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Effect of addition of B or C on thermoelectric properties of heavy fermion intermetallic compound $YbAl_3$

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ABSTRACT

The effect of addition of B or C on thermoelectric properties of $YbAl_3$ was investigated. $YbAl_3$ is well known as one of heavy fermion intermetallic compounds, which generally possess relatively large Seebeck coefficient and extremely low electrical resistivity. $Yb_{1.05}Al_3M_x$ (M = B or C, x = 0–0.10) showed almost single phase with $AuCu_3$-type structure. The Seebeck coefficient and electrical resistivity of $Yb_{1.05}Al_3$ were hardly affected by the addition of B or C, which showed that there was no difference in the carrier density among these compounds. The addition of C, or especially B, was effective for the reduction of the thermal conductivity, which was mainly attributed to the reduction of the lattice contribution. As a result, $Yb_{1.05}Al_3B_{0.10}$ showed a maximum *ZT* of about 0.33 at 323 K, which was a little larger than *ZT* of $Yb_{1.05}Al_3$.

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1. Introduction

In the face of the impending environmental and energy problems, the thermoelectric energy conversion technique, which can convert heat to electricity, has attracted the attention of many researchers. Up until now, SiGe [1], PbTe [2,3], Bi_2Te_3 [4,5] and transition-metal disilisides [6,7] have been investigated as thermoelectric materials. Among them, Bi_2Te_3-based alloy has been employed as the state-of-the-art thermoelectric material over the range around room temperature.

The performance of thermoelectric materials at the temperature of T (K) is shown by the dimensionless figure of merit ZT ($=S^2T/\rho\kappa$), where S is the Seebeck coefficient, ρ is the electrical resistivity and κ is the thermal conductivity for the materials, respectively. On the other hand, ZT is proportional to a part of material parameters, $m^{*3/2}\,\mu/\kappa_{ph}$ when the temperature is fixed [8]. Here, m^* and μ are the effective mass and mobility of the carrier respectively, and κ_{ph} is the lattice thermal conductivity. And so, a material with large effective mass of carrier could be a good thermoelectric material with high performance.

A group of materials with large effective mass of carrier is generally called as a heavy fermion system, and rare-earth of Ce or Yb intermetallic compounds are typical ones. From the derived mathematical function for the transport distribution, Mahan and Sofo proposed that $YbAl_3$ shows a metallic conductivity concluding to high value of power factor [9], and Rowe et al. reported that $YbAl_3$ possesses a power factor double larger than the state-of-the-art thermoelectric materials based on Bi_2Te_3 alloys [10,11]. However, the thermal conductivity of $YbAl_3$ is much higher and the figure of merit of it is lower than that of Bi_2Te_3-based alloys.

$YbAl_3$ crystallizes in a cubic $AuCu_3$-type structure [12]. This structure can be viewed as a cubic defective perovskite structure, where Al forms octahedral network instead of oxygen, Yb occupies the Sr site and the Ti site is left vacant in the perovskite $SrTiO_3$. And so, some elements can be inserted in this empty octahedral site formed by Al atoms. He et al. synthesized $YbAl_3Mn_x$ (x = 0.02–0.10) and investigated their thermoelectric properties [13]. They found that *a*-lattice parameter showed systematic change with increasing doping levels of Mn and the thermal conductivity showed significant drop maintaining a moderate power factor value at around x = 0.02–0.05, and maximum *ZT* of about 0.5 was obtained near x = 0.04. They also investigated the location of the Mn atoms in the crystal structure from the Synchrotron X-ray powder diffraction data, and expected that the substantial static disorder and lattice strain in the structure are probably responsible for lower thermal conductivity of $YbAl_3Mn_x$.

It is well known that the insertion of elements into the empty site in the crystal can reduce the thermal conductivity of the material. In the filled skutterudite compounds RM_4X_{12}, where R is La, Ce or Yb, M is Co, Rh or Ir and X is P, As or Sb, the empty octants of the skutterudite structure formed in the MX_3 framework are filled with rare- earth elements [14,15]. X-ray and neutron structure refinements indicate that the R atoms tend to exhibit exceptionally large thermal parameters, corresponding to the “rattling” of these atoms in an oversized atomic cage [16,17]. This rattling markedly reduces the thermal conductivity of these filled skutterudite compounds.

