Thermoelectric Properties of Novel B_{12} Icosahedra-Containing Compounds

Takao Mori[1,2]
[1] National Institute for Materials Science
Namiki 1-1, Tsukuba, JAPAN 305-0044
[2] PRESTO, Japan Science and Technology Agency
4-1-8 Honcho Kawaguchi, Saitama, Japan.
E-mail: MORI.Takao@nims.go.jp, Phone: +81-29-860-4323

Abstract

$TbB_{44}Si_2$, $ErB_{44}Si_2$, and $YbB_{44}Si_2$ crystals which are isostructural to the magnetic TbB_{50} compound were grown by the floating zone method and high temperature thermoelectric properties Seebeck coefficient, resistivity) measured. These compounds are attractive as high temperature materials due to their stability. For comparison the properties of a ErB_{66} crystal were also measured. Seebeck coefficients in excess of 200 μV/K are observed at temperatures above 1000 K for the $REB_{44}Si_2$ compounds and the conductivity increases rapidly as temperature is increased through variable range hopping. $ErB_{44}Si_2$ had the highest power factor among the compounds measured. The thermal conductivity of $ErB_{44}Si_2$ was evaluated and determined to take the low value of 0.027 W/cm/K at room temperature.

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 B_{12} icosahedra-containing compounds have recently attracted increasing interest, since they are magnetically dilute semiconducting/insulating materials but display a various range of properties such as 1D dimer-like magnetic behavior in TbB_{50}-type compounds [1,2] or spin glass behavior in a layered series of RE-B-C(N) compounds [3,4]. Interestingly, it has been indicated that the B_{12} icosahedral clusters play an important role in mediating the magnetic interaction which is a novel phenomenon. Previously, boron-rich compounds such as the well known doped β-boron and CaB_6 systems have been investigated as possible thermoelectric materials [5-8].

We are interested in B_{12} icosahedral cluster-containing rare earth boride compounds because it has been found for the REB_{66} compound that they exhibit low thermal conductivity [9]. The magnitude of the thermal conductivity of REB_{66} is at least one order lower than the β-boron compounds and many orders lower than the CaB_6-type compounds [9].

The high temperature thermoelectric properties of grown crystals of novel rare earth B_{12} icosahedra-containing compounds were investigated in this work. The series of recently discovered $REB_{44}Si_2$ compounds $TbB_{44}Si_2$, $ErB_{44}Si_2$, $YbB_{44}Si_2$ and a ErB_{66} crystal was also measured for comparison. The thermal conductivity of $ErB_{44}Si_2$ was also evaluated.

Experimental

$REB_{44}Si_2$ (RE= Tb, Er, Yb) crystals were successfully grown by the floating zone method. Recently, interesting new borosilicide compounds like $Gd_5Si_2B_8$ [10] and $Ce_5Si_{3-x}B_x$ [11] have also been synthesized, but this is the most boron-rich compound.

Preparations for crystal growth of $REB_{44}Si_2$ were carried out in the following way. REB_n (n=44) samples were first synthesized by multiple sintering at 2100 K in BN crucibles by the borothermal reduction method:

$Tb_4O_7 + (4n+7)B \rightarrow 4TbB_n + 7BO$,

$RE_2O_3 + (2n+3)B \rightarrow 2REB_n + 3BO$, RE = Er, Yb

Then the samples were crushed, necessary amounts of Si powder added and the mixture synthesized again in the form of feed rods. These feed rods were used in the floating zone (FZ) method in a four xenon lamp ellipsoidal mirror-type image furnace to obtain crystals. Growth was done under Ar gas where the feed and seed crystals were counter-rotated at 40 rpm. REB_{66} and successively grown $REB_{44}Si_2$ crystals were used as seed crystals. Growth rate was kept to 4mm/hr. A part of the grown crystals was crushed and characterized by using high resolution powder x-ray diffractometry (Rigaku Co.; RINT2000) to confirm the $REB_{44}Si_2$ phase. The ErB_{66} crystal was also grown after preparing feed rods by the borothermal reduction sintering. A picture of a grown crystal of $YbB_{44}Si_2$ for example, is shown in Fig. 1.

Figure 1: Picture of $YbB_{44}Si_2$ crystal.

