the vibrational modes associated with carriers forming singlet molecular bipolarons.

Boron carbides belong to a class of distinctively bonded solids, icosahedral boron-rich solids, defined by their

unusual constituents, twelve-atom icosahedral clusters. The valence electrons binding each cluster are sufficiently delocalized to be approximated as electrons confined to the surface of the cluster's circumscribing sphere. These valence electrons fill a succession of states that are each characterized by their orbital angular momenta (s , p , d , and f) [6]. An icosahedron's departure from spherical symmetry splits its f -like levels so that the highest occupied orbitals are a set of fourfold degenerate f -like orbitals. The binding of boron icosahedra is observed to be so strong that B_{12} icosahedra have a strong bielectron affinity: $B_{12} + 2e \rightarrow (B_{12})^{2-}$.

Idealized boron carbide, B_4C , is an insulator that is formally described as $(B_{11}C)^-(CBC)^+$. All of the bonding states of $(B_{11}C)^-$, isoelectronic to $(B_{12})^{2-}$, are filled. Increasing the boron-to-carbon ratio introduces holes on some icosahedra: $(B_{11}C)^- - e \rightarrow (B_{11}C)^0$. Attempts to observe the magnetic moments of these holes both by their electron spin resonance signals and their susceptibility detect only defect spins whose densities are much lower than densities of charge carriers [7,8]. The insensitivity of boron carbides' low-temperature Seebeck coefficients to magnetic field also suggests that the charge carriers lack magnetic moments [9]. These observations imply that holes in boron carbides pair as singlet bipolarons. Pairing of boron carbides' holes is modeled as the disproportionation reaction: $2(B_{11}C)^0 \rightarrow (B_{11}C)^+ + (B_{11}C)^-$, where $(B_{11}C)^+$ represents a bipolaronic hole.

The density of these bipolarons is predicted to peak at the boron carbide $B_{13}C_2$ which is represented as $[(B_{11}C)_{0.5}^+(B_{11}C)_{0.5}^-](CBB)$ [8,10,11]. The fraction of $B_{11}C$ icosahedra occupied by bipolarons is $c = 0.5$ at this composition. The peaking of the conductivity observed at this composition is consistent with its having the maximum carrier density [12]. The lowest bipolaron concentration occurs for $x = 0.15$, where $c = x/2$. Thus, the carrier concentrations in boron carbides are always very high compared with conventional materials manifesting large Seebeck coefficients.

The Seebeck coefficient, α , is experimentally determined by measuring the open-circuit emf induced across

a sample by imposing a temperature gradient. Physically, the Seebeck coefficient measures the entropy transported per charge carrier divided by the carrier's charge [13]. The Seebeck coefficient may be written as the sum of two contributions: α_{presence} , associated with the change in the system's entropy due to the presence of a charge carrier, and $\alpha_{\text{transport}}$, the net energy transported with a carrier divided by qT [14]. In the simplest treatments of the Seebeck effect, $\alpha_{\text{transport}}$ is ignored. In addition, calculations of α_{presence} do not explicitly consider interactions of a carrier with its environment. Then $q\alpha_{\text{presence}}$ equals the change in the entropy-of-mixing associated with adding a charge carrier, $q\alpha_{\text{mix}}$. A simple limit results when all sites are accessible to a carrier and only one carrier can occupy a site at a time. For spinless carriers (e.g., singlet bipolarons) [15]:

$$\alpha_{\text{mix}} = \frac{k_B}{q} \ln\left(\frac{1-c}{c}\right); \quad (1)$$

$k_B/q = 43 \mu\text{V/K}$ when $q = 2e$. With $0.08 < c < 0.5$ for boron carbides, the formula gives the Seebeck coefficient falling from about $100 \mu\text{V/K}$ at $\text{B}_{12.15}\text{C}_{2.85}$ to 0 at B_{13}C_2 .

