

# Effect of transition metal doping and carbon doping on thermoelectric properties of $\text{YB}_{66}$ single crystals

Takao Mori\*, Takaho Tanaka

National Institute for Materials Science, Namiki 1-1, Tsukuba 305-0044, Japan

Received 19 August 2005; received in revised form 23 November 2005; accepted 29 January 2006

Available online 10 March 2006

## Abstract

We have been investigating the high-temperature thermoelectric properties of some novel rare earth borides with a structure containing  $\text{B}_{12}$  icosahedra. Doping effects on the TE properties in such systems were investigated for the first time. A series of Nb-doped  $\text{YB}_{66}$  and C-doped  $\text{YB}_{66}$  single crystals were grown by the floating zone method. The Nb-doped compounds have approximate chemical formulas ranging from  $\text{YNb}_{0.30}\text{B}_{66}$  to  $\text{YNb}_{0.33}\text{B}_{66}$  while the C-doped compound has a formula of  $\text{YB}_{66}\text{C}_{0.6}$ . The effect of Nb-doping on the thermoelectric properties was not monotonic and appears to be complex. As a result of Nb-doping, the room temperature resistivity and the characteristic temperature  $T_0$  were considerably reduced. At room temperature the power factor of the Nb-doped  $\text{YB}_{66}$  sample with 89% site occupancy was three times greater than that of non-doped  $\text{YB}_{66}$ . However, in the important high-temperature region, the non-doped sample actually exhibited the highest power factor for  $T > 550$  K. Furthermore, owing to a structural feature of  $\text{YB}_{66}$ , thermal conductivity actually increases with doping of transition metals. Taking into account all the thermoelectric properties, transition metal doping of  $\text{YB}_{66}$  is therefore not suitable for our purposes. On the other hand, doping of carbon, which is assumed not to go into the same sites as the transition metals, yielded a lowering of the thermal conductivity. Furthermore, contrary to Nb-doping, carbon doping did not result in a reversal of the relative magnitude of resistivity at extremely high temperatures and therefore, an increase in the figure of merit of factor 2 was realized at 1000 K.

© 2006 Elsevier Inc. All rights reserved.

**Keywords:** Borides; Thermoelectric; Doping; Single crystals; Rare earth

## 1. Introduction

Boron-rich cluster compounds are attractive as materials because of their stability under high temperature and “unfriendly” (e.g. acidic, abrasive) conditions. Magnetic properties of some new rare earth borides with a structure containing  $\text{B}_{12}$  icosahedra have recently attracted increasing interest, since they are magnetically dilute semiconducting/insulating f-electron materials but display a wide range of magnetism such as dimer-like magnetic behavior in  $\text{TbB}_{50}$ -type compounds [1,2] or spin glass behavior in a layered series of RE–B–C(N) compounds [3,4] at moderate temperatures. There are indications that the  $\text{B}_{12}$  icosahedral clusters play an important role in mediating magnetic interaction, which is a novel phenomenon. Boron-rich

compounds such as boron carbide, doped  $\beta$ -boron, and  $\text{CaB}_6$  systems have also been investigated as possible thermoelectric materials [5–9].

We have been investigating the potential of these borides recently discovered by us as possible thermoelectric materials, because these rare earth  $\text{B}_{12}$  icosahedral cluster compounds generally exhibit low thermal conductivity [10]. The thermal conductivity of  $\text{REB}_{66}$  is at least one order lower than that of the  $\beta$ -boron compounds and many orders lower than that of the  $\text{CaB}_6$ -type compounds [10].  $\text{REB}_{50}$ -type compounds have been found to have Seebeck coefficients greater than  $200 \mu\text{V/K}$  at temperatures above 1000 K, and low thermal conductivity of  $0.027 \text{ W/cm K}$  at room temperature [11].