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The reduction of the thermal conductivity accompanied with the insertion of atoms into the empty site is a very interesting phenomenon. We have synthesized $YbAl_3M_x$ (M = B or C, x = 0.05–0.10). The radii of these elements are small, and so it is expected that they are easy to enter the empty octahedral site of $YbAl_3$ and rattle in the site, which may result in the reduction of the thermal conductivity of $YbAl_3$. On the other hand, it is also expected that the addition of B or C atom is hard to affect transport properties such as Seebeck coefficient and electrical resistivity of the intermetallic compounds since B and C atoms are nonmetallic elements. We have investigated the effect of the addition of B or C to $YbAl_3$ on the thermoelectric properties.

2. Experimental

The buttons of $Yb_{1+\alpha}Al_3M_x$ (M = B or C, α = 0–0.20, x = 0.05–0.10) compound were synthesized by arc melting of the weighed Yb (99.9% purity), Al (99% purity) and B (99% purity) or C (99% purity) elements according to the desired compositions. For synthesizing $Yb_{1+\alpha}Al_3B_x$ buttons, Yb ingot (2–3 mm in diameter) and B powder (−40 μm) were wrapped in the Al foil (0.025 mm in thickness), and the package was arc-melted under Ar gas atmosphere. In the case of synthesizing $Yb_{1+\alpha}Al_3C_x$ buttons, the C sheet (0.1 mm in thickness) was laid under the package of Al foil during the arc melting. The obtained buttons were ground into fine powders under 180mesh in Ar gas atmosphere, and the powders were packed into graphite dies and sintered by SPS (Spark Plasma Sintering) instrument (SCM SPS-511S) at 923 K for 15 min at a pressure of 100 MPa under a vacuum of about 40 Pa. The sintered samples were wrapped in the tantalum foil and annealed in an evacuated quartz ampoule at 873 K for 168 h.

The phase identification of the obtained samples was made by X-ray diffraction at room temperature. The elemental analysis of the samples was done by EPMA (electron probe micro analyzer). The Seebeck coefficient and electrical resistivity were simultaneously measured by the standard four-probe dc method under a vacuum of 10^{-3} Pa in the temperature range from room temperature to about 573 K. The thermal diffusion coefficient D and the specific heat C_p of the samples were measured by the laser flash method using the thermal constant analyzer (ULVAC TC-7000). The density d of the samples was measured by the Archemedes method. The thermal conductivity κ was calculated from the measured D, C_p and d using the relationship $\kappa = DC_pd$.

3. Results and discussion

The boiling point of Yb (1466 K) is relatively low and it is close to the melting point (1097 K), and so Yb is apt to be lost during the arc melting process [18]. In order to examine the relationship between the nominal composition and the obtained phase for $YbAl_3$, the samples with different nominal compositions were prepared. Fig. 1 shows the X-ray diffraction patterns for the annealed samples with different ratios of Yb to Al, $Yb_{1+\alpha}Al_3$. The X-ray diffraction patterns for the annealed $Yb_{1+\alpha}Al_3$ mainly consist of the diffraction peaks of $YbAl_3$ phase with cubic $AuCu_3$-type structure. As shown in the figure, sleight amounts of Al were detected as an impurity phase in the sample with a nominal composition of $YbAl_3$. On the other hand, $YbAl_2$ phase with cubic $MgCu_2$-type structure appeared in the sample with a nominal composition of $Yb_{1.20}Al_3$. Almost single phase of $YbAl_3$ was obtained in the samples of $Yb_{1.05}Al_3$ and $Yb_{1.10}Al_3$, and so we have decided that the nominal composition of the samples with the added element of M (M = B or C) is $Yb_{1.05}Al_3M_x$.

Fig. 2 shows the X-ray diffraction patterns for the annealed $Yb_{1.05}Al_3B_x$ and $Yb_{1.05}Al_3C_x$ (x = 0.05, 0.10). Almost single phase of $YbAl_3$ phase was obtained in the samples of $Yb_{1.05}Al_3B_x$. Sleight amounts of $YbAl_2$ phase was detected in the samples of $Yb_{1.05}Al_3C_x$.

