Anomalous barium filling fraction and *n*-type thermoelectric performance of $Ba_yCo_4Sb_{12}$

L. D. Chen,[a] T. Kawahara, X. F. Tang, T. Goto, and T. Hirai
Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

J. S. Dyck, W. Chen, and C. Uher
Department of Physics, University of Michigan, Ann Arbor, Michigan 48109

(Received 30 January 2001; accepted for publication 1 June 2001)

Barium-filled skutterudites $Ba_yCo_4Sb_{12}$ with an anomalously large filling fraction of up to $y=0.44$ have been synthesized. The lattice parameters increase linearly with Ba content. Magnetic susceptibility data show that $Ba_{0.44}Co_4Sb_{12}$ is paramagnetic, which implies that some of the Co atoms in $Ba_yCo_4Sb_{12}$ have acquired a magnetic moment. The presence of the two different valence states of Co (Co^{3+} and Co^{2+}) leads to the anomalously large barium filling fraction even without extra charge compensation. All samples show *n*-type conduction. The electrical conductivity increases with increasing the Ba filling fraction. The lattice thermal conductivity of $Ba_yCo_4Sb_{12}$ is significantly depressed as compared to unfilled Co_4Sb_{12}. The dimensionless thermoelectric figure of merit, ZT, increases with increasing temperature reaching a maximum value of 1.1 for $Ba_{0.24}Co_4Sb_{12}$ at 850 K. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1388162]

I. INTRODUCTION

The Co_4Sb_{12}-based filled skutterudites are attracting great attention because of their prospective thermoelectric properties.[1–9] One of the distinguishing characteristics of the filled skutterudites is the significant depression of the lattice thermal conductivity due to the ''rattling'' of the filler atoms positioned in the oversized Sb-dodecahedron voids.[1–3,8–10] The filler atoms also have great influence on the electrical transport and affect parameters such as carrier concentration, carrier mobility, and carrier effective mass. So far, various kinds of atoms, including Ce, La, Nd, Sm, Yb, Ca and Tl, have been used to fill the voids in the search for high thermoelectric performance skutterudites.[2–6,11–14] Such efforts have resulted in striking thermoelectric performance for *p*-type materials with high ZT (dimensionless thermoelectric figure of merit) values of up to 1–1.4 at elevated temperatures (700–900 K).[2,3,5,15]

However, most of the filled skutterudites reported so far are *p*-type materials, though it was predicted that the high conduction-band masses in *n*-type skutterudites hold promise for high thermoelectric performance.[16] There are two approaches for the preparation of *n*-type skutterudites. One is the substitution of Sb with a VIb element (such as Te).[17,18] One can also substitute for Co with Ni, Pt, and/or Pd to obtain *n*-type material.[18,19] Although many studies have been carried out on forming substitutional alloys, there seems to be a limitation to the improvement of *n*-type thermoelectric performance through the formation of substitutional alloys, because the lattice thermal conductivity cannot be depressed enough on account of the mass defect scattering only. The other main approach to obtain *n*-type skutterudites is to fill the voids in the skutterudite structure with foreign species such as rare-earth atoms.[20] In the case of Co_4Sb_{12}-based skutterudites, in order to fill the voids, charge compensation is usually required and is carried out by partially replacing Co^{3+} with Fe^{2+}. The $[Fe_xCo_{4-x}Sb_{12}]$ framework in $M_yFe_xCo_{4-x}Sb_{12}$ (M: metallic filler atom) is isostructural to Co_4Sb_{12}, but is electron deficient as compared to Co_4Sb_{12}. The reason is that Fe mainly takes the 2+ oxidation state.[4] Therefore, when a rare-earth atom (Ln) is used as the filler atom, assuming that each Fe^{2+} provides one hole and each rare-earth atom (Ln) supplies three electrons to the skutterudite structure, the filled skutterudite $Ln_yFe_xCo_{4-x}Sb_{12}$ will only show *n*-type conduction when the filling fraction *y* is larger than $x/3$.[4,5] However, previous work[2–7] showed that when rare-earth atoms are used as filler atoms, a high filling fraction is difficult to achieve and thus most of the $Ln_yFe_xCo_{4-x}Sb_{12}$ samples reported show *p*-type conduction. It is important to search for filled skutterudites with high filling fractions to realize *n*-type material with high thermoelectric performance.