In this work, we attempted to modify these novel rare earth  $\text{B}_{12}$  icosahedral borides to improve their high-temperature thermoelectric properties. We first doped  $\text{YB}_{66}$ , because it is a well known system of which high-quality single crystals can

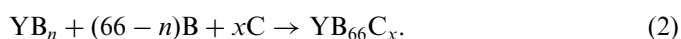
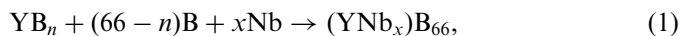
\*Corresponding author. Fax: +81 29 851 6280.

E-mail address: [MORI.Takao@nims.go.jp](mailto:MORI.Takao@nims.go.jp) (T. Mori).

be prepared relatively easily and the doping sites for the transition metal atoms are well known. Nb-doped and C-doped  $\text{YB}_{66}$  single crystals were grown and investigated.

## 2. Experimental

Nb-doped and C-doped  $\text{YB}_{66}$  crystals were successfully grown by the floating zone (FZ) method. Details of the crystal growth for the Nb-doped samples will be presented elsewhere [12]. Feed rods were synthesized by multiple sintering at 1900 K in BN crucibles:



These feed rods were used in the FZ method in a four xenon lamp ellipsoidal mirror-type image furnace to obtain crystals. A fast zone pass was sometimes used to prepare the final feed rods. Growth was done under Ar gas where the feed and seed crystals were counter-rotated at 40 rpm.  $\text{YB}_{66}$  was used as seed crystals. The growth rate was kept to 4 mm/h. Small pieces of the grown crystals were cut off and characterized by single-crystal X-ray diffraction (XRD). An example of a Nb-doped  $\text{YB}_{66}$  crystal is shown in Fig. 1.



Fig. 1. Picture of a Nb-doped  $\text{YbB}_{66}$  crystal.

The  $\text{YB}_{66}$  compound is known to have a homogeneity range [13]. The congruent composition is  $[\text{B}]/[\text{Y}] = 62$ . We found we were able to grow  $\text{YB}_{66}$  crystals with a composition range of  $[\text{B}]/[\text{Y}] \sim 58\text{--}66$ . All the  $\text{YB}_{66}$  crystals grown in this research were prepared at the boron rich end with an actual chemical composition close to  $[\text{B}]/[\text{Y}] \sim 66$ . The  $[\text{B}]/[\text{Y}]$  ratio was determined by wet chemical analysis. The Nb site occupancy was determined from single-crystal XRD data for small pieces cut off the FZ grown crystal, which were corrected with a CCD area detector diffractometer (Bruker SMART APEX, Germany) with graphite monochromated  $\text{MoK}\alpha$  radiation. The intensity data were corrected for Lorentz and polarization effects. The absorption correction applied to the collected data was based on multi-scans. The program SHELXL-97 [14] was used for refinement. The carbon content of C-doped  $\text{YB}_{66}$  was determined with a LECO CS-444LS carbon analyzer. Resistivity and thermoelectric power were measured with an ULVAC ZEM-2. The temperature range of the measurements was from 300 to 1000 K. To determine thermal conductivity, the specific heat and thermal diffusivity coefficient were measured by laser flash method from 300 to 900 K.

## 3. Results and discussion

### 3.1. Nb-doping effects

Four crystals were grown for this part. A non-doped  $\text{YB}_{66}$  crystal and 3 Nb-doped  $\text{YB}_{66}$  crystals. The structure of  $\text{YB}_{66}$  is cubic (space group  $Fm\bar{3}c$ ) with  $a = 23.44 \text{ \AA}$ . It has been studied extensively by Richards [15] and Higashi [16]. The boron framework is basically formed by eight super-icosahedra, each of which consists of 13  $\text{B}_{12}$  icosahedra. Yttrium atoms occupy peanut shaped holes at  $(0.05789, 1/4, 1/4)$  with an occupancy of around 0.65. In the Nb-doped crystals, the Nb atoms occupy the  $(1/4, 1/4, 1/4)$  site (Fig. 2). Three different site occupancies of 89%, 95%, and 97% were achieved. The values of the site occupancies were obtained from the site occupation factors

