Thermoelectric Properties of Hot-pressed Boron Suboxide (B_6O)

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Boron suboxide (B_6O) sintered bodies were prepared by a solid state reaction and a hot pressing method. The thermoelectric properties of B_6O were compared with those of B_4C . The electrical conductivity was smaller than that of B_4C , and the Seebeck coefficient was twice as large as that of B_4C indicating p-type conduction. The hopping conduction of electronic charge carriers was suggested from the temperature dependencies of the electrical conductivity and mobility. The thermal conductivity was greater than that of B_4C . The thermoelectric dimensionless figure-of-merit increased with increasing temperature, and was 0.62×10^{-3} at 1000 K. This value was almost in agreement with that of B_4C .

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1. Introduction

Boron-rich borides are promising as high-temperature thermoelectric materials. They have moderately high electrical conductivity, anomalously large Seebeck coefficient and low thermal conductivity as have been reported for boron carbide,¹⁻⁶⁾ α - AlB_{12} ^{7,8)} and $B_{12}Si$.⁹⁾

Among these boron-rich borides, boron carbide has been most widely studied. Figure 1 illustrates schematic crystal structures of B_4C and B_6O . Boron carbide consists of B_{12} or $B_{11}C$ icosahedrons at the vertices of a rhombohedral unit cell and three-atom chain of CBC or CBB at the center of the rhombohedron.¹⁰⁻¹⁶⁾ Boron carbide has a wide non-stoichiometric composition region from B_4C to $B_{10.5}C$ with different B to C ratio in the icosahedrons and three-atom chains.^{12,14,16)} Carbon-saturated boron carbide, B_4C ($B_{12}C_3$), consists of $B_{11}C$ icosahedrons and CBC three atomic chains ($B_{11}C$ -CBC).^{11,12,14)} It is well-understood that the thermoelectric properties of boron carbide change depending on the non-stoichiometric composition. The structure and properties of $B_{13}C_2$ has been particularly investigated in detail because $B_{13}C_2$ has greatest thermoelectric performance.³⁾ These boron carbides are p-type semiconductor, and the bipolaron hopping between $B_{11}C$ icosahedrons has been proposed to explain the large p-type Seebeck coefficient and small carrier mobility.^{17,18)}

On the other hand, boron suboxide (B_6O) consists of B_{12} icosahedrons and O-O two-atom chain¹⁹⁻²¹⁾ as shown in Fig. 1(b). The structure of B_6O is almost the same as that of B_4C except that (1) the icosahedrons are pure B_{12} , and (2) O-O two-atom chains exist at the center of rhombohedrons. There is neither complicated substitution nor wide-ranged non-stoichiometry in B_6O . Therefore, it is useful to understand not only the characteristics of B_6O but also that of B_4C by comparing B_6O and B_4C .

Table 1 summarizes the research on B_6O published in the

(1) B_4C

(2) B_6O

Fig. 1 Crystal Structure of (1) B_4C and (2) B_6O .

past. The preparation method of B_6O is classified into three categories as shown in Table 1: (1) solid state reaction between B and B_2O_3 , (2) reduction of B_2O_3 and (3) oxidation of B. The high vapor pressure of B_2O_3 at elevated temperatures would cause the B excess composition in the process of (1). The reductants such as Si or Mg would often remain in B_6O as an impurity in the process (2). The oxidant such as ZnO would contaminate B_6O in the process (3). Several researchers have reported the crystal structure^{19-25,30,31)} and some mechanical properties^{26,30,32,36)} of B_6O . Since B_6O is strong covalent nature and easy to decompose at high temperature more than 1973 K,²³⁾ dense B_6O bodies can be hardly obtained. In the present study, moderately dense B_6O bodies were prepared by a hot-pressing method. Their electrical conductivity, Seebeck coefficient and thermal conductivity were

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Table 1 Literature data of boron suboxides (in chronological order).