As for a basic description of the $REB_{44}Si_2$ structure, looking at the rare earth configuration in more detail, in the nearest neighbor direction the rare earth atoms form one dimensional chains in the direction of the c-axis. The chain is an alternating bond, with separation of 4.36 Å and 5.13 Å (for example in the case of $YbB_{44}Si_2$) [12]. These "chains" are separated from one

another in the a-b plane by 7.03 Å. Lattice constants are determined to be a=16.651(5) Å, b=17.661(2) Å, c=9.500(2) Å for $TbB_{44}Si_2$, a=16.600(8) Å, b=17.621(7) Å, c=9.485(5) Å for $ErB_{44}Si_2$, and a=16.636(4) Å, b=17.644(2) Å, c=9.488(2) Å for $YbB_{44}Si_2$.

The structure of ErB_{66} is cubic (space group *Fm3c*) with a=23.408(3) Å. It has been studied extensively by Richards [13] and Higashi [14] and the boron framework is basically formed by eight super-icosahedra, each of which is comprised of thirteen B_{12} icosahedra. Erbium atoms occupy peanut shaped holes at (0.05789,1/4,1/4) with an expected occupancy of around 0.65.

Results and Discussion

The temperature dependence of the resistivity ρ of the $REB_{44}Si_2$ and ErB_{66} compounds are shown in Fig. 2. The logarithmic of ρ is plotted versus $T^{-0.25}$ and although the number of data points is not large it can be seen that the behavior follows a straight line. This is the dependency of Mott's variable range hopping for 3 dimensional systems [15], where $\rho \propto \exp[(T_0/T)^{0.25}]$, and it has typically been observed for boron-rich B_{12} icosahedral systems [16]. Although the room temperature values of the resistivity are high, ρ decreases at an extremely steep rate as temperature is raised, due to the variable range hopping. It can be seen that the resistivity values of the $REB_{44}Si_2$ phase compounds are sizably lower than ErB_{66}.

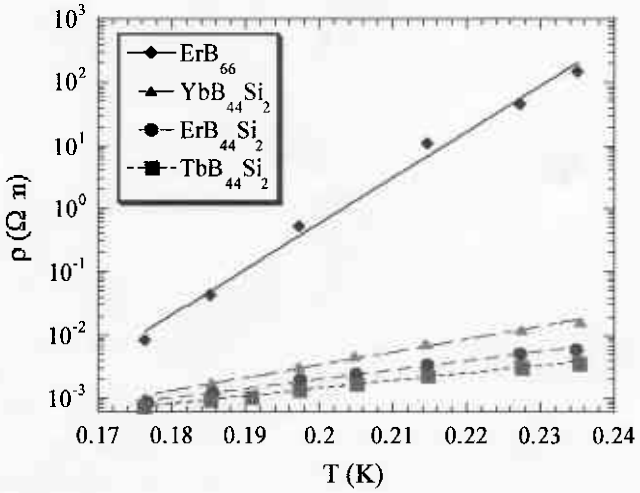

Figure 2: Temperature dependence of the resistivity ρ of $REB_{44}Si_2$; RE=Tb (squares), Er (circles), Yb (triangles) and ErB_{66} (diamonds). The logarithmic of ρ is plotted versus $T^{-0.25}$.

The thermopower of the $REB_{44}Si_2$ and ErB_{66} compounds; the Seebeck coefficients α, are plotted in Fig. 3(a). A sharp contrast of behavior is observed, ErB_{66} takes a very large value of α~700 μV/K near room temperature but decreases sharply as temperature is increased. This temperature dependence is rather peculiar and the reason for the large difference with $REB_{44}Si_2$ is not clear at present.

A view of just the data of the $REB_{44}Si_2$ phase compounds are shown in Fig. 3(b). As temperature is increased, the Seebeck coefficients increase monotonically and take values exceeding 200 μV/K at 1000 K. 1000 K is approximately the measurement limit of our present apparatus, but since the $REB_{44}Si_2$ compounds are stable to temperatures above 1600 K, this temperature dependence is an attractive characteristic for high temperature use.

