Improvement in Thermoelectric Performance of Cu-Doped β-Rhombohedral Boron*1

Yoshiki Takagiwa1,2,*2, Norihide Kuroda3, Erika Imai3, Ikuzo Kanazawa3, Hiroshi Hyodo4, Kohei Soga5 and Kaoru Kimura1

1Department of Advanced Materials Science, The University of Tokyo, Chiba 277–8561, Japan
2National Institute for Materials Science, Tsukuba 305–0047, Japan
3Department of Physics, Tokyo Gakugei University, Tokyo 184–0015, Japan
4Institute for Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980–8577, Japan
5Department of Materials Science and Technology, Tokyo University of Science, Tokyo 125–8585, Japan

The inherently complex crystal structure with its structural vacancies leads to low thermal conductivity, even though boron is a comparatively light element. Metal dopants are found to occupy specific sites; V atoms mainly occupy A1 site,8) while Cu atoms mainly occupy D and E sites.9) Interestingly, V-doping of β-boron was found to enhance the electrical conductivity dramatically, which resulted in a large enhancement of ZT, by acting as an n-type dopant.10) Copper, on the other hand, behaves as a p-type dopant.7,12) To investigate the relationship between the doping sites and the physical properties of the material is therefore of great interest for further enhancement of ZT.

The S of β-boron has a large positive value of ~950 μV K−1 at 373 K, which may be attributed to the fact that carrier compensation driven by the interstitial boron atoms is still insufficient to form a closed shell structure.10,11) Indeed, the σ is rather low, with a value of approximately 10−2 Ω−1 cm−1 at 373 K. Tuning of the carrier concentration by chemical doping is thus necessary to improve σ. To date, the effects of many p-type dopants, including Sr,4) W,4) Zr,2–4) Si,3) Cr,3) and β-boron have been systematically investigated using nominal compositions of CuB105 (x = 0–5). The electrical conductivity increases with increasing x up to 5 at.%, whereas the positive Seebeck coefficient decreases because of an increase in the carrier concentration. Consequently, the power factor is enhanced by a factor of four from 0.006 (x = 0) to 0.038 (x = 4) at 973 K in addition, Cu doping of the interstitial D and E sites contributes a ~50% reduction in the thermal conductivity from 4.3 W m−1 K−1 (x = 0) to 2.1 W m−1 K−1 (x = 5) at 973 K because of increased numbers of phonon scattering events. The dimensionless figure of merit ZT is also enhanced by a factor of six from 0.006 (x = 0) to 0.018 (x = 4) at 973 K in the p-type material. The ZT value obtained is higher than that of the conventional thermoelectric boride B4C.

The effects of Cu doping on the thermoelectric properties of β-rhombohedral boron have been systematically investigated using nominal compositions of CuB105 (x = 0–5). The electrical conductivity increases with increasing x up to 5 at.%, whereas the positive Seebeck coefficient decreases because of an increase in the carrier concentration. Consequently, the power factor is enhanced by a factor of four from 0.006 (x = 0) to 0.038 (x = 4) at 973 K. In addition, Cu doping of the interstitial D and E sites contributes a ~50% reduction in the thermal conductivity from 4.3 W m−1 K−1 (x = 0) to 2.1 W m−1 K−1 (x = 5) at 973 K because of increased numbers of phonon scattering events. The dimensionless figure of merit ZT is also enhanced by a factor of six from 0.006 (x = 0) to 0.018 (x = 4) at 973 K in the p-type material. The ZT value obtained is higher than that of the conventional thermoelectric boride B4C.

1. Introduction

Thermoelectric conversion is a most promising waste-heat recovery method that generates electric power by direct conversion of thermal energy into electrical energy. Low-cost and high-efficiency p- and n-type materials are both required for fabrication of thermoelectric modules. The efficiency of these modules is related to a dimensionless figure of merit, $ZT = \frac{S^2 \sigma T}{\kappa_{\text{total}}}$, where S, σ, $\kappa_{\text{total}}$, and T represent the Seebeck coefficient, the electrical conductivity, the total thermal conductivity, and the temperature, respectively.1) In practical applications, ZT should be above unity at operating temperatures, which roughly corresponds to module efficiency of ~10%.

β-rhombohedral boron (β-boron) is preferred as a high-temperature thermoelectric material because of its high melting point of more than 2300 K. Extensive studies on metal-doped β-boron were performed by Slack et al. in the 1980s2), subsequent studies on several types of metal-doped β-boron have demonstrated the potential of these high-temperature thermoelectric materials.3–5) However, the development of a guiding principle to produce higher values of ZT using a suitable dopant with an optimal carrier concentration for β-boron is still necessary.