Sales *et al.*[13] synthesized Tl-filled skutterudites with moderately high filling fractions (up to $y=0.22$ for $Tl_yCo_4Sb_{12}$), in which Tl is thought to be monovalent. They measured the thermoelectric properties at low temperature and estimated a maximum ZT value of about 0.8 at 800 K for their *n*-type samples. In some other recent work,[21,22] it was reported that, under high pressure, a surprisingly large fraction of IVb elements such as Sn, Pb, and Si can be inserted into the voids of Co_4Sb_{12}. Indeed, $Sn_yCo_4Sb_{12}$ does show *n*-type conduction with low lattice thermal conductivity.[22] However, no high temperature transport data have yet been reported and the thermal stability of these IVb-element-filled compounds is not known. Anno *et al.*,[23] Dilley *et al.*,[12] and Nolas *et al.*[24] synthesized the Yb-filled skutterudites $Yb_yCo_{4-x}M_xSb_{12}$ (M=Pd, Pt), $Yb_yCo_4Sn_xSb_{12-x}$, and $Yb_yCo_4Sb_{12}$, respectively, and reported moderately large filling fractions. The combination of Pd doping with Yb filling resulted in a modestly large ZT value.[23] Nolas *et al.* also

[a]Electronic mail: cld@imr.tohoku.ac.jp

TABLE I. Summary of composition, transport, and crystallographic characteristics of Ba-filled skutterudites at room temperature. All are synthesized by using Co ingot (99.96%) as raw materials.

Nominal composition	Co_4Sb_{12}	$Ba_{0.1}Co_4Sb_{12}$	$Ba_{0.2}Co_4Sb_{12}$	$Ba_{0.3}Co_4Sb_{12}$	$Ba_{0.4}Co_4Sb_{12}$	$Ba_{0.5}Co_4Sb_{12}$
Chemical composition of skutterudite phase by EPMA	Co_4Sb_{12}	$Ba_{0.07}Co_4Sb_{11.88}$	$Ba_{0.16}Co_4Sb_{11.85}$	$Ba_{0.24}Co_4Sb_{11.87}$	$Ba_{0.38}Co_4Sb_{11.74}$	$Ba_{0.44}Co_4Sb_{11.90}$
Lattice constant (Å)	9.0371	9.0491	9.0632	9.0769	9.0902	9.1043
X-ray density (g/cm^3)	7.638	7.650	7.670	7.684	7.735	7.736
Relative density (%)	92.4	97.4	96.7	95.8	89.8	95.8
Electrical conductivity[a] ($S\ m^{-1}$)	1.882×10^3	1.032×10^5	2.138×10^5	3.234×10^5	3.939×10^5	6.378×10^5
Seebeck coefficient ($\mu V\ K^{-1}$)	−628	−139	−132	−88	−70	−68
$\kappa_{lattice}$[a] (W/mK)	8.20	5.76	4.62	3.44	2.47	2.77
Secondary phase by SEM and EPMA	None	None	Trace $CoSb_2$	Trace $CoSb_2$	None	None

[a]Corrected for density.

reported a ZT value of about 1 at 600 K for $Yb_yCo_4Sb_{12}$ by using a calculated lattice thermal conductivity. In our previous study,[25] we succeeded in synthesizing the Ba-filled skutterudite, $Ba_yFe_xCo_{4-x}Sb_{12}$, and observed that Ba has a greater filling fraction than all other filler species. Measurements of the thermoelectric properties showed that $Ba_yCo_4Sb_{12}$ samples are *n*-type materials with promising thermoelectric performance. The present work describes the effect of the Ba filling fraction on the thermal and electrical transport of $Ba_yCo_4Sb_{12}$.