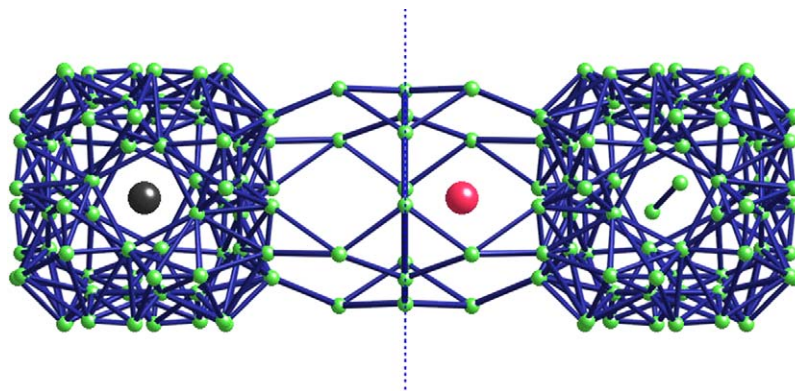


Fig. 2. View of the structure of Nb-doped  $\text{YB}_{66}$  around the doping site of  $(1/4, 1/4, 1/4)$ . Boron atoms (green circles), yttrium atom (red circle) and Nb atom (black circle) are displayed. The Nb atom replaces a short B–B dumbbell pair.

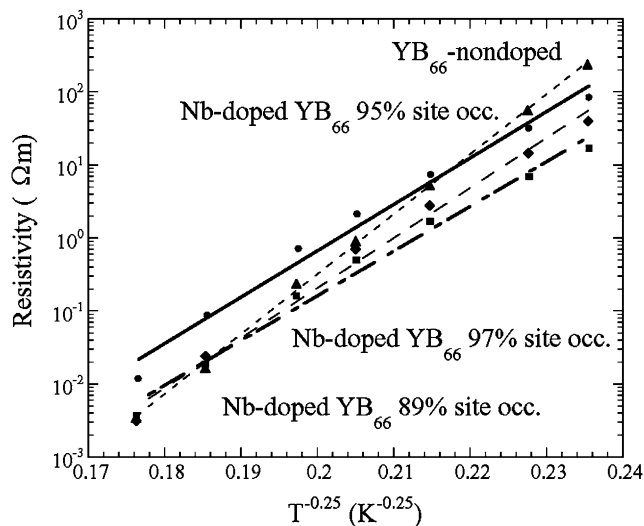


Fig. 3. Temperature dependence of the resistivity  $\rho$  of non-doped (triangles) and Nb-doped  $\text{YB}_{66}$  compounds; 89% occupancy (squares), 95% occupancy (circles), and 97% occupancy (diamonds). The logarithmic of  $\rho$  is plotted versus  $T^{-0.25}$ .

determined from single-crystal XRD analysis and they are  $0.03668 \pm 0.00051$ ,  $0.03938 \pm 0.00039$ ,  $0.04031 \pm 0.00036$ . There are 8 Nb atoms in a unit cell if the sites are fully occupied and the occupancy values in percent are given by multiplying these numbers by  $192/8 \times 100$ . The doped Nb atoms will replace a boron pair in the  $\text{B}_{13}$  site (following the numbering of Higashi [16]) of (0.235, 0.235, 0.235), which is located inside the “ $\text{B}_{80}$  cluster”. As a result of the Nb doping, two new boron sites at  $(x, x, x)$   $x \sim 0.143$  and  $(0.354, 0.271, 0.246)$  were found to appear.

The temperature dependence of the resistivity  $\rho$  of the non-doped and Nb-doped  $\text{YB}_{66}$  compounds are shown in Fig. 3. The logarithm of  $\rho$  is plotted versus  $T^{-0.25}$  and in spite of the paucity of data it can be seen that the graph generally follows a straight line. This is the dependency of Mott’s variable range hopping for 3-dimensional systems [17,18], where

$$\rho = \rho_0 \exp[(T_0/T)^{0.25}] \quad (3)$$

and which has typically been observed for boron-rich  $\text{B}_{12}$  icosahedral systems [19,20]. Although the room temperature values of the resistivity are high,  $\rho$  decreases at an extremely steep rate as the temperature is raised, owing to the variable range hopping. It can be seen that at room temperature Nb doping results in a sizeable reduction in resistivity.

