Thermal conductivity of boron carbides

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Knowledge of the thermal conductivity of boron carbide is necessary to evaluate its potential for high-temperature thermoelectric energy conversion applications. We have measured the thermal diffusivity of hot-pressed boron carbide B_xC samples as a function of composition ($4 \leq x \leq 9$), temperature (300–1700 K), and temperature cycling. These data, in concert with density and specific-heat data, yield the thermal conductivities of these materials. We discuss the results in terms of a structural model that has been previously advanced by two of us (D.E. and C.W.) to explain the electronic transport data. Some novel mechanisms for thermal conduction are briefly discussed.

I. INTRODUCTION

Boron carbides have been utilized extensively in reactor technology for the absorption of thermal neutrons. More recently the high-temperature stability and striking electronic transport properties of these and similar semiconducting material (e.g., the boron-rich borides) have sparked interest in their use for high-temperature thermoelectric energy conversion. We have reported elsewhere[1-4] on the measurement and analysis of the steady-state electronic transport properties of a variety of boron carbides. Here we report on the thermal transport properties of B_xC in the single-phase compositional range $4 \leq x \leq 9$ from 300–1700 K. Previous studies of the thermal conductivity have focused on the single composition B_4C (Refs. 5–8) with the exception of Andryushin *et al.*,[9] who investigated compositions mainly within the two-phase carbon-rich side of B_4C: $x < 4$ in B_xC. They observed a maximum of the thermal conductivity at the B_4C composition. Our interest is in the single-phase region, $4 \leq x \leq 10.4$, containing less carbon.

Over the compositional range $4 \leq x \leq 10.4$, boron carbides are usually viewed as crystallizing in a rhombohedral structure (D_{3d}^5-$R\bar{3}m$), the α-boron structure. This structure consists of deformed icosahedra located at the corners of the rhombohedral unit cell (Fig. 1). As illustrated in Fig. 1, there are direct bonds between the icosahedra. In addition, in α-boron, icosahedra are linked by three-center bonds normal to the trigonal axis. These are not shown in Fig. 1. Rather, Fig. 1 illustrates the situation of the boron carbides in which three-center bond linkages are sometimes replaced by three-atom structural units along the trigonal axis. These are widely thought to be (as illustrated) carbon-boron-carbon chains (CBC).[10] However, carbon-carbon-carbon (CCC) chains have also been suggested.[11] Here the end atoms of the three-atom chain are bonded to three icosahedra in addition to the central member of the

chain. The bonding of the end atom of the chain to three icosahedra plays the role of the three-center bond; it links three icosahedra. For compositions with low carbon content, e.g., B_9C, the three-atom chain may be replaced by a linkage of four boron atoms.[12] Carbon atoms generally reside in the boron carbides as constituents of the three atom chains.[3,10,11,13] They also substitute for boron atoms within the icosahedra.[3,13,14] This structure accommodates to a range of carbon concentrations. In doing this, the unit cell shrinks only slightly with increasing carbon concentration. All compositions within this single-phase region melt at about 2600 K.
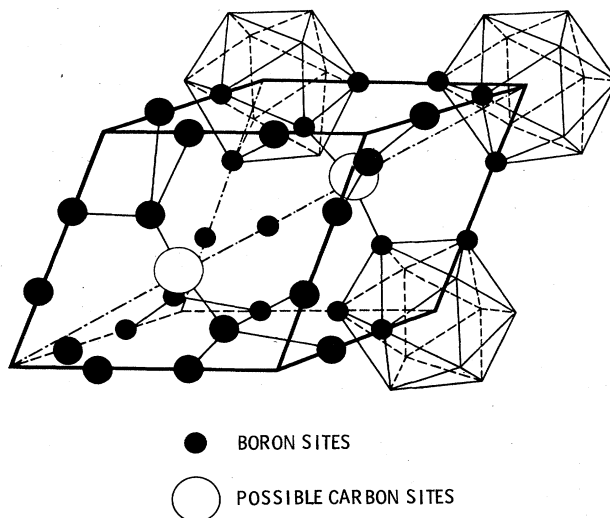

● BORON SITES

◯ POSSIBLE CARBON SITES

FIG. 1. Hypothesized crystal structure for boron carbide. Carbon atoms are distributed among open circles and within icosahedra.

