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THERMAL CONDUCTIVITY BEHAVIOR OF BORON CARBIDES

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ABSTRACT

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 \( B_{1-x}C_x \) samples as a function of composition \( (0.1 \leq x \leq 0.2) \), temperature \( (300 \text{ K to 1700 K}) \) and temperature cycling. These data in concert with density and specific heat data yield the thermal conductivities of these materials. We discuss these results in terms of a structural model that has been previously advanced by two of us (D.E. and C.W.) to explain the electrical transport data. Some novel mechanisms for thermal conduction are briefly discussed.

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 1,2 on the measurement and analysis of the steady-state electrical transport properties of a variety of boron carbides. Here we report on the thermal transport properties of \( B_{1-x}C_x \), in the single-phase compositional range \( 0.1 \leq x \leq 0.2 \) from 300 K to 1700 K. Previous reports 3-7 on the thermal transport properties of boron carbides have concentrated solely on the composition \( B_{0.8}C_{0.2}(B_4C) \).

Over the compositional range \( 0.088 \leq x \leq 0.200 \) boron carbides are usually viewed as crystallizing in a rhombohedral structure (\( D_3d5\overline{m}3m \)), the \( \alpha \)-boron structure, with deformed icosahedra shared at the corners of the unit cell. A structural unit links icosahedra along a cell diagonal. These units are either three-atom chains 8,9 or bridged four-boron atom linkage. 10 Carbon atoms are distributed among the icosahedra and the three-atom chains. 8,9 With increasing carbon content the unit cell shrinks slightly. The melting points of compositions within this single-phase region are about 2600 K.

**EXPERIMENTAL PROCEDURE**

In this study most boron carbide specimens, \( B_{1-x}C_x \), in the single phase regime, \( 0.088 \leq x \leq 0.200 \) were prepared having differing boron to carbon ratios by vacuum (\( 10^{-6} \) to \( 10^{-5} \) torr) hot-pressing (\( \sim 2400 \) K) at 600 psi for two hours using high-purity (B –30 ppm; C –10 ppm maximum impurities) powders (\( \sim 325 \) mesh) in boron-nitride lined graphite dies. Similar samples, examined by X-ray diffraction, were found to be single-phase with lattice constants varying with composition essentially in the manner reported by Bouchacourt and Thevenot. 11

A heat pulse method 12,17 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. 13 The apparatus was satisfactorily calibrated against the results of an International program 14 on thermal diffusivity measurements of ASM-5Q graphite.

**EXPERIMENTAL RESULTS**

The thermal diffusivities of various boron carbides, \( B_{1-x}C_x \),
with compositions \(0.1 \leq x \leq 0.2\) lying within the single-phase region are plotted against temperature in Fig. 1. The general consistency of measurements upon progressive heating of the sample (Temp Inc) with those with subsequent successive cooling (Temp Dec) indicates the insensitivity of these measurements to thermal cycling. Measurements of differently prepared samples of \(B_{0.8}C_{0.2}\) (\(B_4C\)) are also compared in Fig. 1. Here significant differences in the magnitudes of the thermal diffusivities are found. Nonetheless, the temperature dependences of these thermal diffusivities are similar to one another.

The thermal conductivities \((K)\) were obtained from the thermal diffusivities \((\alpha)\) using the relationship \(K = \alpha C_p\), where the specific heat, \(C\), was obtained from the Elwell\(^{15}\) curves in Fig. 2 with \(C\) being treated as constant above 900 K. The sample densities \(\rho\) listed in Table 1 were determined by Archimedes principle and are compared to the theoretical values determined by Bouchacourt and Thevenot.\(^{11}\) These thermal conductivity curves referred to the theoretical densities, are plotted in Fig. 3. Two further samples of \(B_{0.9}C_{0.1}\), i.e., \(B_9C\), (not shown in Fig. 1 for reasons of space) prepared by hot-pressing at higher pressures (-8000 to 9000 psi) for shorter periods (15 min) are also shown for comparison in Fig. 3. As illustrated both by the \(B_{0.8}C_{0.2}\) and \(B_{0.9}C_{0.1}\) samples, the magnitudes of the thermal conductivities depend upon the method of sample preparation. In addition, the thermal conductivity manifests a significant compositional dependence. Here both the magnitude and temperature dependence of the thermal conductivities vary significantly with composition.