Methods	Raw materials	Evaluated properties	Ref.
No detail	No detail	a, b, c, d_{hkl}	22)
Solid state reaction	B + B ₂ O ₃ , B ₂ O ₃ + Si	$a, b, c, d_{hkl}, I/I_0$	23)
Solid state reaction	B + B ₂ O ₃	$a, b, c, d_{hkl}, I/I_0$	24)
Fusion, Plasma arc	B ₂ O ₃ + Mg, B + B ₂ O ₃	$a, b, c, d_{hkl}, I/I_0$	25)
Hot press	No detail	Mechanical properties, κ	26)
Hot press	B + B ₂ O ₃ , B + ZnO	Reaction, Sinterability	27)
Hot press, Solid state reaction	B + B ₂ O ₃	Crystal structure	19)
Oxidation	B + ZnO	Crystal structure	20)
Hot press	B + B ₂ O ₃	Thermodynamic properties	28)
No detail	No detail	Thermoelastic properties	29)
Solid state reaction	amo.-B + ZnO	Crystal structure	21)
Reaction sintering	amo.-B, α -B, B ₂ O ₃	Crystal structure, Bulk Modulus	30)
Solid state reaction	amo.-B, α -B, B ₂ O ₃	Crystal structure	31)
Plasma deposition	B target	Hardness	32)
Solid state reaction	¹⁰ B, ¹¹ B, B(OH) ₃ , etc.	Raman spectra	15)
HP-HT synthesis	B + B ₂ O ₃	Morphology, Structure	33)
HP-HT synthesis	B + B ₂ O ₃	Morphology, Structure	34)
HP-HT synthesis	B + B ₂ O ₃	Morphology, ΔG_f	35)
Solid state reaction, Sintering	B + ZnO	Mechanical Properties	36)
Pulsed laser deposition	B + B ₂ O ₃	Infrared spectra, Raman spectra	37)
Pulsed laser deposition	B + B ₂ O ₃	TEM, SEM	38)
High-pressure sintering	(B + B ₂ O ₃) + c-BN	Mechanical Properties	39)
High-pressure sintering	(B + B ₂ O ₃) + B ₄ C	Mechanical Properties	40)

a, b, c : Lattice parameters, d_{hkl} : interplanar spacing, I/I_0 : Relative diffraction intensity, κ : Thermal conductivity, amo.: Amorphous, HP-HT synthesis: High-pressure, high-temperature synthesis, ΔG_f : Gibbs energy of formation, TEM: Transmission electron microscope, SEM: Scanning electron microscopy.

investigated, and were mainly compared with those of B₄C having similar porosity of B₆O.

2. Experimental Procedure

β -B powder (High purity Chemical Laboratory, 99%) and amorphous B₂O₃ powder (Wako Pure Chemical, 99%) were mixed in the molar ratio of 10:1 (B:O = 4:1) under the B₂O₃ excess condition. The mixed powder was pressed into disk-shaped pellets at 30 MPa, and reacted at 1673 K for 14.4 ks in flowing Ar gas. The pellets were pulverized and heated again at the same condition. This procedure was repeated several times and obtained B₆O powder in single phase, and the remaining B₂O₃ was carefully removed by this heat treatments. The B₆O powder was hot-pressed at 1873 K, 62 MPa for 18 ks in flowing Ar gas with being covered by BN powder to avoid the reaction between B₆O powder and a carbon mold.

Powder X-ray diffraction was carried out to determine the phase and lattice parameters. Pycnometry in distilled water was used to measure the density of B₆O powder. An Archimedian method was applied to determine the porosity of B₆O sintered bodies.