The crystal structure of β-boron is rather complex, as shown in Fig. 1. The large unit cell contains ideally 105 atoms; more accurately, it contains 106.6 atoms when vacant and interstitial site atoms are included. One crystallographic feature indicates the existence of the many interstitial doping sites in this material, such as the A1, D, E, F, and H sites.6,5) The inherently complex crystal structure with its structural

**Keywords:** boron, borides, thermoelectric properties, chemical doping

---

*2Corresponding author, E-mail: TAKAGIWA.Yoshiki@nims.go.jp
Fe,2,3) Co, 3,4) and Cu, 2) on the thermoelectric properties of β-boron have been investigated. While Cu can be doped at levels of more than 4 at.% into β-boron,12) few reports have been published on the effects of Cu doping at more than 1 at.% on the thermoelectric properties of the material. In this paper, we present the thermoelectric properties of β-boron with Cu doping of up to 5 at.% and ZT enhancement based on tuning of the doping concentration.

2. Experimental Procedure

Flakes of pure boron (3N purity; Furuuchi Chemical Co., Tokyo, Japan) were crushed into a coarse-grained powder using a tungsten carbide stamp mill followed by ball milling using a stainless-steel vial and balls. After etching with hydrochloric acid, a high-purity fine powder with no secondary phase was obtained.

Cold-pressed pellet samples containing a mixture of powdered boron and copper (3N purity; Kojundo Chemical Laboratory Co. Ltd., Tokyo, Japan) [nominal compositions: Cu$_{105}$ (x = 0–5)] were melted by arc-melting in an argon atmosphere (NEV-ACD-05; Nissin Giken Co., Saitama, Japan). The mother ingots were crushed into fine powder by ball-milling using the same procedure that was described above. After removal of impurities by etching, fine powder with a particle size of less than 45 μm was used for spark plasma sintering (SPS-515S; Fuji Electronic Industrial Co., Kanagawa, Japan). The powder samples were set in 10-mm-diameter carbon dies with boron nitride spacers and were sintered at 1873 K for 5 min under uniaxial pressure of 45 MPa and an argon atmosphere. The characterization of the samples was performed by powder X-ray diffraction (XRD) measurements using Cu Kα radiation (SmartLab; Rigaku Co., Tokyo, Japan).

The electrical conductivity and the Seebeck coefficient were measured in a helium atmosphere in the temperature range from 373 K to 973 K by the four-probe method and the steady-state temperature gradient method, respectively (ZEM-1; Advance-Riko, Inc., Kanagawa, Japan). The thermal conductivity was obtained by measuring the geometric density, the specific heat and the thermal diffusivity of the material in an argon atmosphere by the laser flash method (TC-7000; Advance-Riko, Inc.).

3. Results and Discussion

Figure 2 shows the XRD patterns for the synthesized Cu$_{105}$ (x = 0–5), together with the calculated peak positions; the patterns indicate that all synthesized samples were of high quality and no secondary phase was observed. To evaluate the doping concentration, the rate of lattice parameter change as a function of x was investigated, as shown in Fig. 3. The lattice parameters of both the a(b) and c axes increase linearly by up to ~0.3% with increasing x, which indicates that the Cu atoms successfully doped the β-boron. However, the observed rate of lattice parameter change is significantly smaller than the rate that was previously reported by Matsuda et al.13) The ~0.3% increase in the lattice parameters presented here can be attributed to interpolated Cu doping of ~2.0 at.% 13) The discrepancy between the nominal and the estimated doping compositions may arise during the sample preparation process: arc-melting and etching.

The temperature dependences of both σ and S for Cu$_{105}$ (x = 0–5) are plotted in Fig. 4. σ is enhanced by one order of magnitude from 1.1 Ω cm$^{-1}$ (x = 0) to 13 Ω cm$^{-1}$ (x = 5) at 973 K. S increases with increasing temperature; however, its absolute value saturates at high temperatures. S at 973 K decreases from 400 μV K$^{-1}$ (x = 0) to 190 μV K$^{-1}$ (x = 5). This trend can be understood based on the increased carrier concentration caused by Cu doping, which shows good qualitative agreement with the increase in the density of states at
concentration because of an alloying effect. Cu$\text{B}_{105}$ in particular has a low $\kappa$ of $\sim$2 W m$^{-1}$ K$^{-1}$ up to 973 K.