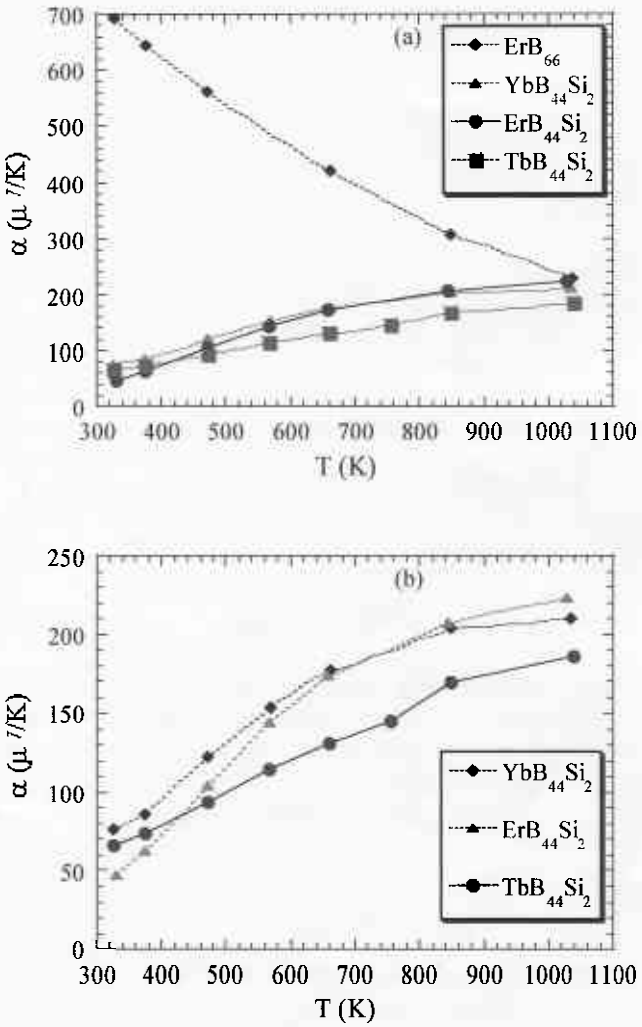

Figure 3: (a)Temperature dependence of the Seebeck coefficient α of $REB_{44}Si_2$; RE=Tb (squares), Er (circles), Yb (triangles) and ErB_{66} (diamonds). (b) is an enlarged plot of only the $REB_{44}Si_2$ data. The lines are a guide to the eye.

Fig. 4 shows the temperature dependence of the power factor, which is equal to α^2/ρ. As expected from the results above, the power factor shows an extremely sharp rise towards the higher temperatures. The power factor of ErB_{66} is much smaller than the $REB_{44}Si_2$ phases due to its high resistivity. $REB_{44}Si_2$ (RE=Tb,Er,Yb) show similar behavior, with $ErB_{44}Si_2$ having the highest power factor value at 1000 K.

To evaluate these new compounds as thermoelectric materials it is important to know the thermal conductivity κ. Unfortunately, the only thermal conductivity measurements carried out on rare earth B_{12} icosahedral compounds to date have been on the REB_{66} compounds. As mentioned before, low values of κ ~ 0.028 W/cmK at room temperature for REB_{66} have been observed [9]. We measured the room temperature

thermal conductivity of $ErB_{44}Si_2$ which has the highest power factor. Although the explicit mechanism for this low thermal conductivity in these rare earth B_{12} icosahedra systems has not been proved yet, the 5 fold symmetry of the boron icosahedra (which are the building blocks of the structure) obviously not translating to the symmetry of the crystal structure may play a role. It has been proposed that the lattice vibrations of crystalline REB_{66} are actually glasslike [9]. The room temperature thermal conductivity values were found to be similar and if we assume that the temperature dependence is also similar, the dimensionless figure of merit value of ZT can be extrapolated to estimate a value of ~0.02 at 1000 K for $ErB_{44}Si_2$. Preparations to measure the thermal conductivity of $REB_{44}Si_2$ up to high temperatures are presently being made.

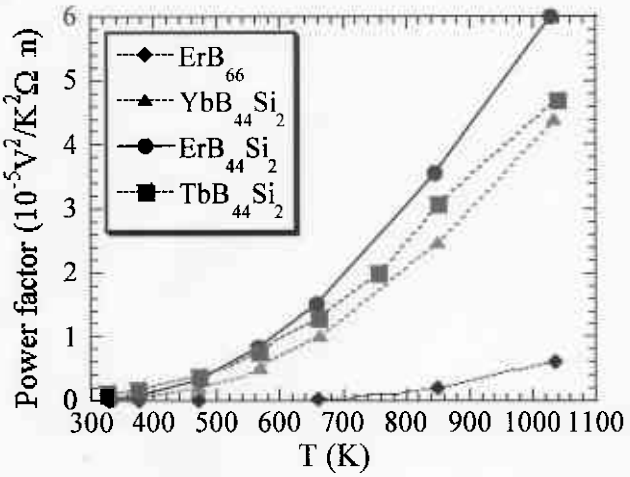

Figure 4: Temperature dependence of the power factor of $REB_{44}Si_2$; RE=Tb (squares), Er (circles), Yb (triangles) and ErB_{66} (diamonds). The lines are a guide to the eye.