The lattice parameters of $Yb_{1.05}Al_3B_{0.05}$ and $Yb_{1.05}Al_3C_{0.05}$ determined by X-ray diffraction are 0.4202 and 0.4204 nm, respectively, which are a little larger than the lattice parameter of $Yb_{1.05}Al_3$, 0.4198 nm. A significant increase of a lattice parameter is not observed in $Yba_{1.05}Al_3B_{0.10}$ and $Yb_{1.05}Al_3C_{0.10}$. He et al. also reported that a larger increase of lattice parameter was observed between $YbAl_3$ and $YbAl_3Mn_{0.05}$; the lattice parameters of $YbAl_3$, $YbAl_3Mn_{0.05}$ and $YbAl_3Mn_{0.10}$ are 0.42015, 0.4207 and 0.4208 nm, respectively [13]. The lattice parameters reported by He et al. are

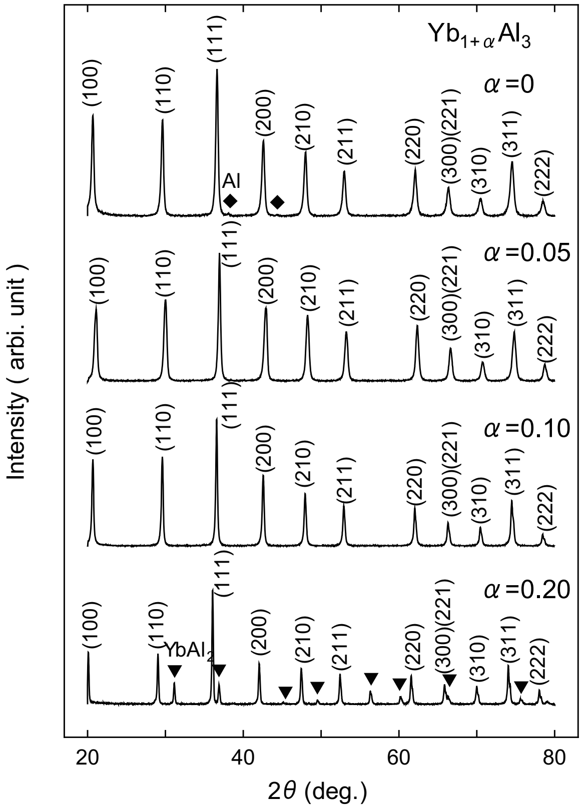

Fig. 1. X-ray diffraction patterns for the annealed $Yb_{1+\alpha}Al_3$ (α = 0–0.20).

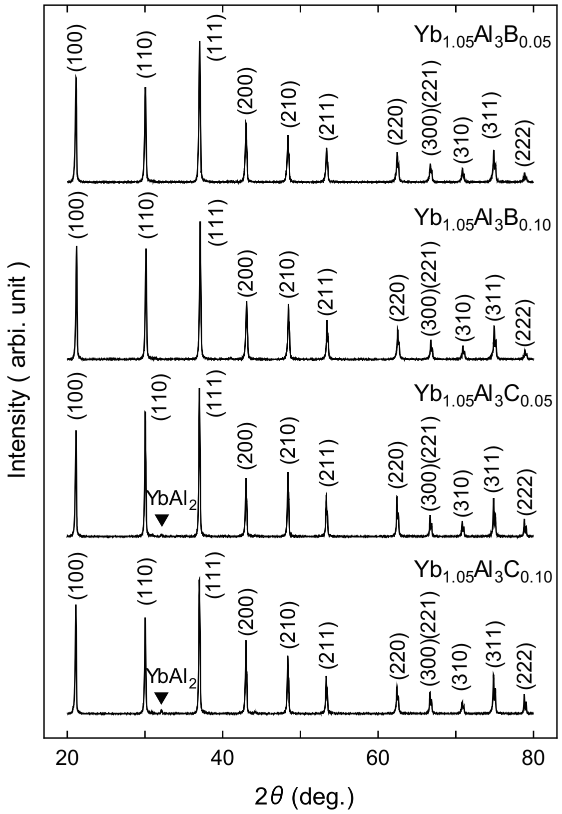

Fig. 2. X-ray diffraction patterns for the annealed $Yb_{1.05}Al_3B_x$ and $Yb_{1.05}Al_3C_x$ (x = 0.05–0.10).