II. EXPERIMENT

Highly pure metals of Ba (99.9%, plate), Sb powder (99.9999%), and Co shot (99.96% with Ni as the main impurity) or Co powder (99.99%, Ni free) were used as the starting materials. A binary compound of Sb_3Ba was first synthesized by reacting Sb and Ba elements in a carbon crucible under a flowing Ar atmosphere at 903 K for 96 hrs. The prereacted Sb_3Ba was mixed with Co and additional Sb and then melted at 1323 K for 24 h with subsequent quenching in a water bath. The obtained ingots were ground into fine powder, and pressed into cylindrical pellets. The pellets were then annealed at 973 K for 72–216 h to form a completely homogeneous skutterudite phase. The obtained powder was then sintered into a dense polycrystalline solid by using a plasma activated sintering (PAS) technique (Sodic Co. Ltd: PAS-V-K) at 873 K for 15 min in a graphite die.

The constituent phases of the samples were determined by powder X-ray diffractometry (Rigaku: RAD-C, Cu $K\alpha$). Chemical composition of the skutterudite phase was determined by using electron probe microanalysis (EPMA). Electrical conductivity (σ) was measured by a four-probe method in a flowing Ar atmosphere. Thermoelectromotive force (ΔE) was measured at five different temperature gradients ($0 \leqslant \Delta T \leqslant 10$ K) for a given temperature, and the Seebeck coefficient (α) was obtained from the slope of the ΔE vs ΔT plot. Thermal conductivity (κ) was measured by a laser flash method (Shinkuriko: TC-7000) in a vacuum over the temperature range of 300–900 K. The measurement of thermal conductivity at low temperature (2–300 K) was carried out by using a longitudinal steady-state method. Magnetic susceptibility was measured between 10 and 300 K in a magnetic field of 1.0 T using a Quantum Design magnetometer. In the magnetic measurement, the sample was placed inside of a polyethylene capsule and straw and the background susceptibility of the capsule and straw was corrected for.

III. RESULTS

The prereacted Sb_3Ba was stable in air and easily handled. The resulting powder obtained after melting $Sb_3Ba+Sb+Co$ with subsequent annealing at 973 K was single phase as determined by x-ray analysis, while the EPMA and scanning electron microscopy (SEM) observation showed that several samples contained trace amount (<2 vol %) of $CoSb_2$ as a secondary phase (Table I). The Co:Sb ratios in the skutterudite phase determined by EMPA are very close to the stoichiometric value (4:12) and are independent of Ba content. Table I summarizes the composition and physical properties of the Ba-filled skutterudites at room temperature.

Figure 1 shows the relationship between lattice parameter and Ba content (y). Lattice parameters increase linearly with y in the region of $y=0$–0.44. The Rietveld refinement of the x-ray diffraction data verified that Ba fills the Sb voids to form the skutterudite structure (Im3).[25] From the linear relation between lattice parameter and filling fraction, it can be said that the filling fraction of Ba in the $Ba_yCo_4Sb_{12}$ samples prepared by the melting method extends at least to $y=0.44$, which is a rather higher limit than that usually associated with rare- earth and other filler atoms in the Co_4Sb_{12}-based filled skutterudites without extra compensation (such as substitution of Fe for Co).[4,9,13] The results of EPMA composition (Table I) confirmed that the anomalously large Ba-filling fraction does not cause nonstoichiometry in the Co/Sb ratio. As a possible explanation for the present high content of Ba in Co_4Sb_{12} structure, we proposed[26] that cobalt is in a mixed

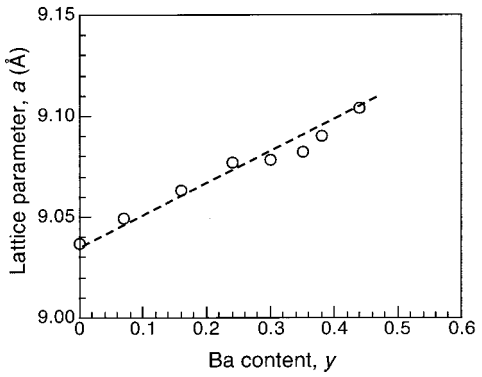

FIG. 1. Relationship between lattice parameter and Ba content for $Ba_yCo_4Sb_{12}$.