II. EXPERIMENTAL PROCEDURE

The boron carbide specimens of this study were prepared by vacuum $(10^{-6}-10^{-5}$ Torr) hot pressing (~2400 K) at 6000 psi for 2 h using high-purity (B with ~30 ppm and C with ~10 ppm maximum impurities) powders (352 mesh) in boron-nitride-lined graphite dies. Similar samples, examined by x-ray diffraction, were found to be of a single phase. The lattice constants vary with nominal composition in a manner similar to that reported by Bouchacourt and Thevenot.[15]

A heat-pulse method[16,17] was employed to determine the thermal diffusivities. Here a He-Ne laser or xenon flash lamp applies a heat pulse to one side of a sample. An InSb infrared detector or thermocouple measures the temperature rise of the rear surface of the sample. Where necessary, corrections were applied for heat losses and finite pulse times.[18] The apparatus was satisfactorily calibrated against the results of an international program[19] on thermal diffusivity measurements of ASM-5Q graphite.

III. EXPERIMENTAL RESULTS

The thermal diffusivities of various boron carbides (B_xC, with $4 \leq x \leq 9$) are plotted against temperature in Fig. 2. The general consistency of measurements upon progressive heating of the sample ($\triangle$) with those with subsequent successive cooling (∇) indicates the insensitivity of these measurements to thermal cycling. In addition to data on our hot-pressed samples, we include data from commercial sam-
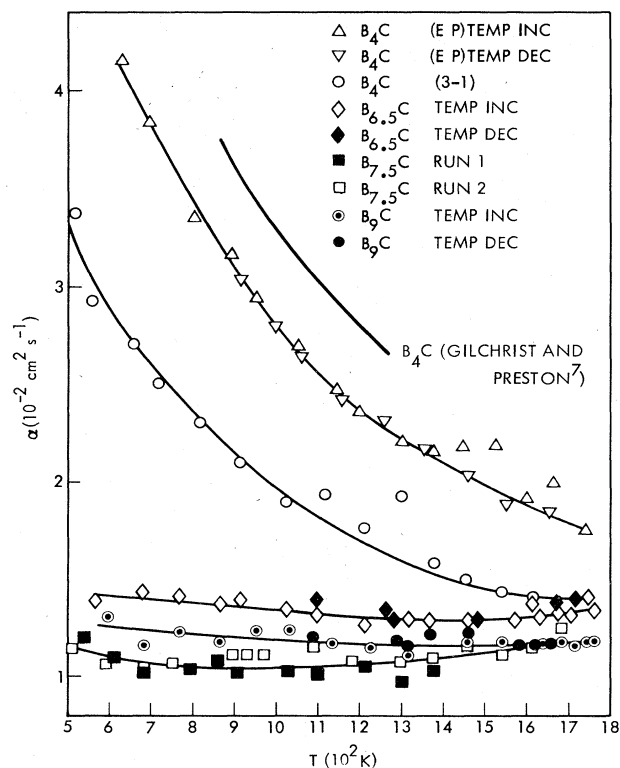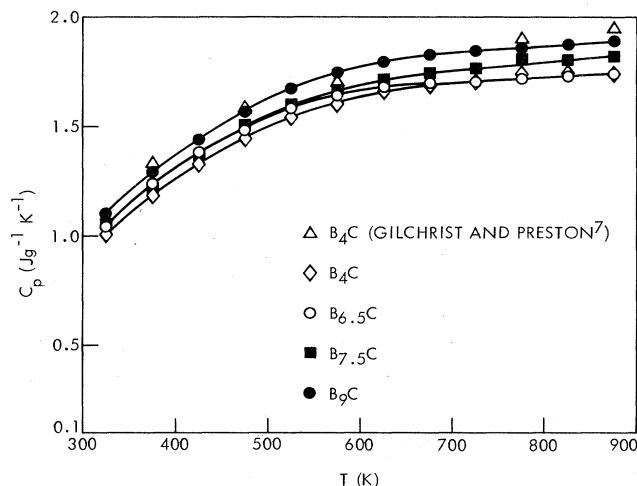

