Journal of Solid State Chemistry **154**, 229–231 (2000)
doi:10.1006/jssc.2000.8840, available online at http://www.idealibrary.com on IDEAL®

Transport Phenomena of $YB_{41}Si_{1.2}$

Yoshio Ishizawa and Takaho Tanaka*

Department of Materials Science, Iwaki Meisei University, 5-5-1 Iino, Chuohdai, Iwaki, Fukushima 970-8551, Japan, and
**National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*

Received September 9, 1999; in revised form January 10, 2000; accepted January 20, 2000

$YB_{41}Si_{1.2}$ was grown by a floating zone method with infrared heating. The crystal structure of $YB_{41}Si_{1.2}$ belongs to the orthorhombic system. The electrical resistivity, the Hall coefficient, and the Seebeck coefficient have been investigated from liquid nitrogen temperature to room temperature. The temperature dependence of the electrical resistivity was expressed as $\exp[(T_0/T)^{1/4}]$ and indicates semiconductive nature. The Hall mobility was estimated to an order of 0.1 cm^2/V s or lower. The combined data of the Hall mobility and the electrical resistivity indicates that electrical conduction is not of the band conduction type but of hopping type. The Seebeck coefficient is almost temperature independent between 110 and 290 K with a value of about 180 μV/K. For temperatures lower than 110 K, the Seebeck coefficient decreases rapidly with decreasing temperature. The figure of merit of the thermoelectric conversion of $YB_{41}Si_{1.2}$ was estimated and discussed using present data. © 2000 Academic Press

Key Words: **$YB_{41}Si_{1.2}$; boron-rich solid; electrical resistivity; Hall coefficient; Seebeck coefficient; figure of merit; thermoelectric conversion.**

INTRODUCTION

A new boron-rich compound of the Y–B–Si system, $YB_{41}Si_{1.2}$, was synthesized recently by Tanaka *et al.* (1). The crystal structure of $YB_{41}Si_{1.2}$ was determined by single-crystal X-ray diffractometry (2). $YB_{41}Si_{1.2}$ has an orthorhombic crystal structure (space group *Pbam*) composed of B_{12} icosahedra and $B_{12}Si_3$ polyhedral units. The lattice constants are $a = 1.6674$ nm, $b = 1.7667$ nm, and $c = 0.95110$ nm. The unit cell includes eight formulas with 346 atoms. The specific gravity is 2.668 g/cm^3.

$YB_{41}Si_{1.2}$ is a semiconductor with a room temperature electrical resistivity of about 0.7 Ω cm, which increases with decreasing temperature. The thermal conductivity of $YB_{41}Si_{1.2}$ is expected to be low because there are many atoms in the unit cell like most boron-rich solids. In the case of YB_{66} and β-rhombohedral boron (β-boron), the thermal conductivity at room temperature is 2.5×10^{-2} W/cm K (3) and 3.5×10^{-1} W/cm K (4), respectively. Such semiconductors with low thermal conductivity should be checked for the figure of merit of the thermoelectric conversion. Therefore, it is interesting to investigate the temperature dependence of the electrical resistivity and Seebeck coefficient. It is then possible to estimate the figure of merit of the thermoelectric conversion using both this data and available thermal conductivity data for boron-rich solids.

Moreover, the electrical conduction mechanism is also interesting because boron-rich solids such as YB_{66} and β-boron have amorphous-like transport properties (5, 6). Therefore, the Hall mobility was also studied and discussed in connection with the temperature dependence of the electrical resistivity.

EXPERIMENTAL

The crystals of $YB_{41}Si_{1.2}$ were grown with the floating zone technique using a Xenon image furnace (1). Feed rods with composition of $YB_{45}Si_{1.5}$ were sintered in vacuum at 1700°C and then arc-melted to obtain high-density rods. A small pellet with composition of $YB_{40}Si_{3.5}$ which was used for the molten zone in the floating zone crystal growth was also made by the same technique as the feed rods. A double zone pass was necessary in order to grow the crystal. The first zone pass was effective to obtain uniform composition and diameter of the feed rod. The crystal growth was carried out through the second zone pass process. Both the feed rod and the growing crystal were driven downward at 10 mm/h and counterrotated at 30 rpm. The composition in the middle part of the grown crystal was $YB_{44}Si_{1.0}$.

A $2.5 \times 1.0 \times 8.0$-mm sample was cut from the grown crystal using a diamond cutter. The sample orientation was not determined since the crystal included cracks, and it was necessary to cut out a portion of the crystal and avoid these cracks. The cut surface was cleaned using nitric acid.

The electrical resistivity, the Hall effect, and the Seebeck effect measurements were performed from liquid nitrogen to room temperature using standard techniques. The maximum magnetic field is 1.4 T during the Hall effect

0022-4596/00 $35.00

measurement. Electrical contacts between the sample and lead wires were made using a silver conductive paint.