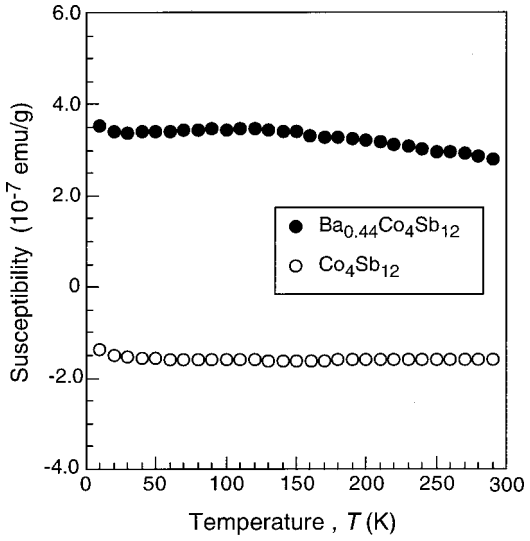

FIG. 2. Temperature dependence of magnetic susceptibility of Co_4Sb_{12} and $Ba_{0.44}Co_4Sb_{12}$.

valence state, Co^{3+} and Co^{2+}. If this is the case, some of the Co atoms will have a d^7 electron configuration (Co^{2+}) and therefore an uncompensated electron spin leading to a paramagnetic behavior. To verify it, we made measurements of magnetic susceptibility and the data are shown in Fig. 2. Co_4Sb_{12} has a negative susceptibility of about -1.6×10^{-7} emu/g, temperature independent in the studied temperature range. This agrees well with the data reported in previous studies.[20,27,28] On the other hand, $Ba_{0.44}Co_4Sb_{12}$ has a positive susceptibility of $2.5-3.5\times10^{-7}$ emu/g which slightly decreases with increasing temperature. In this sample, no impurity phase is observed by either x-ray diffraction or microanalysis. The small magnetic susceptibility is considered to be contributed by a few percent of Co atoms with a magnetic d^7 state, because Ba should take a nonmagnetic s^2p^6 state. This result indicates the possibility of mixed valence for Co atoms in $Ba_yCo_4Sb_{12}$. The mixed valence of Co may be the main cause for the anomalously high Ba filling fraction. If so, this gives us an interesting angle on the study of filled skutterudites. For the exact description of the relationship between Co mixed valence and Ba content, further experimental and theoretical study is necessary.

The carrier concentration and electrical conductivity are known to be sensitive to the level of Ni impurity in the cobalt raw material.[26,29] Co_4Sb_{12} prepared from highly pure Co (Ni free) usually shows *p* type conduction. In the present experiment, the unfilled Co_4Sb_{12} sample prepared by using Co shot (99.96%) as raw material shows *n*-type conduction and has an electron concentration of 5.34×10^{24} m^{-3} at room temperature due to the Ni impurity in the Co. When a small amount of Ba is added to the voids of Co_4Sb_{12}, additional electrons are donated by barium. Figure 3 shows the temperature dependence of electrical conductivity for $Ba_yCo_4Sb_{12}$. Electrical conductivity increases as the Ba content increases. This is due to the increase in electron concentration because Ba provides two electrons to the skutterudite structure as discussed above.

Figure 4 shows the temperature dependence of the See-

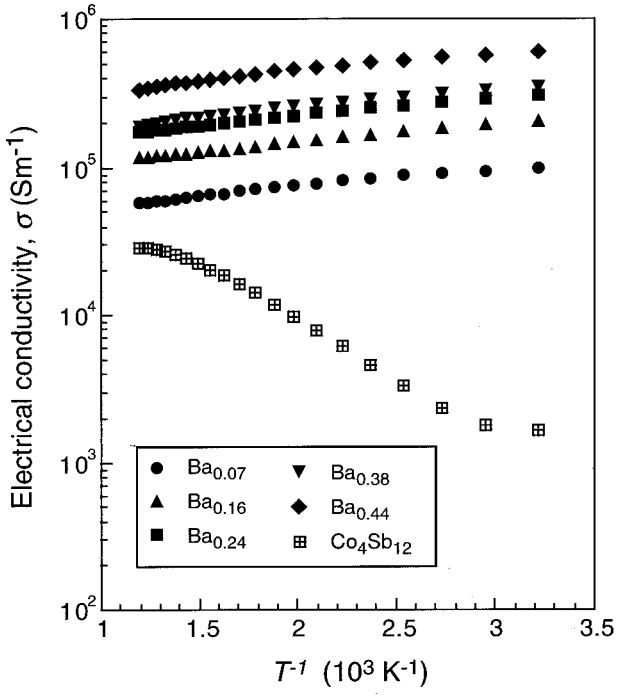

FIG. 3. Temperature dependence of electrical conductivity for $Ba_yCo_4Sb_{12}$.