FIG. 3. The specific heat (C_p) of boron carbides vs temperature (T).

ples of B_4C produced by Eagle-Picher (the EP samples), and the data of Gilchrist and Preston[7] on their high-density (2.38 gm cm^3) B_4C sample. We note that the Gilchrist-Preston data on low-density (1.85 gm cm^3) B_4C are almost exactly coincident with our 2.38-gm cm^3 sample results (98% of theoretical density). Furthermore, our samples differ from the Eagle-Picher samples in that ours are reactively hot pressed, while the EP samples are fabricated by hot pressing prefabricated B_4C powders. Gilchrist and Preston's data are typical of a considerable body of data in the literature.[4-8] All of the published data are on commercial-grade material or on material with unspecified preparation. As such, they are poorly characterized. Therefore, we cannot definitively account for the differences in magnitude between the various B_4C samples. We suspect that our samples have less long-range crystalline order. This would account for our lower thermal diffusivities. There are two points we wish to stress. First, although there are significant differences in the *magnitudes* of the thermal diffusivities of various samples of B_4C, the *temperature dependences* of thermal diffusivities of various samples of B_4C are similar to one another. Second, the temperature dependences of the thermal diffusivities of B_4C are quite distinct from those of boron carbides with significantly less carbon, e.g., B_9C.

The specific heats C_p, shown in Fig. 3, were measured by a differential scanning calorimeter (Dupont model 1090), using sapphire as a standard. The thermal conductivities (κ) were obtained from the thermal diffusivities (α), using

FIG. 2. The thermal diffusivity (α) of boron carbides as a function of temperature (T). (EP refers to Eagle-Picher commerical-grade boron carbide.)

TABLE I. Boron carbide densities.

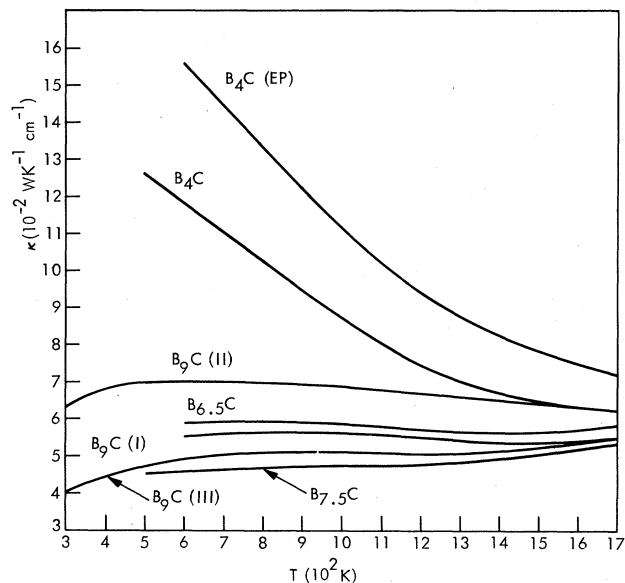| Specimen	Experimental density (g/cm^3)	Percent of the theoretical density
B_4C (EP)	2.44[a]	97
B_4C	2.38	98
$B_{6.5}C$	2.38	96
$B_{7.5}C$	2.48	100
B_9C	2.43	98
B_9C	2.33	94

[a]Average of three samples.

FIG. 4. The thermal conductivity (κ) of boron carbides as a function of temperature (T).

the relationship $\kappa = C_p \alpha \rho$, with C_p being treated as constant above 900 K. The sample densities (ρ) listed in Table I were determined by the Archimedes principle, and are compared with the theoretical values determined by Bouchacourt and Thevenot.[15] No allowance was made for the decrease of density with increasing temperature, since the volume expansion is only of the order of 2%[7] over the whole temperature range studied. This is well within the estimated error of our measurement of thermal conductivity ($\pm 5\%$). The thermal conductivity curves are plotted in Fig. 4. Two further samples of B$_9$C, II and III (excluded from Fig. 2 for clarity), prepared by hot pressing at higher pressures (~ 8000 to 9000 psi) for shorter periods (15 min), are also shown in Fig. 4.[20] As illustrated by both the B$_4$C and B$_9$C samples, the magnitudes of the thermal conductivities depend upon the method of sample preparation. However, despite the sample-to-sample variations, both the magnitudes and temperature dependences of the thermal conductivities vary significantly with composition. This we view to be of the most interest.