The characteristic temperature  $T_0$  (Table 1) follows the relationship

$$k_{\text{B}}T_0 = 1.5/[D(E_{\text{F}})\xi^3], \quad (4)$$

where  $D(E_{\text{F}})$  is the density of states at the Fermi level and  $\xi$  is the localization length [18]. We note that Nb-doping results in a lower  $T_0$  meaning that  $D(E_{\text{F}})$  increases, or the localization length  $\xi$  elongates. The heavy doping end of 95% and 97% showed an increase in  $T_0$  but this could be

Table 1

Characteristic temperatures of non-doped and Nb-doped  $\text{YB}_{66}$

	Site occupancy (%)	$T_0$ ( $10^8$ K)
$\text{YB}_{66}$	0	12.8
Nb- $\text{YB}_{66}$	89	3.95
Nb- $\text{YB}_{66}$	95	4.57
Nb- $\text{YB}_{66}$	97	6.19

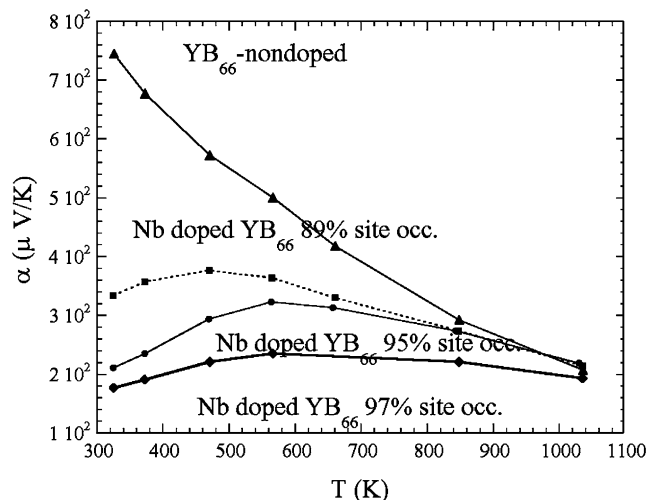


Fig. 4. Temperature dependence of the Seebeck coefficient  $\alpha$  of non-doped (triangles) and Nb-doped  $\text{YB}_{66}$  compounds; 89% occupancy (squares), 95% occupancy (circles), and 97% occupancy (diamonds). The lines are a guide to the eye.

due to the fact that we sacrificed crystal quality to some extent in order to attain this high site occupancy, as a higher growth rate was necessary (to reduce escape of Nb into the feed rod).

The  $T_0$  value of the non-doped  $\text{YB}_{66}$  is higher than that reported previously, which may be because our sample is at the boron-rich end [12,13].

The thermopower of the non-doped and Nb-doped  $\text{YB}_{66}$  compounds, the Seebeck coefficient  $\alpha$ , is plotted in Fig. 4. As expected for a variable range hopping system [21–23], the non-doped  $\text{YB}_{66}$  with the highest  $T_0$  has the largest Seebeck factor. Less well understood is the behavior of the Nb-doped 89% site occupancy sample, which takes the largest  $\alpha$  among the doped samples (over the whole temperature range) while having the smallest  $T_0$ , which is strange for a VRH system [21–23]. This could be due to the crystal quality of the most heavily doped samples, as noted above.

We now consider temperature dependence. Non-doped  $\text{YB}_{66}$  has an unusual temperature dependence with a steep decrease as the temperature increases. The problem of the temperature dependence of the Seebeck factor in variable range hopping systems has been theoretically investigated before [21–23]. Assuming a linear density of states, Zvyagin obtained [21] a temperature dependence of

$$\alpha \propto (T_0 T)^{1/2} d(\ln D(E))/dE|_{E_{\text{F}}}, \quad (5)$$

where  $D(E)$  is the density of states and  $d(\ln D(E))/dE|_{E_F}$  is the value of derivative at the Fermi level. Overhof also determined [22] a temperature dependence of