beck coefficient. All samples have negative Seebeck coefficients consistent with Hall measurements. The magnitude of the Seebeck coefficient decreases with Ba content. For the samples with $y=0.16-0.44$, the magnitude of the thermopower monotonically increases with increasing temperature. The $Ba_{0.07}Co_4Sb_{12}$ sample, which has a low carrier concentration, shows a maximum value in thermopower at about 700–800 K. In the case of unfilled Co_4Sb_{12}, the absolute negative Seebeck coefficient decreases as temperature in-

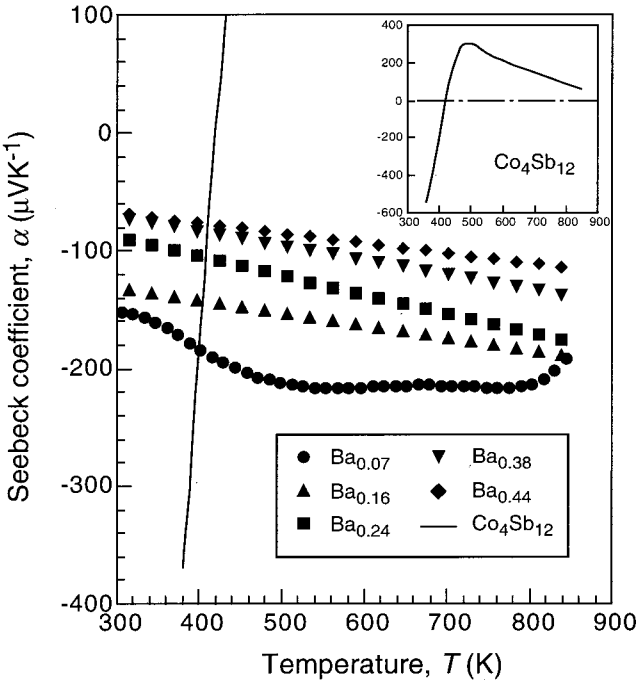

FIG. 4. Temperature dependence of Seebeck coefficient for $Ba_yCo_4Sb_{12}$.

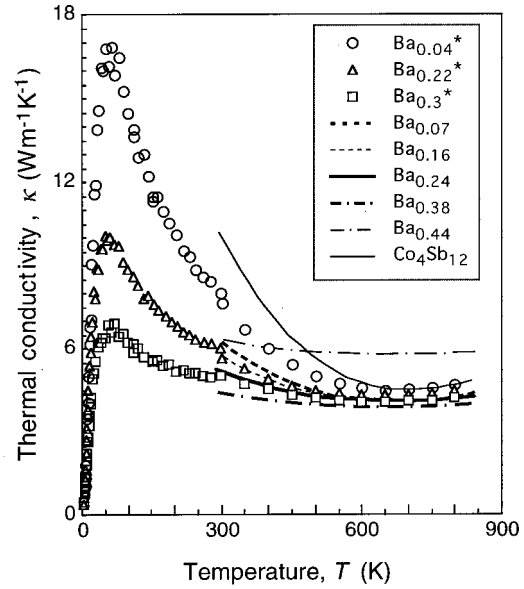

FIG. 5. Temperature dependence of thermal conductivity. * Samples prepared by using Ni-free Co powder (99.99%) as raw materials.

creases. At high temperatures, it turns *p* type due to an onset of intrinsic conduction seen also in the temperature dependence of the electrical conductivity (Fig. 3) and Hall measurements. For all samples, the relation $\mu \propto T^{-3/2}$ at $T>50$ K is confirmed, implying that the charge carriers are mainly scattered via acoustic phonons.[26] The calculated electron effective mass is between $2m_e$ and $4m_e$,[26] which is similar to those previously reported for *n*-type Co_4Sb_{12} and related filled compounds.[13,18,20]