RESULTS AND DISCUSSION

The temperature variation of the electrical resistivity ρ is shown in Fig. 1. The room temperature resistivity is about 0.7 Ω cm. The resistivity increases with decreasing temperature, indicating that $YB_{41}Si_{1.2}$ is a semiconductor. The temperature dependence of the resistivity does not show thermal activation type conduction. The observed resistivity is expressed as $\rho_0 \exp[(T_0/T)^{1/4}]$, where T_0 is a characteristic temperature. The electrical resistivity plotted on a logarithmic scale vs $T^{-1/4}$ relation is shown in Fig. 2. The characteristic temperature T_0 was evaluated to be 3.8×10^6 K. This $T^{-1/4}$ behavior of the electrical resistivity holds well for $T > 160$ K, indicating possibly that a three-dimensional variable range hopping-type conduction exists. This temperature dependence was also observed in other boron-rich solids such as YB_{66} (5) and β-boron (6). In the case of YB_{66} and DyB_{66}, the $T^{-1/4}$ dependence holds up to 900 K (5). Also in the electrical resistivity of Li- or Cu-doped β-boron, the same $T^{-1/4}$ temperature dependence was observed at temperatures between 30 and 300 K (7).

The Hall coefficient measurements of $YB_{41}Si_{1.2}$ were carried out at temperatures between 77 K and room temperature in order to estimate the carrier mobility. However, the Hall voltage was too small to be detected with the present experimental setup. The Hall coefficient was estimated to be 1 cm^3/C or lower at both 77 K and room temperature. Therefore, the Hall mobility is derived as 0.1 cm^2/V s or lower. Such a low mobility value means that standard band conduction mechanism does not apply to $YB_{41}Si_{1.2}$. The combined data of the low mobility value and the observed $T^{-1/4}$ temperature dependence of the electrical resistivity indicates that variable range hopping conduction exists in $YB_{41}Si_{1.2}$.

The temperature variation of the Seebeck coefficient of $YB_{41}Si_{1.2}$ is shown in Fig. 3. The Seebeck coefficient exhibits p-type behavior and is almost temperature independent at temperatures between 110 and 290 K with values of about 180 μV/K. For $T < 110$ K, the Seebeck coefficient decreases rapidly with decreasing temperature.

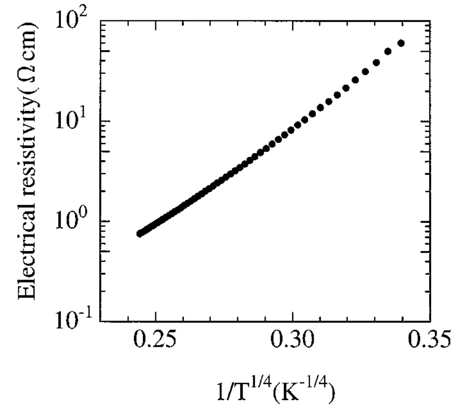

FIG. 2. Electrical resistivity vs $1/T^{1/4}$ relation of $YB_{41}Si_{1.2}$.

Since there are 346 atoms in the unit cell, the thermal conductivity of $YB_{41}Si_{1.2}$ is assumed to be low as in the case of most boron-rich solids with several hundreds of atoms in the unit cell. Therefore, it is interesting to estimate the figure of merit of the thermoelectric conversion. The figure of merit (Z) is expressed as follows (8):

$$Z = \alpha^2/\rho\kappa.$$

Here, α is the Seebeck coefficient, ρ is the electrical resistivity, and κ is the thermal conductivity. First, it is useful to calculate the power factor (P), which is given by

$$P = \alpha^2/\rho.$$

The power factor α^2/ρ was calculated using present data of the electrical resistivity and the Seebeck coefficient and is

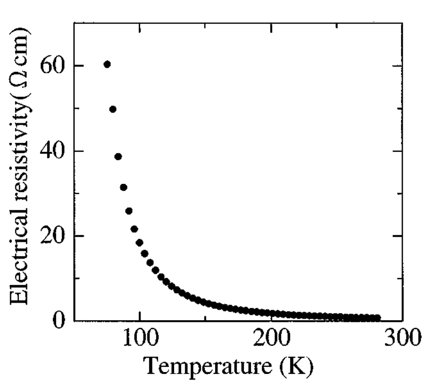

FIG. 1. Electrical resistivity of $YB_{41}Si_{1.2}$ as a function of temperature.

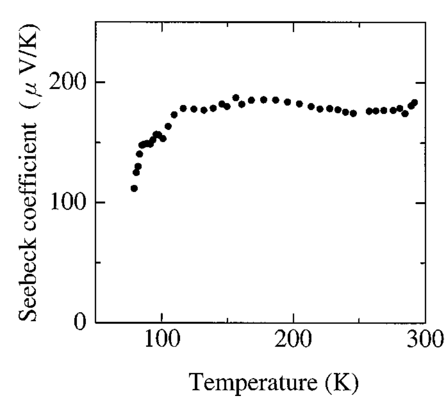

FIG. 3. Seebeck coefficient of $YB_{41}Si_{1.2}$ as a function of temperature.