$$\alpha \propto T^{1/2}. \quad (6)$$

In cases where  $E_F$  is in the vicinity of a minimum in the density of states with a symmetric distribution, the temperature dependence is given as

$$\alpha \propto T^{-Y}, \quad (7)$$

where  $Y$  is a constant, as determined by Pollak [23]. We note that the unusual temperature dependence of  $\alpha$  in non-doped  $YB_{66}$  changes dramatically with doping, and the Nb-doped samples exhibit a temperature dependence compatible with  $\alpha \propto T^{1/2}$  before decreasing at the high temperature end of our measurements. Not knowing the explicit band structure of doped  $YB_{66}$  we can only speculate, but the significant changes in the temperature dependence indicate that our doping has a strong influence on the band structure around the Fermi energy, possibly beyond a rigid band filling. For systems like a-Si and a-Ge a comprehensive investigation was carried out by Lewis [24]. We note that the unusual temperature dependence we observe most clearly in non-doped  $YB_{66}$  is similar to that of a-Ge, but the temperature scale of our data is about an order of magnitude higher.

Fig. 5 shows the temperature dependence of the power factor, which is equal to  $\alpha^2/\rho$ . The power factors of these  $YB_{66}$  systems increase but show saturation towards higher temperatures, whereas the  $REB_{44}Si_2$  system we investigated previously shows an extremely sharp rise towards temperatures beyond 1000 K [11].

At room temperature, the Nb-doped  $YB_{66}$  compound with 89% occupancy shows an increase of the power factor by factor 3 over the non-doped sample. However, in the

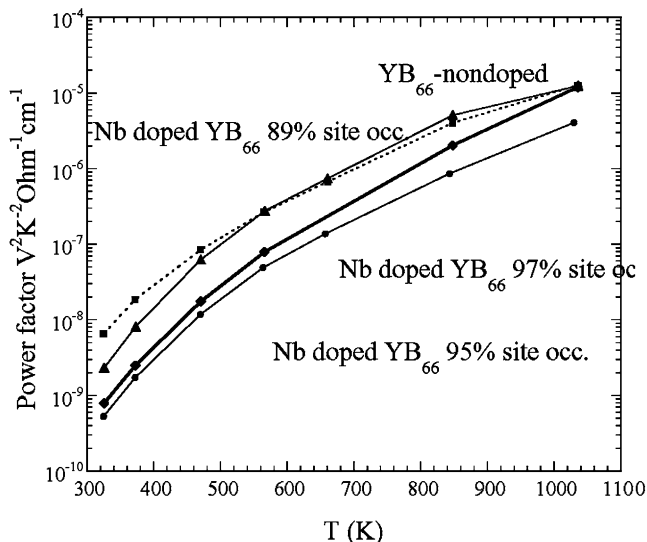


Fig. 5. Temperature dependence of the power factor of non-doped (triangles) and Nb-doped  $YB_{66}$  compounds; 89% occupancy (squares), 95% occupancy (circles), and 97% occupancy (diamonds). The lines are a guide to the eye.

important high-temperature region (for these compounds) the non-doped sample actually exhibits the highest power factor for  $T > 550$  K. This result is interesting as it shows that in the case of these compounds it is worth striving for a high  $T_0$  even at the price of a higher resistivity and thus a lower power factor at room temperature. As demonstrated here, even though  $\rho_0$  will increase, at high temperatures there can be reversals owing to the increase of  $T_0$  and the variable range hopping mechanism.

Taking into account the power factor results, in order to evaluate these new compounds as thermoelectric materials it is also necessary to know the behavior of the thermal conductivity  $\kappa$ . As mentioned before, low values of  $\kappa \sim 0.028$  W/cm K at room temperature for  $REB_{66}$  have been observed [10]. The doping of a Nb atom into the Wyckoff position  $8a$  of the  $YB_{66}$  structure will replace a boron pair, which has been speculated [12] to lower the thermal conductivity. Through this Nb doping the thermal conductivity is increased by a factor of 2, which is detrimental to thermoelectric applications. Taking the results obtained here and the thermal conductivity results into account, the  $YB_{66}$  system is judged not to be a feasible system to pursue among these rare earth boron cluster compounds. We are presently investigating transition metal doping in the more promising [11]  $REB_{44}Si_2$  system.