IV. DISCUSSION

The electronic transport properties of these boron carbides have been studied in detail.[1–4] It is concluded that the boron carbides are weakly degenerate semiconductors, in which the predominant charge carriers are small bipolarons, which hop between nonequivalent carbon-containing icosahedra (B$_{11}$C). This nonequivalence arises from two sources. First, carbon atoms can be distributed among nonequivalent positions within B$_{11}$C icosahedra. Second, only a fraction of the available intericosahedral chain locations are generally filled by CBC chains. Ideally, at the high-carbon end of the single-phase region B$_4$C, each intericosahedral chain position is filled by a CBC chain, and each

icosahedron contains a single carbon atom B$_{11}$C. Thus, apart from the nonequivalence of the carbon locations within icosahedra, B$_4$C resembles an ideal crystal.

The present thermal-conductivity study also supports this view. As shown in Fig. 4, at the highest carbon concentration B$_4$C, the thermal conductivity is not only at its largest, but is also a decreasing function of temperature. By contrast, with lower carbon concentrations, the thermal conductivities are much smaller, with much weaker temperature dependences. The lower weakly temperature-dependent thermal conductivities of samples with low carbon concentrations are similar to those of glasses (e.g., fused quartz). However, the thermal conductivities of the B$_4$C samples have temperature dependences characteristic of a crystal. This is consistent with the view that at the B$_4$C composition all available intericosahedral chain positions are filled by CBC chains. At lower carbon concentrations only a fraction of the available chain locations are filled. Since these carbon-containing intericosahedral chains are relatively stiff, the absence of such structural units should affect the thermal conductivity. In particular, thermal transport through such a defect structure should resemble that through a disordered material.

Further support for this interpretation is found in studies of neutron-irradiated B$_4$C. Namely, neutron irradiation has been reported to disrupt the intericosahedral chains, producing disorder of the type we envision in samples of low carbon content.[21] Gilchrist and Preston report that upon neutron irradiation[7] the thermal conductivity of B$_4$C comes to resemble that of our samples of low carbon concentration. This is, indeed, what we would expect.

The thermal conductivity of these solids arises from two sources. First, even in the absence of charge carriers, heat is transferred directly between atoms of the solid. Second, the motion of a charge carrier through a solid can also be associated with a heat flow. In the boron carbides, the electronic transport represents a very distinctive type of small-polaron hopping.[1–4] The associated thermal conductivity is distinctive as well. In particular, vibrational energy is transported with a charge carrier as it hops between nonequivalent sites. The average energy carried with a hopping carrier, E_T, is $C(kT)^2$, where the constant C is defined by $C = zJ^2/16E_b^3$, z is the number of nearest neighbors, J is the intersite transfer energy, and E_b is the small bipolaron binding energy characterizing an average B$_{11}$C icosahedron. Thus, the transported energy increases with temperature. Preliminary considerations indicate that the electronic contribution to the thermal conductivity is a product of this energy E_T, the electronic diffusion constant D, and the rate of change of the carrier density with temperature (dn/dT), i.e., $\kappa_T = E_T D(dn/dT)$. This yields a very small electronic contribution to the thermal conductivity, which increases with temperature and is ~ 15 mW/K cm at 1600 K. This is about one-third of the lowest measured value of the total thermal conductivity. Hence, we ignore the electronic contribution to the thermal conductivity relative to the lattice contribution.

Finally, we note that the random removal of the (stiff) intericosahedral chains should greatly alter the nature of the lattice contribution to the thermal conductivity. In particular, in this situation, a significant fraction of the vibrational modes becomes localized. In a purely harmonic system, these modes will not participate directly in the passage of vibrational energy. However, anharmonic forces provide a

means of transferring energy between local and nonlocal vibrational modes. This facilitates the thermal transport.[22,23] Hence, contrary to customary (phonon scattering) treatments of thermal conductivity, the thermal conductivity increases as the anharmonic coupling strength increases. While such behavior has been shown in theoretical models,[22,23] it has not heretofore been reported in actual solids. The boron carbides B_xC, of low carbon concentrations (e.g., $x = 9$–6.5), may be examples of this distinctive type of thermal transport. We are currently investigating whether or not the observed behavior is attributable to such anomalous thermal transport.