Several apparatus were employed to measure boron carbides' Seebeck coefficients over the temperature range 6–900 K. Rectangular samples, ≈ 8 mm by ≈ 5 mm by ≈ 2 mm, were cut from fully dense hot-pressed boron carbide cylinders. Samples' compositions, homogeneity, and absence of large carbon inclusions were confirmed by chemical analysis, Raman spectroscopy, and electron probe microanalysis [11,12].

Seebeck coefficients of boron carbides of several compositions are shown in Fig. 1 as a function of temperature above 300 K. Reproducibility among different apparatus, denoted by different symbols, is very good. These measurements, and others omitted in Fig. 1 for clarity, yield approximately parallel curves that gradually fall from 300 K to nearly temperature-independent values above 650 K. Boron carbides' Seebeck coefficients at 773 K are plotted as a function of carbon concentration in Fig. 2.

The smallest value of boron carbides' high-temperature Seebeck coefficients occurs near B_{13}C_2 as predicted by Eq. (1) with $c = 0.5$. Furthermore, the variation of the Seebeck coefficient with carbon concentration relative to the B_{13}C_2 minimum is in rough agreement with the prediction of Eq. (1). However, the Seebeck coefficient at $c = 0.5$ is far from 0, the value predicted by Eq. (1) for $c = 0.5$. These results suggest that the conventional, carrier-density dependent contribution to the Seebeck coefficient, α_{mix} , is augmented by a relatively large contribution that is insensitive to carrier density.

Measurements of boron carbides' Seebeck coefficients were extended to low temperatures with another apparatus. Figure 3 shows that the Seebeck coefficient of a B_{13}C_2 sample between 6 and 900 K is characterized by a peak at 250 K in addition to a temperature-independent

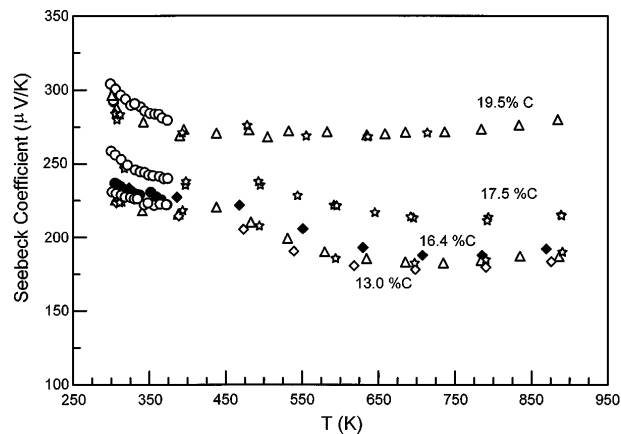


FIG. 1. Seebeck coefficients of boron carbides of a few illustrative compositions as functions of temperatures. Different symbols refer to measurements of the same sample using different experimental apparatus. Circles and stars: samples held between Cu anvils with Cu leads and type-K thermocouples. Triangles and diamonds: samples held between graphite anvils with Pt leads and type-S thermocouples. Plotted values are corrected for the Seebeck coefficient of the reference metal. Measurements above 400 K were made under an atmosphere of gettered Ar to prevent oxidation of samples and leads. Data for the 16.4 atomic percent (a/o) C sample are indicated by filled symbols to distinguish them from data for the 13.0 a/o C sample.

plateau at high temperatures. The temperature dependencies of the Seebeck coefficients of other compositions are similar to Fig. 3. This unusual temperature dependence is consistent with carrier-induced softening augmenting the Seebeck coefficient [16].