### 3.2. C-doping effects

A  $YB_{66}C_{0.6}$  crystal was grown and the properties compared with that of the non-doped  $YB_{66}$  crystal. It was impossible to determine exactly which sites the doped carbon atoms occupy, although it is assumed that they replace boron atoms. Fig. 6(a) and (b) plot the resistivity and the Seebeck coefficient, respectively. C-dope resulted in a modest lowering of the characteristic temperature  $T_0$ .  $T_0 = 7.76 \times 10^8$  K for  $YB_{66}C_{0.6}$  compared to  $T_0 = 12.8 \times 10^8$  K for non-doped  $YB_{66}$ . The room temperature resistivity shows a sizeable drop, and as a result the resistivity of C-doped  $YB_{66}$  does not vary much from the undoped compound at the important extreme high temperatures, unlike the Nb-doped case, in which there was a reversal of the relative magnitudes of resistivity. The Seebeck coefficient behaves in a way corresponding to the resistivity and also does not vary much upon doping in the high-temperature region.

We could not find high-temperature thermal conductivity values for  $YB_{66}$ ; however, those for  $GdB_{66}$  were measured [10]. In Fig. 5 of Ref. [10], it appears that a smooth extrapolation to the high-temperature region from 300 to 1000 K of the measured thermal conductivity of  $YB_{66}$  will yield similar values of  $\kappa$  as that of  $GdB_{66}$ . Therefore, as an approximation, we use the measured  $\kappa$  values of  $GdB_{66}$  as representative of non-doped  $YB_{66}$  to compare with those of our C-doped  $YB_{66}$  compound (Fig. 7(a)). The thermal conductivity undergoes a sizeable decrease upon C-doping and we attribute this to disorder arising from the carbon atoms replacing boron in the

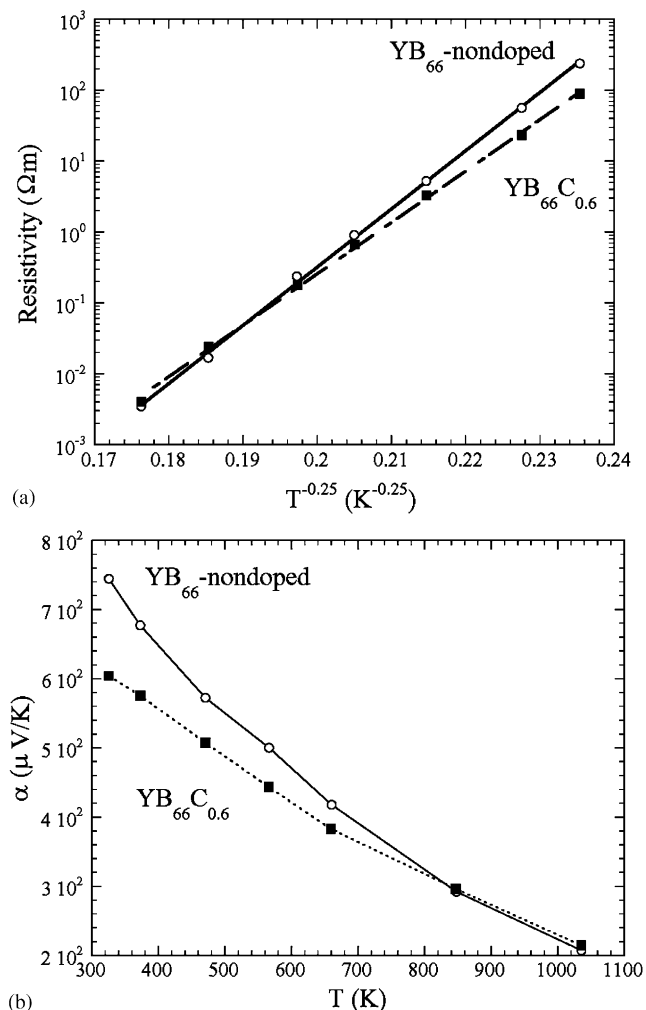


Fig. 6. Temperature dependence of (a) resistivity  $\rho$  and (b) Seebeck coefficient of non-doped (triangles) and C-doped  $\text{YB}_{66}$  compounds (squares). In the case of  $\rho$  the logarithmic is plotted versus  $T^{-0.25}$ .