Figure 5 shows the temperature dependence of thermal conductivity. The Ba content dependence of lattice thermal conductivity (κ_L) at room temperature is shown in Fig. 6. Compared to the unfilled Co_4Sb_{12}, the thermal conductivity of $Ba_yCo_4Sb_{12}$ is greatly depressed, especially in the low temperature region. The $Ba_{0.44}Co_4Sb_{12}$ sample has an abnormally large value of total thermal conductivity, especially at high temperatures, though its lattice thermal conductivity remains small. A large electronic contribution to the thermal conductivity arising from the high electrical conductivity (see Fig. 3) is responsible for the large total thermal conductivity. The lattice thermal conductivity decreases with Ba content. However, the lattice thermal conductivity remains relatively large in comparison to skutterudites filled with rare-earth atoms (Ce, La, Yb)[2–5] and others species (Tl, Sn, Y)[13,22,30] which have smaller ionic radii than barium. Indeed, the thermal parameters of Ba atoms in the voids are known to be smaller than those of other filler atoms.[25] That is to say, the larger Ba ions provide less scattering and thus a weaker influence on the lattice thermal conductivity. To depress the lattice thermal conductivity of $Ba_yCo_4Sb_{12}$-based compounds further, substitution (e.g., Ni on the lattice sites of Co, which will provide additional phonon scattering) and multi-filling approaches (e.g., filling with both Ba and Ce ions) might be prospective avenues for exploration. Such experiments are now in progress.

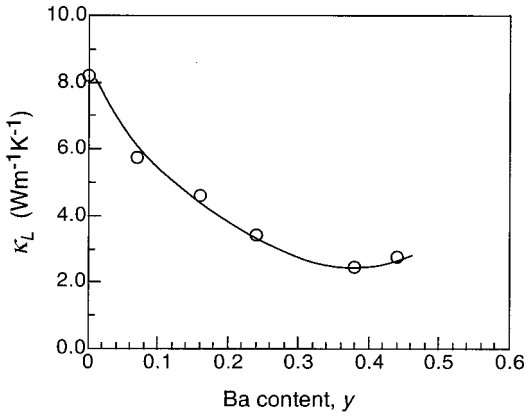

FIG. 6. Relationship between lattice thermal conductivity and Ba content for $Ba_yCo_4Sb_{12}$.

Concerning the effect of the filling fraction on the lattice thermal conductivity, two main viewpoints have been advanced. Sales *et al.*[13] suggested that the thermal resistivity ($1/\kappa_{\text{Lattice}}$) varies as $y^{1/3}$ based on a simple model of acoustic phonon scattering by the rattlers. They reported that this is the case in the $Tl_yCo_4Sb_{12-x}Sn_x$ structure where the Tl content varies over a wide range of $y=0$–1. However, in Sales's discussion,[13] it must be noted that the substitution of Sn for Sb, needed for charge compensation, was not taken into account. Indeed, as can be seen in Ref. 13, the Sn content does increase with Tl content. This concomitant Sb substitution effect will also depress the lattice thermal conductivity due to the additional phonon scattering similar to that caused by the substitution of Fe for Co[4,7] or the substitution of Te for Sb.[18] The other viewpoint was proposed independently by Nolas *et al.*[9] and Meisner *et al.*[10] and is based on an argument that a random distribution of rattlers (i.e., a partial filling) should be more effective in scattering phonons than an arrangement in which all of the voids are filled (i.e., 100% filling). Meisner *et al.* reported that for optimally filled $Ce_yFe_xCo_{4-x}Sb_{12}$ skutterudites (Ce filling fraction at a maximum for a given Fe concentration), Ce scatters most effectively near $y\approx 0.7$. In the case of La-filled skutterudites, Nolas *et al.* observed a minimum lattice thermal conductivity at a filling fraction of 0.25–0.3. Minima in the lattice thermal conductivity were subsequently observed[15,31] also for $Ce_yFe_xCo_{4-x}Sb_{12}$ and $Ba_yFe_xCo_{4-x}Sb_{12}$ samples with Fe content fixed at $x=1$ and 1.6. In the present experiment, the lattice thermal conductivity displays an apparent shallow minimum near $y=0.35$–0.4. To verify the trend, samples having a larger filling fraction are necessary. However, in the present work we were unable to synthesize samples with a filling fraction larger than 0.45.