Carrier-induced shifts of vibrational frequencies occur when the electronic energies of self-trapped carriers vary nonlinearly with atomic displacements [17]. In particular, the electronic energy of a singlet stabilized by lifting orbital degeneracy with a symmetry-breaking deformation

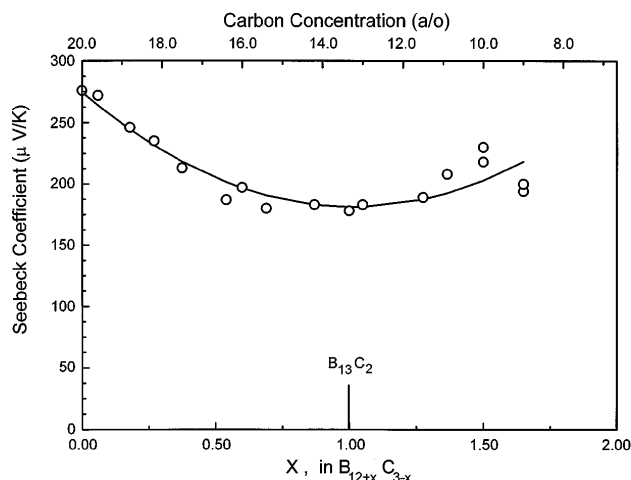


FIG. 2. Seebeck coefficients of boron carbides as a function of carbon concentration at 773 K. The solid line is a guide for the eye.

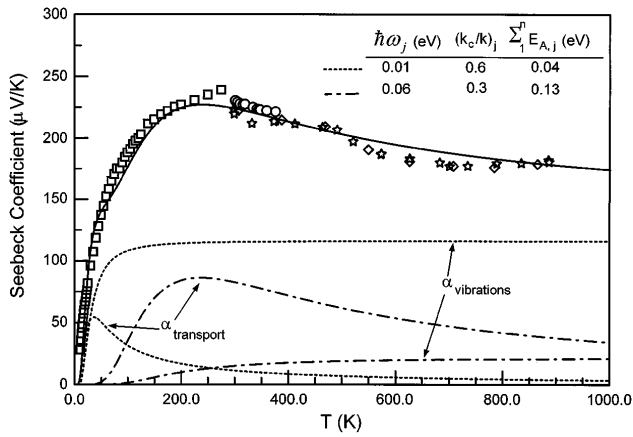


FIG. 3. Temperature dependence of the Seebeck coefficient of a boron carbide of composition $B_{13}C_2$ ($x = 1$) between 6 and 900 K. Squares represent data obtained in a low-temperature apparatus, with the sample held in vacuum between Cu anvils with Cernox thermometers. Reference leads were superconducting Nb_3Sn below 18 K and Cu above 18 K. Other symbols are the same as those of Fig. 1. Contributions from $\alpha_{\text{vibrations}}$ and $\alpha_{\text{transport}}$, Eqs. (2) and (3), for carriers' interactions with six low-energy modes (0.01 eV, $n = 6$) and one higher-energy mode (0.06 eV, $n = 1$) illustrate a fit to the observations. Because $c = 0.5$ for this composition of boron carbide, the contribution from α_{mix} , Eq. (1), is 0.

always falls nonlinearly with the distortion [6]. Through this effect singlet bipolarons associated with degenerate orbitals soften the symmetry-breaking vibrations to which their carriers are coupled. In our case, stabilization of a singlet bipolaron on a boron-rich icosahedron results from lifting the degeneracy arising from its orbitally degenerate f -like frontier orbitals [6].

Carrier-induced softening produces contributions to both α_{presence} and $\alpha_{\text{transport}}$ [16]. The contribution to α_{presence} is produced by the increase in vibrational entropy arising from carrier-induced lowering of the Hooke's law constant associated with the j th vibrational mode from k_j to $k_{j,c}$. This contribution is

$$\alpha_{\text{vibrations}} = \left(\frac{k_B}{q}\right) \sum_j \left(\frac{k_j - k_{j,c}}{k_j + k_{j,c}}\right) \times \left[\frac{(\hbar\omega_j/2k_B T)}{\sinh(\hbar\omega_j/2k_B T)}\right]^2, \quad (2)$$