[1]C. Wood and D. Emin, Phys. Rev. B **29**, 4582 (1984).

[2]D. Emin and C. Wood, in *Proceedings of the 18th Intersociety Energy Conversion Engineering Conference, Aug. 21–26, 1983, Orlando, FL* (American Institute of Chemical Engineers, New York, 1983), Vol. 1, pp. 222–225.

[3]D. Emin, G. A. Samara, and C. Wood, in Proceedings of the 17th International Conference on the Physics of Semiconductors, San Francisco, CA, Aug. 6–10, 1984 (unpublished).

[4]D. Emin, G. A. Samara, L. J. Azevedo, E. L. Venturini, H. H. Madden, G. C. Nelson, J. A. Shelnutt, B. Morosin, M. Moss, and C. Wood, in *Proceedings of the Eighth International Symposium on Boron, Borides, Nitrides, and Related Compounds* [J. Less-Common Met. (to be published)].

[5]H. W. Deem and C. F. Lucks, Battelle Memorial Institute Report No. BMI-731, 1951 (unpublished); Nucl. Sci. Abstr. **6**, 915 (1952).

[6]J. C. Hedge, C. Kostenko, and J. I. Lang, Illinois Institute of Technology Research Institute, Technical Documentary Reports No. ASD-TDR-63-597 and No. AD-424375, 1963 (unpublished); Chem. Abstr. **61**, 10422d, (1964).

[7]K. E. Gilchrist and S. D. Preston, High Temp.-High Pressures **11**, 643 (1979).

[8]D. E. Mahagin, J. L. Bates, and D. E. Baker, Hanford Engineering and Development Laboratory Report No. HEDL-TME 73-78, 1973 (unpublished).

[9]A. I. Andryushin, R. A. Belyaev, Yu. V. Vavilov, M. S. Kvashnevskaya, and R. S. Lishanskaya, Inzh. Fiz. Zh. **32**, 414 (1977) [J. Eng. Phys. **32**, 254 (1977)].

[10]G. Will and K. H. Kossobutzki, J. Less-Common Met. **47**, 43 (1976).

[11]K. H. Clark, and J. L. Hoard, J. Am. Chem. Soc. **65**, 2115 (1943).

[12]H. L. Yakel, Acta Crystallogr. B **31**, 1797 (1975).

[13]W. N. L. Lipscomb, J. Less-Common Met. **82**, 1 (1981).

[14]E. L. Muetterties, *The Chemistry of Boron and its Compounds* (Wiley, Chichester, 1967), p. 57.

[15]J. Bouchacourt and F. Thevenot, J. Less-Common Met. **82**, 227 (1981).

[16]W. J. Parker, R. J. Jenkins, C. P. Butler, and G. L. Abbott, J. Appl. Phys. **32**, 1679 (1961).

[17]R. E. Taylor, High Temp.-High Pressures **11**, 43 (1979).

[18]R. C. Heckman, J. Appl. Phys. **44**, 1455 (1973).

[19]M. L. Minges, Int. J. Heat Mass Transfer **17**, 1365 (1974).

[20]From thermal-diffusivity data supplied by R. E. Taylor, Purdue University, and confirmed by JPL, using the flash method. An absolute determination of thermal conductivity by G. Slack, General Electric Corporate Research and Development, yielded a fairly temperature-independent value of $\sim 0.068 \pm 0.002$ W/K cm for B_9C in the vicinity of room temperature in essential agreement with B_9C (II).

[21]C. W. Tucker and P. Senio, Acta Crystallogr. **8**, 371 (1955).

[22]D. N. Payton, M. Rich, and W. M. Visscher, Phys. Rev. **160**, 706 (1967).

[23]D. N. Payton, M. Rich, and W. M. Visscher, in *Localized Excitations in Solids*, edited by R. F. Wallis (Plenum, New York, 1968), p. 657.