compound framework. Since in Ref. [10], the only overlapping point at 300 K of measured  $\kappa$  of  $\text{YB}_{66}$  is actually larger than that of  $\text{GdB}_{66}$ , this conclusion appears to be sound despite the approximation. We next tried to estimate the figure of merit. We used values of  $\text{GdB}_{66}$  extrapolated from smooth polynomials to determine the figure of merit  $ZT$  of  $\text{YB}_{66}$  for comparison and plotted this in Fig. 7(b).

Overall, taking into account all the effects of doping, we can see in Fig. 7(b) that at the high-temperature limit which we are interested in, there is about a factor 2 increase of the figure of merit through C-doping. C-dope appears to be a valid route when considering modification of the rare earth boron-rich borides to improve their thermoelectric properties.

#### 4. Conclusions

A series of heavily Nb-doped  $\text{YB}_{66}$  single crystals and a C-doped  $\text{YB}_{66}$  single crystal were grown by the FZ method and their high-temperature thermoelectric properties were

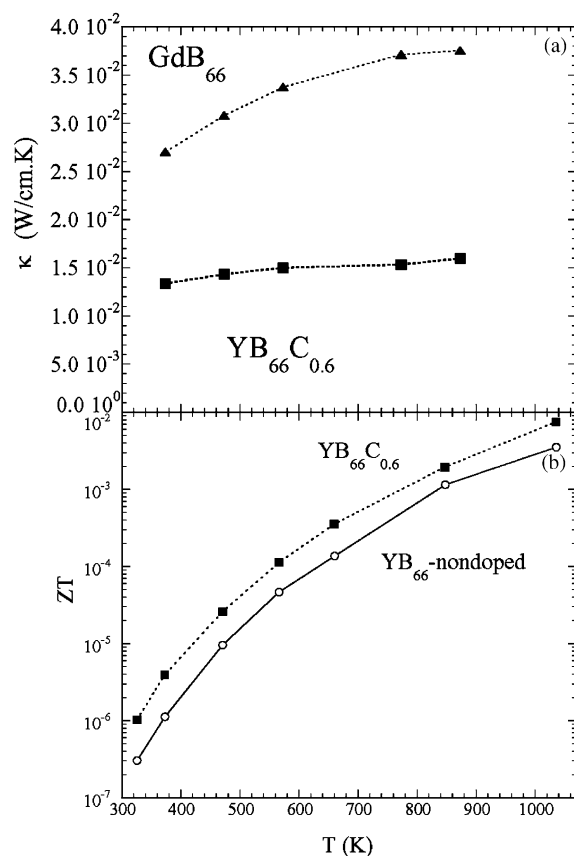


Fig. 7. Temperature dependence of (a) thermal conductivity and (b) calculated figure of merit of non-doped (triangles) and C-doped  $\text{YB}_{66}$  compounds (squares). The lines are a guide to the eye. It was assumed that the values of thermal conductivity for  $\text{GdB}_{66}$  in Ref. [12] apply to  $\text{YB}_{66}$  also.