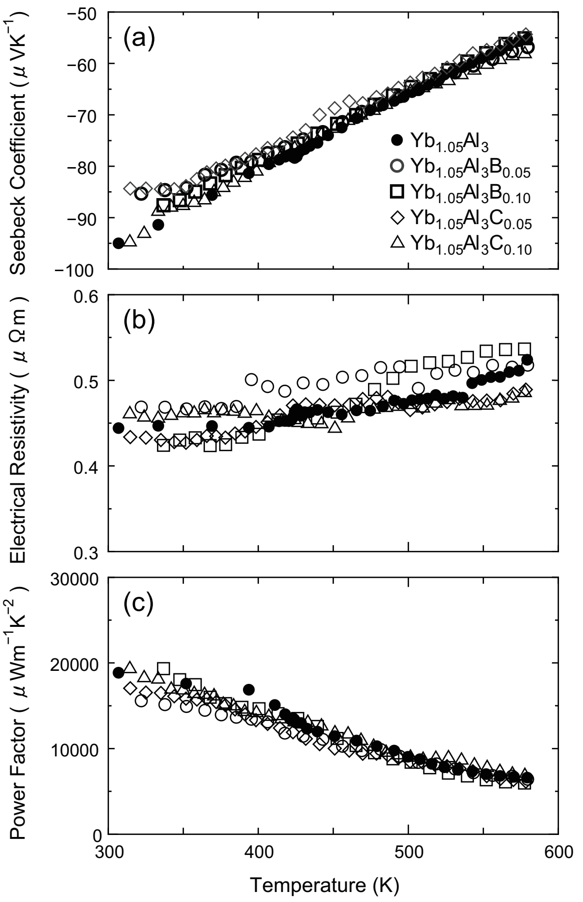

Fig. 3. Temperature dependence of the (a) Seebeck coefficient, (b) electrical resistivity and (c) power factor for the annealed $Yb_{1.05}Al_3$, $Yb_{1.05}Al_3B_x$ and $Yb_{1.05}Al_3C_x$ ($x = 0.05–0.10$).

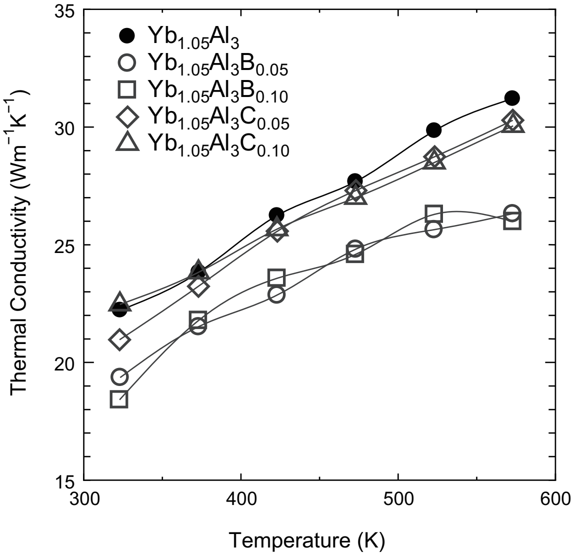

Fig. 4. Temperature dependence of the thermal conductivity for the annealed $Yb_{1.05}Al_3$, $Yb_{1.05}Al_3B_x$ and $Yb_{1.05}Al_3C_x$ ($x = 0.05–0.10$).

somewhat larger than those by us. The analyzed content of C in the matrix grains of $Yb_{1.05}Al_3C_x$ by EPMA is much larger than the nominal content. It is generally difficult to make a precise estimation of the content of C owing to the contaminated organic matter in the samples. On the other hand, the analyzed content of B in the matrix grains of $Yb_{1.05}Al_3B_x$ by EPMA is 0.04–1.2 at.%, and there is a variation in the analyzed data among crystal grains. The nominal content of B in $Yb_{1.05}Al_3B_{0.10}$ is 2.4 at.%, and so the analyzed content is smaller than the nominal content. These results by X-ray diffraction and EPMA show that the added B or C can be inserted into the empty octahedral site in the $YbAl_3$ crystal, but only a part of the added atoms might be inserted. The relative density of the sintered $Yb_{1.05}Al_3M_x$ is 96–98%, and as for the relative density, there is no systematic dependency on the content of x.

Fig. 3(a) and (b) shows the temperature dependence of the Seebeck coefficient and electrical resistivity for $Yb_{1.05}Al_3$, $Yb_{1.05}Al_3B_x$ and $Yb_{1.05}Al_3C_x$, respectively. The sign of the Seebeck coefficient for these compounds is negative, and the absolute value of the Seebeck coefficient decreases monotonously with an increase of temperature. The absolute value of the Seebeck coefficient is somewhat reduced by the addition of B or C to $YbAl_3$, but the systematic dependency on the added element about the Seebeck coefficient is not observed. The electrical resistivity for these compounds is very low among most of the thermoelectric materials. It is difficult to measure the low electrical resistivity with a high degree of accuracy by our measuring instrument, and so the measured data are somewhat spread. The electrical resistivity generally increases with an increase of temperature, i.e., it shows a metallic behavior. As seen from the figure, there is almost no difference in the behavior of the electrical resistivity among these samples. These results on the Seebeck coefficient and electrical resistivity show that the carrier density of $YbAl_3$ is hardly affected by the addition of B or C.

