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Isotope effects on thermal diffusivity of boron carbide

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Abstract

Thermal diffusivities for the isotope-enriched samples, which are $^{10}B_4\,^{12}C$, $^{10}B_4\,^{13}C$, $^{11}B_4\,^{12}C$ and $^{11}B_4\,^{13}C$, were measured by laser flash method over the temperature range from 290 to 1770 K. Thermal conductivity decreased with the molar weight of boron carbide. The heat transfer in boron carbide is considered to be mainly caused by acoustic phonons. As heavier isotopes were substituted for lighter ones, the phonon velocity in B_4C decreased and so did the thermal conductivity. Consequently, total heat transfer by phonons is thought to decrease with molar weight. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Isotope effect; Thermal diffusivity; Thermal conductivity; Boron carbide

1. Introduction

Boron carbide (B_4C) is used as the many functional materials, such as the neutron absorber with large neutron cross-section of ^{10}B in a nuclear reactor, the anticorrosion and refractory material at high temperature with high hardness and high melting temperature. Recently, B_4C and its composite have been expected as the thermoelectric materials, which transform thermal energy directly to electrical energy at high temperatures. The wide application and high efficiency of B_4C are due to its large thermoelectrical figure of merit Z,

$$Z = \alpha^2 \frac{\sigma}{\kappa}, \tag{1}$$

where α is the Seebeck coefficient, κ the thermal conductivity and σ the electrical conductivity. Thermal conductivity in Eq. (1) is represented by Eq. (2) with heat capacity C_p, thermal diffusivity a and density ρ,

$$\kappa = C_p\, a\, \rho. \tag{2}$$

Therefore, thermal diffusivity or thermal conductivity is one of the key quantities to evaluate the figure of merit for thermoelectricity. The dependence of thermal conductivity of B_4C on the concentration of ^{10}B isotope was measured at 350 K by Karumidze and Shengelia [1] and the increase in the thermal conductivity was reported to be remarkable at higher concentration region of the ^{10}B isotope. They concluded that as the average boron mass decreases the bonding energy per unit mass increases therefore, the thermal conductivity increases. However the origin of the boron isotope effect has not been clear and the effect of carbon isotope has not been studied.

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In the present study, the thermal diffusivities for the isotope-enriched samples, which are $^{10}B_4{}^{12}C$, $^{10}B_4{}^{13}C$, $^{11}B_4{}^{12}C$ and $^{11}B_4{}^{13}C$, were measured over a wide range of temperatures from 290 to 1770 K to discuss the isotope effect of B and C for the thermal conductivity in boron carbide.

2. Experimental

2.1. Sample preparation and characterization

The powders of enriched ^{10}B (99.75%) and ^{11}B (99.52%) supplied by Trace Sciences International (Canada) and ^{12}C (99.9%) and ^{13}C (99.2%) supplied by ISOTEC (USA) were used for the sample preparation. Disk samples, with diameter of 10 mm, thickness of approximately 1.8 mm and very high (more than 99%) relative theoretical densities, were prepared by spark plasma sintering method (SPS-520S, Sumitomo Coal Mining) under the pressure of 37 MPa at 2273 K for 30 min in argon atmosphere. The sample densities are summarized in Table 1. The phases of samples were identified by X-ray diffraction analysis and diffraction peaks of B_4C were only observed for each sample.

2.2. Thermal diffusivity measurement

Thermal diffusivities of $^{n}B_4{}^{m}C$ (n=10 or 11, m=12 or 13) samples were measured by laser flash method (LF/TCMFA8510SP4, Rigaku) from 290 to 1770 K. The thermal diffusivity measurements were carried out three times at each temperature step in a vacuum of less than 2×10^{-4} Pa. The thermal diffusivities of the samples were determined from the rear-surface temperature responses of samples, which were measured by an In–Sb infrared detector, by using logarithmic method [2].

Table 1
Boron carbide densities

Specimen	Experimental density (g/cm^3)
$^{10}B_4{}^{12}C$	2.28
$^{10}B_4{}^{13}C$	2.34
$^{11}B_4{}^{12}C$	2.48
$^{11}B_4{}^{13}C$	2.53

Heat capacities of each samples were measured with a differential scanning calorimeter (DSC-220, Seiko Instruments, Japan) installed in a globe box over the temperature range from 300 to 700 K in a argon gas flow. As the reference material for the heat capacity measurement, a NBS Al_2O_3 pellet was used.

3. Results and discussion

The thermal diffusivities of $^{10}B_4{}^{12}C$, $^{10}B_4{}^{13}C$, $^{11}B_4{}^{12}C$ and $^{11}B_4{}^{13}C$ pellets are shown in Fig. 1 with the data of Glichrist and Preston for natural B_4C [3]. Thermal diffusivity decreases with temperature, as was expected. The difference in the molar heat capacities between the lightest $^{10}B_4{}^{12}C$, and the heaviest $^{11}B_4{}^{13}C$ was obtained to be small in our preliminary results. Therefore, the thermal conductivities were calculated by Eq. (2) using the heat capacity value that was previously measured for the natural B_4C sample in our laboratory [4], assuming the negligibly small isotope effect on the heat capacity. Since the theoretical density (TD) of each sample was almost the same, the density normalization of thermal conductivity was not carried out. As shown in Fig. 2, the thermal conductivity of each sample increases as the

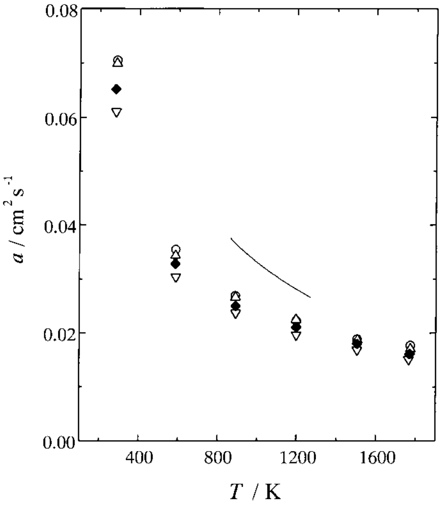

Fig. 1. Thermal diffusivity of boron carbide. $^{10}B_4{}^{12}C$ (○), $^{10}B_4{}^{13}C$ (△), $^{11}B_4{}^{12}C$ (▽), $^{11}B_4{}^{13}C$ (◆), [3] (—).