investigated. The doped samples were compared with a grown non-doped  $\text{YB}_{66}$  crystal. The influence of Nb-doping on the thermoelectric properties was not monotonic and appears to be complex. For example, the Nb-doped 89% site occupancy sample takes the largest  $\alpha$  among the doped samples (over the whole temperature range) but also has the smallest  $T_0$ . This could be due to the crystal quality of the most heavily doped samples, which was inferior since a higher growth rate was necessary to reduce escape of Nb into the feed rod. At room temperature the Nb-doped  $\text{YB}_{66}$  sample with 89% site occupancy yielded a factor 3 increase over the power factor of non-doped  $\text{YB}_{66}$ . However, in the important high-temperature region (for these compounds) the non-doped sample actually exhibited the highest power factor for  $T > 550$  K. Furthermore, thermal conductivity actually increases with doping of transition metals because of a special structural feature of  $\text{YB}_{66}$ . The results indicate that transition metal doping of  $\text{YB}_{66}$  is not a feasible route to improving thermoelectric properties. On the other hand, C-doping was shown to result in a reduction of thermal conductivity and a factor 2 increase of the figure of merit at high temperatures. C-doping appears to be an attractive doping route to improve the thermoelectric properties of these rare earth boron cluster compounds. C-doping to

modify the more promising  $\text{REB}_{44}\text{Si}_2$  system is now underway.

### Acknowledgments

The authors are grateful to Y. Yajima for technical help. This work was supported in part by PRESTO, Japan Science and Technology Agency (4-1-8 Honcho Kawaguchi, Saitama, Japan).

### References

- [1] T. Mori, J. Appl. Phys. 95 (2004) 7204–7206.
- [2] T. Mori, T. Tanaka, J. Phys. Soc. Japan 68 (1999) 2033–2039.
- [3] T. Mori, A. Leithe-Jasper, Phys. Rev. B 66 (2002) 214419 1-6.
- [4] T. Mori, H. Mamiya, Phys. Rev. B 68 (2003) 214422 1-5.
- [5] C. Wood, D. Emin, Phys. Rev. B 29 (1984) 4582–4587.
- [6] H. Werheit, R. Schmechel, V. Fueffel, T. Lundstrom, J. Alloys Comp. 262–263 (1997) 372–380.
- [7] T. Nakayama, J. Shimizu, K. Kimura, J. Solid State Chem. 154 (2000) 13–19.
- [8] Y. Ishizawa, T. Tanaka, J. Solid State Chem. 154 (2000) 229–231.
- [9] M. Takeda, Y. Kurita, K. Yokohama, MRS Symposium Proceedings, vol. 793, Thermoelectric Materials, 2003 Research and Applications, Boston, MA, December 2003, pp. 219–224.
- [10] D.G. Cahill, H.E. Fischer, S.K. Watson, R.O. Pohl, G.A. Slack, Phys. Rev. B 40 (1989) 3254–3260.
- [11] T. Mori, J. Appl. Phys. 97 (2005) 093703 1-4.
- [12] T. Tanaka, et al., submitted for publication.
- [13] G.A. Slack, D.W. Oliver, G.D. Brower, J.D. Young, J. Phys. Chem. Solids 38 (1977) 45.
- [14] G.M. Sheldrick, SHELX-97: A Program for Solution and Refinement of Crystal Structures, University of Goettingen, Goettingen, Germany, 1997.
- [15] M. Richards, et al., Acta Crystallogr. 25 (1969) 237.
- [16] I. Higashi, K. Kobayashi, T. Tanaka, Y. Ishizawa, J. Solid State Chem. 133 (1997) 16–20.
- [17] A.L. Efros, M. Pollak, Electron-Electron Interactions in Disordered Systems, North-Holland, Amsterdam, 1985 pp. 409–482.
- [18] N.F. Mott, J. Non-Cryst. Solids 1 (1968) 1–28.
- [19] O.A. Golikova, Phys. Stat. Sol. A 101 (1987) 277–279.
- [20] H. Werheit, A. Moldenhauer, J. Solid State Chem. 177 (2004) 586–591.
- [21] I.P. Zvyagin, Phys. Stat. Sol. B 58 (1973) 443–449.
- [22] H. Overhof, Phys. Stat. Sol. B 67 (1975) 709–714.
- [23] M. Pollak, B.I. Halperin, Solid State Commun. 13 (1973) 869–872.
- [24] A.J. Lewis, Phys. Rev. B 13 (1976) 2565–2575.