Hot-pressed B₆O bodies were cut into three sizes for measurement ($3 \times 3 \times 12 \text{ mm}^3$ for Seebeck coefficient and electrical conductivity, $\phi 10 \times 1.5 \text{ mm}^3$ for thermal conductivity, and $3 \times 6 \times 0.5 \text{ mm}^3$ for Hall coefficient). The Seebeck coefficient (α) was determined from the slope of the linear relationship between thermoelectric power and temperature difference in Ar gas at 300 to 1000 K. The electrical conductivity (σ) was

measured by a d.c. four-probe method in Ar gas at 300 to 1000 K. The Hall coefficient measurement was carried out by a Van der Pauw method in vacuum at 300 to 1000 K. The thermal conductivity (κ) was measured by a laser flush method (TC-7000, Shinku Riko) in vacuum at 290 to 1060 K.

The figure-of-merit (Z) was calculated using eq. (1) from Seebeck coefficient (α), electrical conductivity (σ) and thermal conductivity (κ).

$$ZT = \alpha^2 \sigma T / \kappa. \quad (1)$$

3. Results and Discussion

Figure 2 presents the powder X-ray diffraction pattern for a hot-pressed B₆O body. Every peak was identified as B₆O and no trace of B₂O₃ was observed. The lattice parameters of B₆O were determined as $a = 0.538 \text{ nm}$ and $c = 1.233 \text{ nm}$ (in hexagonal expression), and the density of B₆O (ρ_{obs}) was 2.587 Mg m^{-3} , meaning the porosity of 33%. Rizzo *et al.*²³⁾ reported that B₆O evaporated significantly at more than 1973 K. The high vapor pressure of B₂O₃ which formed by the decomposition of B₆O into B and B₂O₃ could be a main reason for the difficulty of sintering.

Figure 3 shows the temperature dependence of the Seebeck coefficient for the hot-pressed B₆O, comparing with that of B₄C^{1,3-6)} whose porosity is indicated in parentheses. Significant effect of density on the Seebeck coefficient was not observed. The positive Seebeck coefficient of B₆O means that the carrier in B₆O is hole. The Seebeck coefficient of B₆O increased with increasing temperature. The Seebeck coefficient

Fig. 2 Powder X-ray diffraction pattern of hot-pressed B_6O . Fig. 3 Temperature dependence of Seebeck coefficient for hot-pressed B_6O . (Numerals in parentheses mean porosity of the specimens).

cient of B_6O was twice as great as that of B_4C and reached to $500 \mu VK^{-1}$ at 1000 K. Although the Seebeck coefficient of some B_4C was independent of temperature, it generally increased with increasing temperature. Wood *et al.*¹⁾ proposed a model to explain the temperature dependence of B_4C using small polaron hopping conduction mechanism, and gave eq. (2).

$$\alpha = (T\Delta S + E_T)/qT = A + BT \quad (2)$$

where ΔS is average charge of entropy, E_T the average vibrational energy, q the charge of carrier, and A and B constants. The temperature dependence of Seebeck coefficient for B_6O may be explained by eq. (2). This might be also verified by small mobility as shown later.

Figure 4 shows the temperature dependence of electrical conductivity for the hot-pressed B_6O and B_4C .^{1,3,5,6)} The electrical conductivity of B_6O was $1.1 \times 10^2 \text{ Sm}^{-1}$ at 1020 K. The electrical conductivity of fully dense B_6O will be greater, because those of B_4C were affected by porosity. The electrical conductivity of B_6O increased with increasing temperature. The temperature dependence was similar with that of B_4C ,¹⁾ obeying eq. (3) for a hopping conduction:

$$\sigma = (C/T) \exp(-E_a/k_B T) \quad (3)$$

Fig. 4 Temperature dependence of the electrical conductivity for hot-pressed B_6O . (Numerals in parentheses mean porosity of the specimens). Fig. 5 Temperature dependence of Hall mobility for hot-pressed B_6O . (Numerals in parentheses mean porosity of the specimens).

where C is a constant, k_B is Boltzmann constant, and E_a is activation energy for electrical conductivity. The activation energy for B_6O , E_a , was 0.28 eV. This value was greater than those for B_4C (0.14 to 0.18 eV).