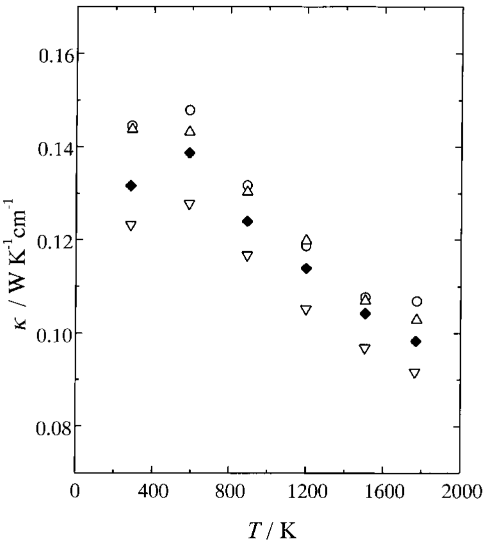

Fig. 2. Thermal conductivity of boron carbide. $^{10}B_4{}^{12}C$ (○), $^{10}B_4{}^{13}C$ (△), $^{11}B_4{}^{12}C$ (▽), $^{11}B_4{}^{13}C$ (◆).

temperature below 400 K and then decreases above 500 K. Since the Debye temperature of boron carbide is 750 K [5], the decrease of thermal conductivity in boron carbide is considered to be caused by the collision of the phonon. In order to make clear the isotope effect on the thermal conductivity, the thermal conductivities at 290 and 1770 K against molar weight of B_4C are shown in Fig. 3 with the data of Karumidze and Shengelia [1] for B_4C at 350 K with several boron-isotope ratios. It is seen from Fig. 3 that the thermal conductivity κ depends on the molar weight of boron carbide and decreases with the molar weight. The molar weight dependences on thermal conductivity at 290 and 1770 K in this study are similar and they are smaller than that of Karumidze and Shengelia [1].

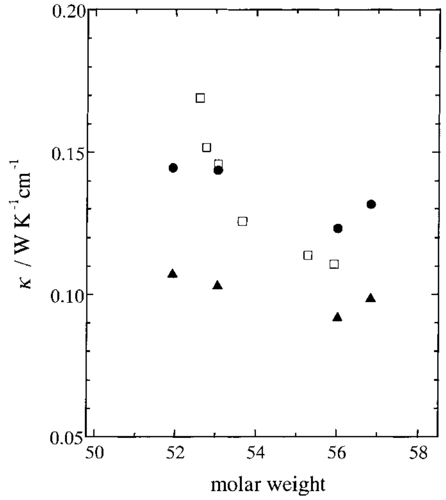

Fig. 3. Molar weight dependence on thermal conductivity: at 290 K (this study) (●), at 1770 K (this study) (▲), at 350 K [1] (□).

The crystal structure of B_4C belongs to rhombohedral, which can be also treated as hexagonal. This structure consists of deformed icosahedra located at the corners of the rhombohedral unit cell. In addition, icosahedra are linked by three-center bonds normal to the trigonal axis. The icosahedra and three-atom bond are generally thought to be $B_{12}C$ icosahedra and carbon–boron–carbon chains (CBC), respectively [6]. Here the end atoms in the three-atom chain are bonded to three icosahedra in addition to the central member of the chain. The bonding of the end atom in the chain to three icosahedra plays the role of the three-center bond; it links three icosahedra. Since the electronic contribution to the total thermal conductivity of B_4C is very small, the relative electronic contribution to the thermal conductivity may be ignored [7]. In general, phonon–phonon scattering (Umklapp process) and phonon–impurity (substituted impurity) scattering are dominant mechanisms of thermal resistance in ceramics above room temperature. The heat transfer in boron carbide is considered to be mainly caused by acoustic phonons. The heat transfer by phonons in ceramics depends on the average phonon velocity, which is thought to be approximately equal to the velocity of sound in ceramics, and the phonon mean free path. The velocity of sound in ceramics decreases with atomic weight [8], and this supposes that the average phonon velocity decreases with atomic weight. This decrease of phonon velocity may cause the decrease of thermal conductivity in ceramics and total heat transfer by phonons may decrease with molar weight of boron carbide. The difference between the molar weight dependences on thermal conductivity in this study and that of Karumidze and Shengelia [1] is thought to be caused by the isotope effect of carbon isotopes which consists the three-center bonds and links three icosahedra. The thermal conductivity of $^{11}B_4{}^{13}C$ seems to be larger than that of $^{11}B_4\,^{12}C$ in Fig. 3. The mechanism of isotope effects on the thermal conductivity of boron carbide is not clear at moment.

4. Conclusions

The thermal diffusivities of several boron carbides (B_4C) which consist of enriched boron and carbon isotope, were measured by laser flash method in the temperature range from 290 to 1770 K. The thermal conductivities were calculated from the thermal diffusivities, the heat capacities of our previous paper and the densities. The thermal conductivities decreased with molar weight of B_4C. The decrease of the thermal conductivity may be caused by the decrease of phonon velocity, which may be due to the substitution of heavy isotopes for light ones.

Acknowledgements

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