Rowe et al. reported that the absolute values of the Seebeck coefficient and electrical resistivity for sintered $YbAl_3$ are 75 μV/K (at 300 K)–50 μV/K (at 600 K) and 0.8 μΩ m (at 300 K)–1 μΩ m (at 600 K), respectively [10,11]. There is almost no difference in values of the Seebeck coefficient between in Rowe's and our reports, but the electrical resistivity in our report is a little smaller than that in Rowe's report. On the other hand, Daal et al. reported that the Seebeck coefficient and electrical resistivity for single crystal of $YbAl_3$ at 300 K are −90 μV/K and 0.45 μΩ m, respectively [17]. Our results are close to Daal's results on single crystal. The relative density of Rowe's sample is 88%, which is smaller that of our sample. The difference in values of the electrical resistivity is considered to be due to the difference in the density of samples; the sintered sample with larger density generally shows smaller electrical resistivity. It is known that the sintering by SPS is useful for obtaining a dense sample with high density at relative low sintering temperature and for a short time [19].

Fig. 3(c) shows the temperature dependence of the power factor for $Yb_{1.05}Al_3$, $Yb_{1.05}Al_3B_x$ and $Yb_{1.05}Al_3C_x$. The power factor decreases with an increase of temperature, and there is almost no difference in the power factor values among these compounds. The power factor of $Yb_{1.05}Al_3C_{0.10}$ shows a maximum value of about 20,000 $\mu W\,m^{-1}\,K^{-2}$ at 323 K, which is much larger than the power factor of Bi_2Te_3 system ever reported [5].

In order to estimate the dimensionless figure of merit of *ZT* for the samples, the thermal conductivity is measured. Fig. 4 shows the temperature dependence of the total thermal conductivity, κ_{total} for $Yb_{1.05}Al_3$, $Yb_{1.05}Al_3B_x$ and $Yb_{1.05}Al_3C_x$. The thermal conductivity of these compounds is very high for the thermoelectric materials and it generally increases with an increase of temperature. κ_{total} for $Yb_{1.05}Al_3C_x$ is somewhat smaller than that for $Yb_{1.05}Al_3$, and κ_{total} for $Yb_{1.05}Al_3B_x$ is more reduced. This result seems to show that the addition of B or C to $YbAl_3$ is effective for the reduction of thermal conductivity. The total thermal conductivity κ_{total} of the material generally consists of κ_{ph} and κ_{car}, where κ_{ph} is the lattice contribution and κ_{car} is the carrier contribution to the thermal conductivity. In order to determine which component between lattice and carrier governs the thermal conductivity of these compounds, κ_{ph} and

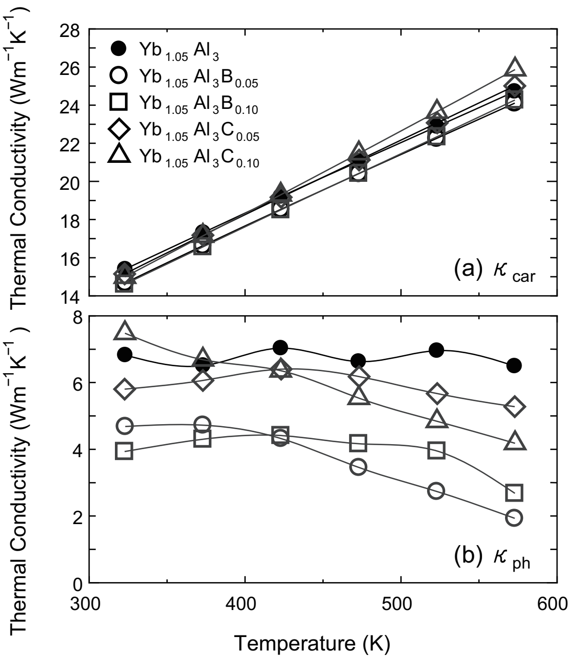

Fig. 5. Temperature dependence of (a) κ_{car} and (b) κ_{ph} for the annealed $Yb_{1.05}Al_3$, $Yb_{1.05}Al_3B_x$ and $Yb_{1.05}Al_3C_x$ ($x = 0.05–0.10$).