Figure 7 shows the ZT values of several samples. Within the temperature range of 300–900 K, ZT increases with temperature for all samples. The highest figure of merit is observed for the $Ba_{0.24}Co_4Sb_{12}$ sample where the ZT value reaches about 1.1 at 850 K. This is one of the highest values reported for *n*-type filled skutterudites. It is expected that further work on the optimization of composition, especially on the further depression of lattice thermal conductivity by multifilling or substitutional effect, would result in even

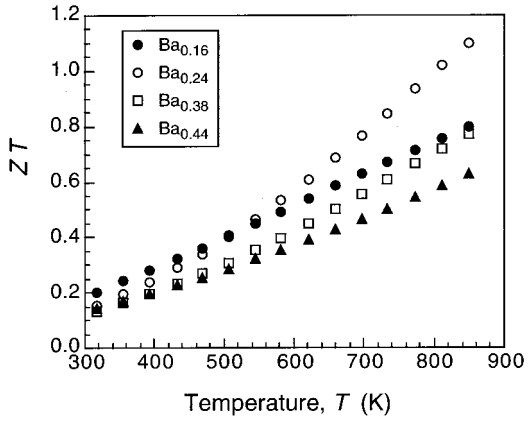

FIG. 7. Typical results of dimensionless figure of merit (ZT) as a function of temperature for $Ba_yCo_4Sb_{12}$.

higher performance *n*-type skutterudite material based on Ba filling.

IV. SUMMARY

Barium-filled skutterudite compounds with a wide range of Ba filling fractions have been synthesized. The $Ba_yCo_4Sb_{12}$ samples show a paramagnetic susceptibility suggesting the possibility of mixed valence of Co atoms. The mixed valence of Co in this system might be the reason why one observes an anomalously large Ba filling fraction. Further magnetic and transport measurements are needed to ascertain the exact magnetic state of Co in Ba-filled skutterudites. The lattice thermal conductivity decreases with Ba filling fraction and falls well below the values corresponding to unfilled Co_4Sb_{12}. The highest value of the figure of merit ($ZT=1.1$) is measured at 850 K for the composition $Ba_{0.24}Co_4Sb_{12}$. Further suppression of lattice thermal conductivity would result in even higher performance *n*-type skutterudite material filled with barium.

ACKNOWLEDGMENTS

This work was partly supported by a research grant from the Mazda Foundation, Japan, and the Research Foundation for Materials Science, Japan. Work at the University of Michigan was supported by the DARPA Grant No. N00014-98-3-0011. The authors thank Dr. T. Caillat of Jet Propulsion Laboratory, California Institute of Technology, for his helpful discussion. The authors thank Y. Murakami of IMR, Tohoku University for performing EPMA analysis.