**Table 1. Boron Carbide Densities**

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Experimental Density (gm/cm(^3))</th>
<th>Percent Theoretical Density (gm/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(B_4C) EP</td>
<td>2.44(^a)</td>
<td>97</td>
</tr>
<tr>
<td>(B_4C) 3-1</td>
<td>2.38</td>
<td>98</td>
</tr>
<tr>
<td>(B_6.5C(143-1))</td>
<td>2.38</td>
<td>96</td>
</tr>
<tr>
<td>(B_7.5C(144-1))</td>
<td>2.48</td>
<td>100</td>
</tr>
<tr>
<td>(B_9C(147-1))</td>
<td>2.43</td>
<td>98</td>
</tr>
<tr>
<td>(B_9C(20-1))</td>
<td>2.33</td>
<td>94</td>
</tr>
</tbody>
</table>

\(^a\)Average of three samples.
It should be noted that we have utilized Elwell's specific heat data since his samples, while not ours, were prepared in a manner similar to ours. However, even if the specific heat were to differ substantially, (i.e., be such as those of Gilchrist and Preston of Fig. 2) the fall of the thermal conductivity of the $B_0.8C_{0.2}$ with increasing temperature would only be somewhat milder than that shown in Fig. 3. In fact, as shown in Fig. 3, the thermal conductivity of our $B_0.8C_{0.2}$ falls with increasing temperature in a manner similar to that found by other researchers.

DISCUSSION

The electrical transport properties of these boron carbides have been studied in detail. It is concluded that the boron carbides are nearly degenerate semiconductors in which the predominant charge carriers (holes) form small polarons and hop between inequivalent positions in the solid. The dependence of the Seebeck coefficient on carbon concentration suggests that the holes hop between sites associated with carbon atoms. In this
Fig. 3. The Thermal Conductivity (K) of Boron Carbides as a Function of Temperature (T)
case the inequivalence of hopping sites corresponds to jumps between chains and icosahedra. Thus carbon atoms occupy these two types of sites at all carbon compositions within the single-phase region. This contradicts the idea of some that $x = 0.133 \left( B_{13}C_2 \right)$ represents an "ideal" composition in which two carbon atoms reside on each intericosahedral chain, with the icosahedra remaining devoid of carbon atoms. The present thermal conductivity studies also supports the view that carbon atoms generally occupy both kinds of sites.

As shown in Fig. 3, the high temperature thermal conductivities of the boron carbides are generally moderately low ($\sim 0.1 \text{ to } 0.01 \text{ W/K-cm at } 1000 \text{ K}$). At the highest carbon concentrations, $x = 0.200 \left( B_{10}C \right)$ the thermal conductivity is not only at its largest but also is a decreasing function of increasing temperature. At lower carbon concentrations, $x = 0.100, 0.133$ and $0.176$, the thermal conductivities are much smaller with much weaker temperature dependences. The smaller weakly temperature dependent thermal conductivities of these materials with lower carbon concentrations are similar to those of glasses (e.g., silica). However the thermal conductivity of the high-carbon concentration material ($x = 0.200, B_{10}C$) is characteristic of the lattice thermal conductivity of a crystal. This suggests that at the high carbon concentration carbon atoms occupy all available sites. In this situation the thermal transport should be that of a well ordered crystal. At lower carbon concentrations the carbon atoms occupy only a fraction of the available locations. The thermal transport through such a defect structure then resembles that through a disordered material. The fact that the thermal transport through the $x = 0.133$ composition ($B_{13}C_2$) resembles that through an amorphous structure belies this being an "ideal" composition with only chains being occupied by carbon atoms. Thus both the electronic and thermal transport suggests a consistent picture of the carbon occupancy of the boron carbides.

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. The associated thermal conductivity is distinctive as well. In particular, vibrational energy is transported with a charge carrier as it hops between inequivalent sites. The average energy carried with a hopping carrier, $E_T$, is $C \Delta T^2$, where the constant $C$ is defined by $C = \frac{\pi^2 k_B^2}{16E_b^3}$, $\Delta$ is the number of nearest neighbors, $J$ is the intersite transfer energy and $E_b$ is the small-polaron binding energy characterizing an average site in the material. Thus the energy carried 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., $\kappa_T = E_TD(dn/dT)$. This yields an 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 value we measure.

Finally we note that the disorder in the masses and spring constants associated with carbon atoms being distributed among distinct sites can greatly alter the nature of the lattice contribution to the thermal conductivity. In particular, in this situation a significant fraction of the vibrational modes become 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. 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, it has not, heretofore, been reported in actual solids. The boron carbides, $B_{1-x}C_x$, of low carbon concentrations (e.g., $x = 0.100, 0.133$ and $0.176$) may be examples of this distinctive type of thermal transport. We are currently investigating this possibility further.

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REFERENCES

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18. Data supplied by D. Elwell, Stanford University, using a Dupont Differential Scanning Calorimeter.

19. 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, G. E. Research yielded a fairly temperature independent value of $-0.068 \pm 0.002$ W/K-cm for $B_{0.9}C_{0.1}$ in the vicinity of room temperature in essential agreement with $B_{0.9}C_{0.1}$ (20-1).