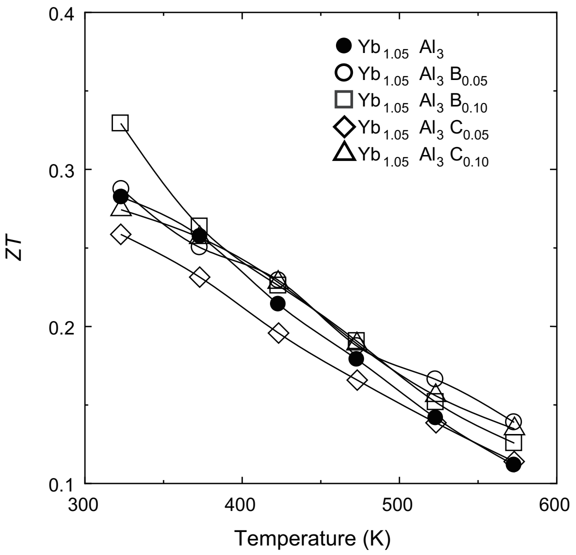

Fig. 6. Temperature dependence of ZT for the annealed $Yb_{1.05}Al_3$, $Yb_{1.05}Al_3B_x$ and $Yb_{1.05}Al_3C_x$ ($x = 0.05–0.10$).

κ_{car} are estimated by the Wiedemann–Franz relationship following our procedure in a previous report [20]. By the Wiedemann–Franz relationship κ_{car} corresponds to LT/ρ, where L is the Lorentz number. The Lorentz number L was calculated using the reduced Fermi energy, which was estimated from the Seebeck coefficient and the Fermi–Dirac integral. Acoustic-mode phonon scattering was estimated. κ_{ph} was obtained by subtracting κ_{car} from κ_{total}. κ_{car} and κ_{ph} are shown in Fig. 5(a) and (b) as a function of the temperature, respectively. The value of κ_{car} is much larger than that of κ_{ph}, i.e., the thermal conductivity in these compounds is mainly governed by the carrier component. As seen from the figure, there is almost no difference in κ_{car} among these compounds. This shows that the carrier density is hardly affected by the addition of B or C to $YbAl_3$, which is consistent with the results of the Seebeck coefficient and electrical resistivity. On the other hand, κ_{ph} of $Yb_{1.05}Al_3C_x$ is somewhat smaller than that of $Yb_{1.05}Al_3$, and κ_{ph} of $Yb_{1.05}Al_3B_x$ is more reduced. This result shows that the addition of C, or especially B, is effective for the reduction of κ_{ph}.

Fig. 6 shows the temperature dependence of the corresponding *ZT* for $Yb_{1.05}Al_3$, $Yb_{1.05}Al_3B_x$ and $Yb_{1.05}Al_3C_x$. *ZT* decreases monotonously with an increase of temperature. Unfortunately, a considerable improvement is not attained by the addition of B or C to $YbAl_3$. $Yb_{1.05}Al_3B_{0.10}$ shows a maximum *ZT* of about 0.33 at 323 K, which is a little larger than *ZT* of $Yb_{1.05}Al_3$.

4. Conclusion

The lattice component of the thermal conductivity of $YbAl_3$, which is one of heavy fermion intermetallic compounds, is reduced by the addition of B or C, while the Seebeck coefficient and electrical resistivity of it are not so affected by the addition of B or C. These results show that the addition of B or C to $YbAl_3$ is effective for the reduction of the thermal conductivity and that the carrier density of $YbAl_3$ is hardly affected by the addition of B or C.

In this study, a considerable improvement in *ZT* was not attained by the addition of B or C to $YbAl_3$. The samples prepared in this study are inhomogeneous; there is a variation in the analyzed content of B in the matrix of $Yb_{1.05}Al_3B_x$ and the analyzed content is smaller than the nominal content. It is necessary to improve the process of sample preparation. For example, the rapid quench from high temperature may be effective for increasing the content of B in $Yb_{1.05}Al_3B_x$ as carried out in the synthesis of the rare-earth filled skutterudite compounds [14].

It is interesting that the addition of light and small elements such as B or C is effective for the reduction of the thermal conductivity of $YbAl_3$. In general, the addition of heavy elements is effective for the reduction of the thermal conductivity, as observed in the rare-earth filled skutterudite compounds, in which the “rattling” of the rare-earth elements in an oversized atomic cage [16,17]. In the case of $YbAl_3$ with an addition of B or C, another mechanism for reducing the thermal conductivity may be operative. In order to clarify the mechanism, further investigation of the crystal structure, for example by the neutron or Synchrotron X-ray powder diffraction, will be necessary.

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