where the sum is taken over the vibrational modes. Carrier-induced softening also produces a heat of transport contribution to the Seebeck coefficient, $\alpha_{\text{transport}}$, equal to the vibrational energy transferred in a hop divided by qT . For hopping between the equivalent sites of a crystal, it is found that

$$\alpha_{\text{transport}} = \left(\frac{1}{qT}\right) \sum_j \left\{ E_b^{j,c} \frac{[\csc h^2(\hbar\omega_j \sqrt{k_{j,c}/k_j}/2k_B T) - \csc h^2(\hbar\omega_j/2k_B T)]}{[\coth(\hbar\omega_j \sqrt{k_{j,c}/k_j}/2k_B T) + \sqrt{k_{j,c}/k_j} \coth(\hbar\omega_j/2k_B T)]^2} \right\} \rightarrow \left(\frac{1}{qT}\right) \sum_j E_b^{j,c} \frac{k_j(k_j - k_{j,c})}{(k_j + k_{j,c})^2} = \left(\frac{1}{qT}\right) \sum_j \frac{(k_j - k_{j,c})}{(k_j + k_{j,c})} E_A^j, \quad (3)$$

where $E_b^{j,c}$ is the contribution to the bipolaron's binding energy associated with the carrier's interaction with the j th vibrational mode of the softened site [16]. The expression after the arrow in Eq. (3) is obtained at high temperatures, $k_B T > \hbar\omega_j/3$, where hopping can be described semiclassically. In this domain the bipolaron's jump rate is Arrhenius with the activation energy being the sum of contributions from each mode, $E_A^j \equiv E_b^{j,c} [k_j/(k_j + k_{j,c})]$ [16]. The net hopping activation energy in boron carbides is taken to be the high-temperature activation energy of the dc conductivity, 0.17 eV.

As illustrated in Fig. 3, these two extraordinary contributions to the Seebeck coefficient are characterized by distinct temperature dependencies. With increasing temperature, $\alpha_{\text{vibrations}}$ rises with temperature to reach a plateau at a temperature above about half of the phonon temperature. By contrast, $\alpha_{\text{transport}}$ rises with temperature to a peak at about one-third of the phonon temperature and then falls as $1/T$.

Figure 3 shows these contributions for the carrier's interactions with vibrational modes having two different energies. Summing $\alpha_{\text{vibrations}}$ and $\alpha_{\text{transport}}$ yields a temperature dependence that closely resembles boron car-

bides': rising with increasing temperature to a peak, then falling to a temperature-independent plateau. For example, these formulas are used to obtain a fit to our experimental data shown by the solid curve of Fig. 3. This fit uses the parameter values listed in Fig. 3 for the fractional softening of one moderately low frequency mode and six degenerate low-frequency modes. Spreading carriers' interactions with low-energy vibrations over several frequencies rather than approximating them as degenerate could smooth the inflection in the calculated curve near 50 K.

We note the slight increase in boron carbides' Seebeck coefficients at the highest temperatures in Figs. 1 and 3. We associate this effect with the observed [8] thermal dissociation of bipolarons into separated polarons, "pair breaking." Because broken pairs give an extra contribution to the entropy of mixing, pair breaking can increase boron carbides' high-temperature Seebeck coefficients [18].

In summary, we have presented reproducible measurements of boron carbides' Seebeck coefficients as functions of temperature and carbon concentration. The expected variation of boron carbides' Seebeck coefficient with carrier density is augmented by a large contribution

that is insensitive to carrier density. The unusual temperature dependence of this novel contribution suggests its origin lies in boron carbides' bipolaronic holes. Singlet bipolarons can substantially soften vibrational modes with which they interact. Boron carbides' Seebeck coefficients are well described as arising from carrier-induced softening. The large enhancement of boron carbides' Seebeck coefficient enables their functioning as efficient high-temperature thermoelectrics despite having high carrier densities. We speculate that large softening effects may be found in other systems whose localized charge carriers pair among degenerate orbitals of multiatom sites, e.g., aromatic molecular solids or defect-related states in oxides.

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