Conclusions

The thermoelectric properties of novel $REB_{44}Si_2$ (RE=Tb,Er,Tm,Yb) compounds and a ErB_{66} sample were investigated at high temperatures from 300 K to 1000 K. $REB_{44}Si_2$ had the higher power factors and it was observed to increase steeply as temperature was increased. Seebeck coefficients exceeding 200 μV/K were observed at 1000 K. The room temperature thermal conductivity of a $REB_{44}Si_2$ compound was also evaluated for the first time and found to take the low value of 0.027 W/cm/K at room temperature which is similar to what has been determined previously for REB_{66}. The results indicate that further work on these types of rare earth higher borides for possible usage as high temperature thermoelectric materials is merited.

Acknowledgments

Dr. T. Tanaka is acknowledged for assisting the crystal growth.

References

1. Mori, T., "Doping Effect in a Magnetic TbB_{50}-type B_{12} Cluster Compound", *J. Appl. Phys.*, Vol. 95, No. 11 (2004), pp. 7204-7206.
2. Mori, T. *et. al.* "Magnetic Properties of Terbium B_{12} Icosahedral Boron-Rich Compounds" *Journal of the Physical Society of Japan* 68 (1999) 2033-2039.
3. Mori, T. *et. al,* "Magnetism of the Trigonal B_{12} Cluster Compound $REB_{17}CN$ (RE=Er, Ho)", *J. Appl. Phys.*, Vol. 93 (2003), pp. 7664-7666.
4. Mori, T. *et. al,* "Dynamical Properties of a Crystalline Rare-Earth Boron Cluster Spin-Glass System", *Phys. Rev. B*, Vol. 68, No. 20 (2003), 214422.
5. Werheit, H. *et. al,* "On the Electronic Properties of β-Rhombohedral Boron Interstitially Doped with 3d Transition Metal Atoms", *J. Alloys Comp.*, Vol. 262-263 (1997), pp. 372-380.
6. Nakayama, T. *et. al,* "Thermoelectric Properties of Metal Doped β-Rhombohedral Boron", *J. Solid State Chem.*, Vol. 154 (2000), pp. 13-19.
7. Ishizawa, Y. *et. al,* "Transport Phenomena of $YB_{41}Si_{1.2}$", *J. Solid State Chem.*, Vol. 154 (2000), pp. 229-231.
8. Takeda, M. *et. al,* "Synthesis and High Temperature Thermoelectric Properties of Alkaline-Earth Metal Hexaborides MB_6 (M=Ca,Sr,Ba)", *MRS Symp. Proc. Vol. 793 Thermoelectric Materials 2003 Research and Applications*, Boston, MA, Dec. 2003, pp. 219-224.
9. Cahill, D. G. *et. al,* "Thermal Properties of Boron and Borides", *Phys. Rev. B*, Vol. 40, No. 5 (1989), pp.3254-3260.
10. Babizhetskyy, V. *et. al,* "$Gd_5Si_2B_8$: A ternary rare-earth-metal silicide boride compound", *Angew. Chem. Int. Ed.*, Vol. 43, No. 15 (2004), pp. 1979-1983.
11. Jardin, R. *et. al,* "Influence on the physical behavior of boron substitution in Ce_5Si_3", *J. Alloys Comp.*, Vol. 359 (2003), pp. 35-40.
12. Higashi I. *et. al,* "Crystal Structure of $YB_{41}Si_{1.2}$", *J. Solid State Chem.*, Vol. 133 (1997), pp. 11-15.
13. M. Richards *et. al, Acta Crystallogr.* 25 (1969) 237.
14. I. Higashi *et. al,* "Structure refinement of YB_{62} and YB_{56} of the YB_{66}-type structure" *J. Solid State Chem*, 133 (1997) pp. 16-20.
15. Efros, A. L. *et al,* Electron-Electron Interactions in Disordered Systems, North-Holland (Amsterdam, 1985), pp. 409-482.
16. O. A. Golikova, "Semiconductors with Complex Lattice and the Amorphization Problem" *Phys. Stat. Sol.* A101 (1987) pp. 277-279.