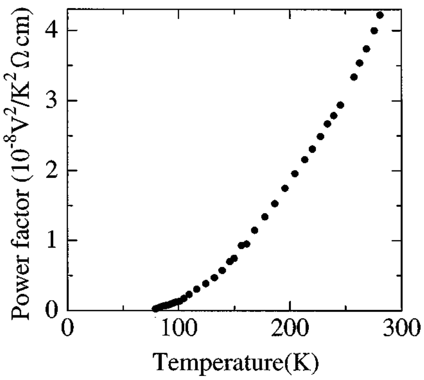

FIG. 4. Temperature dependence of the power factor α^2/ρ of $YB_{41}Si_{1.2}$.

shown in Fig. 4. The power factor increases monotonously from the value of 2.48×10^{-10} ($V^2/K^2\ \Omega$ cm) at liquid nitrogen temperature to the value of 4.22×10^{-8} ($V^2/K^2\ \Omega$ cm) at room temperature.

The thermal conductivity values of most boron-rich solids are between 10^{-1} and 10^{-2} W/cm K (3, 4, 9, 10). The room temperature thermal conductivity of YB_{66} and GdB_{66} is the lowest with a value of 2.5×10^{-2} W/cm K (3), while those of B_4C and $B_{12}P_2$ are about 2×10^{-1} W/cm K (9, 10). The thermal conductivity of β-boron is 3.5×10^{-1} W/cm K (4) at room temperature. Although the thermal conductivity of $YB_{41}Si_{1.2}$ is not measured yet, it is of interest to estimate the figure of merit (Z) using available data of the above-mentioned boron-rich solids. The thermal conductivity of YB_{66} is the lowest, so the estimated figure of merit calculated using data of YB_{66} gives the maximum or nearly maximum value. Using the value of 2.5×10^{-2} W/cm K, the figure of merit of $YB_{41}Si_{1.2}$ was estimated to be 1.69×10^{-6} K^{-1}. As the thermal conductivity of YB_{66} at liquid nitrogen temperature is almost the same as that of the room-temperature value, the figure of merit at liquid nitrogen temperature was estimated to be 9.92×10^{-9} K^{-1}. If the value of the thermal conductivity of β-boron is used instead, then the figure of merit at room temperature becomes 1.20×10^{-7} (K^{-1}).

For practical use, the figure of merit of the thermoelectric conversion should have values higher than 1×10^{-3} (K^{-1}). The present estimated figure of merit is 10^{-3} lower than a useful one. There are a few points to be considered to improve the figure of merit. In the case of $YB_{41}Si_{1.2}$, the maximum value of the figure of merit is expected to occur at a higher temperature than room temperature. This expectation is clearly seen from the temperature dependence of the power factor. A further step is to lower the electrical resistivity by carrier doping. Moreover in order to evaluate the real figure of merit, it is necessary to measure the actual thermal conductivity of $YB_{41}Si_{1.2}$.

CONCLUSION

The electrical resistivity, the Hall coefficient and the Seebeck coefficient of $YB_{41}Si_{1.2}$ were investigated from liquid nitrogen to room temperature. The temperature dependence of the electrical resistivity shows a semiconducting-like nature. It has been found that the resistivity obeys $\rho = \rho_0 \exp[(T_0/T)^{1/4}]$ above 160 K. The Hall mobility was estimated to be of an order of 0.1 cm^2/V s or lower. The combined data of the Hall mobility and the electrical resistivity indicates that electrical conduction is not mediated by band electrons but can be accounted for by a variable range hopping machanism. The Seebeck coefficient is almost temperature independent between 110 and 290 K, having a value of about 180 μV/K. The power factor in the figure of merit of the thermoelectric conversion amounts to 4.22×10^{-8} $V^2/K^2\ \Omega$ cm at room temperature. Thus, the figure of merit was estimated to be 1.69×10^{-6} K^{-1} using the thermal conductivity of YB_{66} at room temperature. A few points were proposed to improve the figure of merit.

REFERENCES

1. T. Tanaka, S. Okada, and Y. Ishizawa, *J. Solid State Chem.* **133,** 55 (1997).
2. I. Higashi, T. Tanaka, K. Kobayashi, Y. Ishizawa, and M. Takami, *J. Solid State Chem.* **133,** 11 (1997).
3. P. A. Medwick, R. O. Pohl, and T. Tanaka, *Jpn. J. Appl. Phys. Series* **10,** 106 (1994).
4. D. G. Cahill, H. E. Fischer, S. K. Watson, and R. O. Pohl, *Phys. Rev. B* **40,** 3234 (1989).
5. H. Werheit and U. Kuhlmann, *AIP Conf. Ser.* **231,** 125 (1990).
6. O. A. Golikova, *Phys. Stat. Sol.* (a) **101,** 277 (1987).
7. H. Matsuda, T. Nakayama, K. Kimura, H. Ino, Y. Murakami, H. Suematsu, and I. Higashi, *Jpn. J. Appl. Phys. Series* **10,** 39 (1994).
8. C. Wood, *Mat. Res. Soc. Proc.* **97,** 335 (1987).
9. G. A. Slack, D. W. Oliver, and F. H. Horn, *Phys. Rev. B* **4,** 1714 (1971).
10. P. R. H. Turkes, E. T. Swartz, and R. O. Pohl, *AIP Conf. Proc.* **140,** 346 (1985).