Figure 5 demonstrates the temperature dependence of Hall mobility for the hot-pressed B_6O . The Hall mobility of B_6O increased from 10^{-5} to $10^{-4} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ with increasing temperature from 290 to 800 K. The mobility of non-generated semiconductor typically for Si single crystal at 300 K is $8 \times 10^{-2} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ which decreased with increasing temperature.⁴¹⁾ The mobility of B_6O and B_4C was 1/10000 to 1/1000 times less than that of Si, and had opposite temperature de-

Fig. 6 Temperature dependence of Hall carrier concentration for hot-pressed B₆O. (Numerals in parentheses mean porosity of the specimens).

pendence to Si. The significantly small mobility and its positive temperature dependence are indicative of the small polaron hopping conduction, because the carriers should be mobile with dragging lattice vibration (*i.e.* phonon) and would be thermally activated at higher temperatures by phonons. The activation energy of 0.09 eV for B₆O was greater than that of 0.05 eV for B₄C, suggesting more significant nature of small polaron hopping than that of B₄C.

Figure 6 demonstrates the temperature dependence of carrier concentration for the hot-pressed B₆O. The carrier concentration of B₆O was one to two orders of magnitude smaller than that in B₄C and increased with increasing temperature. The positive value of Hall coefficient was consistent with the polarity of Seebeck coefficient. The hole concentration of B₆O was smaller than that of B₄C, which would justify the greater Seebeck coefficient of B₆O than that of B₄C.

Figure 7 shows the temperature dependence of thermal conductivity for the hot-pressed B₆O, comparing with those for reported values of B₆O²⁶⁾ and B₄C.^{2,5,6)} The thermal conductivity of the hot-pressed B₆O decreased with increasing temperature. This trend was similar to those of reported values, indicating that the transport of phonons are dominant. The thermal conductivity of hot-pressed B₆O was slightly smaller than the reported value of B₆O (10% porosity),²⁶⁾ probably due to the effect of porosity. Sintered B₄C (38% porosity)⁵⁾ showed smaller thermal conductivity than the hot-pressed B₆O (33% porosity). Since the porosity is similar between these two specimens, the thermal conductivity of B₆O may be basically greater than that of B₄C. Single crystal B₄C had much greater thermal conductivity than those of sintered B₄C. The grain boundary and porosity could decrease the thermal conductivities of B₄C and B₆O. Further study should be necessary to prepare highly dense B₆O to understand the intrinsic nature of B₆O.

Figure 8 presents the temperature dependence of dimensionless figure-of-merit (*ZT*) for the hot-pressed B₆O comparing with those reported for B₄C and B₆O. The *ZT* value for the

Fig. 7 Temperature dependence of thermal conductivity for hot-pressed B₆O. (Numerals in parentheses mean porosity of the specimens).

Fig. 8 Temperature dependence of dimensionless figure-of-merit for hot-pressed B₆O. (Numerals in parentheses mean porosity of the specimens).

hot-pressed B₆O increased with temperature, and reached to 0.62×10^{-3} at 1000 K. This value was almost in agreement with that of B₄C,⁵⁾ having the similar porosity.

4. Conclusion

B₆O bodies with 33% porosity in single phase were prepared by hot-pressing. Lattice parameters were $a = 0.538$ nm, $c = 1.233$ nm. The thermoelectric properties of the hot-pressed B₆O were compared with those of B₄C.

(1) The electrical conductivity is lower than that of B₄C. The small mobility and its positive temperature dependence

suggests the small polaron hopping conduction.

(2) The Seebeck coefficient is twice as great as that of B₄C.

(3) The thermal conductivity may be greater than that of B₄C.

(4) The dimension-less figure-of-merit (*ZT*) increases with increasing temperature, and reaches to 0.62×10^{-3} at 1000 K. This value is almost in agreement with that of B₄C having the similar porosity.

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