[1] C. Uher, in *Semiconductors and Semimetals* (Academic, New York, 2001), Vol. 69, pp. 139–253.
[2] B. C. Sales, D. Mandrus, and R. K. Williams, Science **272**, 1325 (1996).
[3] B. C. Sales, D. Mandrus, B. C. Chakoumakos, V. Keppens, and J. R. Thompson, Phys. Rev. B **56**, 15081 (1997).
[4] B. X. Chen, J. H. Xu, C. Uher, D. T. Morelli, G. P. Meisner, J.-P. Fleurial, T. Caillat, and A. Borshchevsky, Phys. Rev. B **55**, 1476 (1997).
[5] J.-P. Fleurial, T. Caillat, and A. Borshchevsky, *Proceedings of the 16th International Conference of Thermoelectrics* (IEEE, New York, 1997), p. 1.
[6] X. Tang, L. Chen, T. Goto, T. Hirai, and R. Z. Yuan, Sci. China, Ser. B: Chem. **43**, 306 (2000).
[7] X. Tang, L. Chen, T. Goto, and T. Hirai, J. Jpn. Inst. Met. **63**, 1412 (1999).
[8] B. C. Chakoumakos, B. C. Sales, D. Mandrus, and V. Keppens, Acta Crystallogr., Sect. B: Struct. Sci. **B55**, 341 (1999).
[9] G. S. Nolas, J. L. Cohn, and G. A. Slack, Phys. Rev. B **58**, 164 (1998).
[10] G. P. Meisner, D. T. Morelli, S. Hu, J. Yang, and C. Uher, Phys. Rev. Lett. **80**, 3551 (1998).
[11] J. W. Kaiser and W. Jeitschko, J. Alloys Compd. **291**, 66 (1999).
[12] N. R. Dilley, E. D. Bauer, M. B. Maple, and B. C. Sales, J. Appl. Phys. **88**, 1948 (2000).
[13] B. C. Sales, B. C. Chakoumakos, and D. Mandrus, Phys. Rev. B **61**, 2475 (2000).
[14] G. S. Nolas, H. B. Lyon, J. L. Cohn, T. M. Tritt, and G. A. Slack, *Proceedings of the 16th International Conference of Thermoelectrics* (IEEE, New York, 1997), p. 321.
[15] X. Tang, L. Chen, T. Goto, and T. Hirai, J. Mater. Res. **16**, 837 (2001).
[16] L. Nordstrom and D. J. Singh, Phys. Rev. B **53**, 1103 (1996).
[17] Y. Nagamoto, K. Tanaka, and T. Koyanagi, in *Proceedings of the 17th International Conference of Thermoelectrics* (IEEE, New York, 1998), p. 302.
[18] T. Caillat, A. Borshchevsky, and J.-P. Fleurial, J. Appl. Phys. **80**, 4442 (1996).
[19] H. Anno, K. Matsubara, Y. Notohara, T. Sakakibara, and H. Tashiro, J. Appl. Phys. **86**, 3780 (1999).
[20] D. T. Morelli, G. P. Meisner, B. X. Chen, S. Q. Hu, and C. Uher, Phys. Rev. B **56**, 7376 (1997).
[21] H. Takizawa, K. Miura, M. Ito, T. Suzuki, and T. Endo, J. Alloys Compd. **282**, 79 (1999).
[22] G. S. Nolas, H. Takizawa, T. Endo, H. Sellinschegg, and D. C. Johnson, Appl. Phys. Lett. **77**, 52 (2000).
[23] H. Anno, and K. Matsubara, in *Recent Research Developments in Applied Physics* (Transworld Research Network, India, 2000), Vol. 3.
[24] G. S. Nolas, M. Kaeser, R. T. Littleton IV, and T. M. Tritt, Appl. Phys. Lett. **77**, 1855 (2000).
[25] L. Chen, X. Tang, T. Goto, and T. Hirai, J. Mater. Res. **15**, 2276 (2000).
[26] L. Chen, T. Kawahara, X. Tang, T. Goto, T. Hirai, J. S. Dyck, W. Chen, and C. Uher, in *Proceedings of the 19th International Conference of Thermoelectrics* (IEEE, New York, 2000).
[27] H. Anno, K. Hatada, H. Shimizu, K. Matsubara, Y. Notohara, T. Sakakibara, H. Tashiro, and K. Motoya, J. Appl. Phys. **83**, 5270 (1998).
[28] D. T. Morelli, T. Cailat, J.-P. Fleurial, A. Borshchevsky, J. Vandersande, B. Chen, and C. Uher, Phys. Rev. B **51**, 9622 (1995).
[29] K. Matsubara, T. Sakakibara, Y. Notohara, H. Anno, H. Shimizu, and T. Koyanagi, in *Proceedings of the 15th International Conference of Thermoelectrics* (IEEE, New York, 1996), p. 96.
[30] X. Tang, L. Chen, S. Oribe, W. Pan, T. Goto, and T. Hirai, J. Jpn Soc. Powder Powder Metallurgy **47**, 958 (2000).
[31] X. Tang, Thesis of Tohoku University, 2000, p. 93.