The increase in $S^2\sigma$ and the reduction in $\kappa_{\text{total}}$ induce a $ZT$ enhancement by a factor of six from 0.006 ($x = 0$) to 0.038 ($x = 4$) at 973 K (Fig. 7) in the $p$-type material, which is considerably higher than the value (0.01) of the conventional thermoelectric boride $\text{Bi}_2\text{C}$. Previous results indicate that a $ZT$ of 0.26 can be achieved for $\text{Cu}_1\text{B}_{105}$ at 1300 K, which further encourages us to evaluate the thermoelectric properties of this material at temperatures above 1000 K.

$E_F, N(E_F)$: When the previous work on $\text{Cu}_1\text{B}_{105}$ is taken into account, the present value of $\sigma$ is one order of magnitude lower than that of Slack’s work, although the absolute value and the temperature dependence of $S$ are almost identical. This behavior can be explained by the difference in density between the arc-melted high density samples (relative density: >90%) and our SPS samples (70–75%). While the arc-melted samples contain visible cracks and pores, this microstructure does not exceed 4 at.%. However, higher temperature consolidation introduces cracks into the sintered samples. It will thus be necessary to establish suitable SPS conditions to synthesize disk samples with higher densities than the relative densities of the present samples.

With regard to $p$-type Co-doping, a $\text{Co}_1\text{B}_{105}$ sample exhibited higher $\sigma$ and lower $\kappa$ when compared with the corresponding values of $\text{Cu}_1\text{B}_{105}$. This indicates that Co can introduce more carriers into $\beta$-boron than Cu, which may be caused by different site preferences; Co atoms occupy both the $A_1$ and $E$ sites, while Cu atoms mainly occupy the $D$ and $E$ sites. However, tuning of the carrier concentration by Cu doping may be more suitable because the doping limit can exceed 4 at.%. $S^2\sigma$ increases monotonically with increasing temperature (Fig. 5). The maximum $S^2\sigma$ is enhanced by a factor of four from 22 $\mu$W m$^{-1}$ K$^{-2}$ ($x = 0$) to 90 $\mu$W m$^{-1}$ K$^{-2}$ ($x = 4$). However, a slight reduction in $S^2\sigma$ is observed for the sample with $x = 5$ because of the large reduction of $S$. In this case, $\text{Cu}_4\text{B}_{105}$ is found to have a suitable carrier concentration.

The values of $\kappa_{\text{total}}$ as a function of temperature are displayed in Fig. 6. Since the $\sigma$ of Cu-doped $\beta$-boron show rather low values of $\sim$10$^3$ $\Omega$ cm$^{-1}$ at 973 K, the main contribution to $\kappa$ is thus the lattice component that was estimated from the Wiedemann–Franz law. $\kappa$ decreases with increasing Cu concentration because of an alloying effect. $\text{Cu}_3\text{B}_{105}$ in particular has a low $\kappa$ of $\sim$2 W m$^{-1}$ K$^{-1}$ up to 973 K.

$E_F, N(E_F)$, $\kappa_{\text{total}}$, $S^2\sigma$: From $\kappa_{\text{total}}$ from 4.3 W m$^{-1}$ K$^{-1}$ ($x = 0$) to 2.1 W m$^{-1}$ K$^{-1}$ ($x = 5$) at 973 K. $ZT$ was enhanced by a factor of six from 0.006 ($x = 0$) to 0.038 ($x = 4$) at 973 K in the $p$-type material. The obtained $ZT$ value was found to be higher than that of the conventional thermoelectric boride $\text{Bi}_2\text{C}$.

4. Conclusions

The effects of Cu doping on the thermoelectric properties of $\beta$-rhombohedral boron have been investigated systematically for nominal compositions of $\text{Cu}_x\text{B}_{105}$ ($x = 0–5$). $\sigma$ and $S$ increased and decreased with increasing $x$, respectively, because of the increased carrier concentration, which corresponded to an increase in $N(E_F)$. $S^2\sigma$ was enhanced by a factor of four from 22 $\mu$W m$^{-1}$ K$^{-2}$ ($x = 0$) to 90 $\mu$W m$^{-1}$ K$^{-2}$ ($x = 4$) at 973 K. In addition, Cu doping of the interstitial $D$ and $E$ sites contributed to a ~50% reduction in $\kappa_{\text{total}}$ from 4.3 W m$^{-1}$ K$^{-1}$ ($x = 0$) to 2.1 W m$^{-1}$ K$^{-1}$ ($x = 5$) at 973 K. $ZT$ was enhanced by a factor of six from 0.006 ($x = 0$) to 0.038 ($x = 4$) at 973 K in the $p$-type material. The obtained $ZT$ value was found to be higher than that of the conventional thermoelectric boride $\text{Bi}_2\text{C}$.

Acknowledgments

This work was supported by KAKENHI (Grant Nos. 24360262 and 26709051) from the Japan Society for the Promotion of Science (JSPS).

REFERENCES
