Low thermal conductivity and high thermoelectric figure of merit in *n*-type $Ba_xYb_yCo_4Sb_{12}$ double-filled skutterudites

X. Shi,[1,a)] H. Kong,[1] C.-P. Li,[1] C. Uher,[1] J. Yang,[2,b)] J. R. Salvador,[3] H. Wang,[4] L. Chen,[5] and W. Zhang[5,c)]

[1]*University of Michigan, Department of Physics, Ann Arbor, Michigan 48109, USA*
[2]*Materials and Processes Laboratory, General Motors R&D Center, Warren, Michigan 48090, USA*
[3]*Optimal Inc., 14492 Sheldon Road, Suite 300, Plymouth, Michigan 48170, USA*
[4]*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*
[5]*State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, People's Republic of China*

(Received 31 March 2008; accepted 13 April 2008; published online 5 May 2008)

Filled skutterudites are one of the most promising thermoelectric materials for power generation applications. The choice and concentration of filler atoms are key aspects for achieving high thermoelectric figure of merit values. We report on the high temperature thermoelectric properties in the double-filled skutterudites $Ba_xYb_yCo_4Sb_{12}$. The combination of Ba and Yb fillers inside the voids of the skutterudite structure provides a broad range of resonant phonon scattering and consequently a strong suppression in the lattice thermal conductivity is observed. A dimensionless thermoelectric figure of merit of 1.36 at 800 K is achievable for *n*-type $Ba_xYb_yCo_4Sb_{12}$. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2920210]

Thermoelectricity has great potential for applications such as energy conversion of waste heat into electricity and solid state heating and cooling. The efficiency of advanced thermoelectric technology is governed by the materials dimensionless thermoelectric figure of merit $ZT=S^2\sigma T/\kappa$, which is defined by the following transport parameters: absolute temperature T, thermopower S, electrical conductivity σ, and thermal conductivity κ. Reducing the lattice thermal conductivity (κ_L) is an important factor in obtaining high efficiency energy conversion in all thermoelectric materials.[1,2]

Skutterudites[3] are among a handful of systems that are being intensely pursued in hopes of developing more efficient thermoelectric materials than those currently in use such as Bi_2Te_3/Sb_2Te_3 compounds, PbTe alloys, and Si–Ge. Binary skutterudite compounds crystallize as a body-centered-cubic structure and have interstitial voids at the 2*a* positions (12 coordinated) in the crystal lattice. Filling these voids with foreign ions such as rare earths,[4–11] alkali,[12] or alkaline earths[13–15] (thus forming filled skutterudites) has been shown to be an effective way to reduce κ_L.[4–15] The weakly bound filler ions with their independent, Einstein-like vibrations interact with the normal modes of the structure and dramatically suppress κ_L. This type of κ_L suppression has been explained by the phonon resonance scattering mechanism.[16,17] Each filler ion represents a phonon resonance scattering center with a particular frequency and only those normal phonon modes that have frequencies close to this local resonant frequency can strongly interact with the vibrational modes of the fillers. The objective is to scatter as wide a spectrum of normal phonons as possible. Therefore, filling the skutterudite structure with ions that have different localized frequencies (multifilling) might be more effective in further lowering κ_L.

Recently, Yang *et al.* calculated the spring constants and resonance frequencies for various fillers in $CoSb_3$.[18] They found that a lower κ_L and higher ZT is achieved for Ba and La (or Ce) fillers in double-filled skutterudites (DFS) due to the large difference in their resonant phonon frequencies. Based on the calculations in Ref. 18, filling Ba and Yb into the voids of skutterudites should be even more effective in scattering phonons because the spring constants and resonant frequencies for Yb and Ba differ more than other possible filler pair combinations. Furthermore, the filling fraction limits for Ba and Yb in $CoSb_3$ are well experimentally[13,19–21] and theoretically[22,23] studied and both fillers independently yield high ZTs.[13,19,21] In this report, we present a high temperature thermoelectric property study on polycrystalline $Ba_xYb_yCo_4Sb_{12}$ compounds. We have found that double filling with Ba and Yb is indeed more efficient in scattering lattice phonons than single filled skutterudites and other double-filler combinations. Hence such an approach leads to an enhancement in ZT.

The details of sample synthesis can be found elsewhere.[13] X-ray diffraction patterns and electron probe microanalysis (EPMA) show trace amounts of ytterbium oxide. To designate the samples, we use the actual chemical compositions derived from EPMA (see Table I). Thermoelectric transport measurements were carried out at both the University of Michigan and Oak Ridge National Laboratory. Discrepancies, if any, are less than 5%. We have also made Hall effect measurements in a cryostat equipped with a 5.5 T superconducting magnet.

Figure 1 shows the T dependence of σ, S, and κ for $Ba_xYb_yCo_4Sb_{12}$. The respective room temperature properties are listed in Table I. All samples show heavily doped semiconductor behavior except for $Ba_{0.03}Co_4Sb_{12}$. The filling fraction and carrier concentration (see Table I) for this sample are very low and it exhibits a crossover to intrinsic

a)Electronic mail: xunshi@umich.edu.
b)Electronic mail: jihui.yang@gm.com.
c)Electronic mail: wqzhang@mail.sic.ac.cn.

TABLE I. Actual compositions as determined by EPMA and room temperature values of thermal conductivity, lattice thermal conductivity, electrical conductivity, thermopower, power factor, and carrier concentration for $Ba_xYb_yCo_4Sb_{12}$ skutterudites.

Actual composition	κ (W/m K)	κ_L (W/m K)	σ (S/cm)	S (μV/K)	$S^2\sigma$ (μW/cm K^2)	n (10^{20} cm^{-3})
$Ba_{0.03}Co_4Sb_{12.05}$	5.4	5.1	399	−220	19.3	0.5
$Ba_{0.15}Yb_{0.01}Co_4Sb_{12.08}$	4.3	3.0	1798	−125	28.1	2.8
$Ba_{0.11}Yb_{0.03}Co_4Sb_{12.07}$	3.2	1.9	1787	−115	23.6	3.7
$Yb_{0.12}Co_4Sb_{12.11}$	2.7	2.2	765	−146	16.3	2.3
$Ba_{0.05}Yb_{0.09}Co_4Sb_{12.13}$	2.8	2.0	1126	−158	28.1	2.9
$Ba_{0.08}Yb_{0.09}Co_4Sb_{12.12}$	2.5	1.0	2068	−126	32.8	3.2
$Ba_{0.11}Yb_{0.08}Co_4Sb_{12.08}$	2.4	0.9	2114	−107	24.2	4.4

conduction near 450 K. For DFS, increasing the void filling markedly increases σ without a large negative impact on S; consequently, high power factor ($S^2\sigma$) values are achieved in several DFS reported here. Good electrical transport properties in Ba-filled skutterudites have been previously reported[13] and our present data show that the beneficial effect of Ba is maintained in $Ba_xYb_yCo_4Sb_{12}$. The power factors of $Ba_{0.05}Yb_{0.09}Co_4Sb_{12.13}$ and $Ba_{0.08}Yb_{0.09}Co_4Sb_{12.12}$ are close to 45 μW/cm K^2 at high temperatures, which is comparable to the value of the best Ba-filled skutterudites.[13]

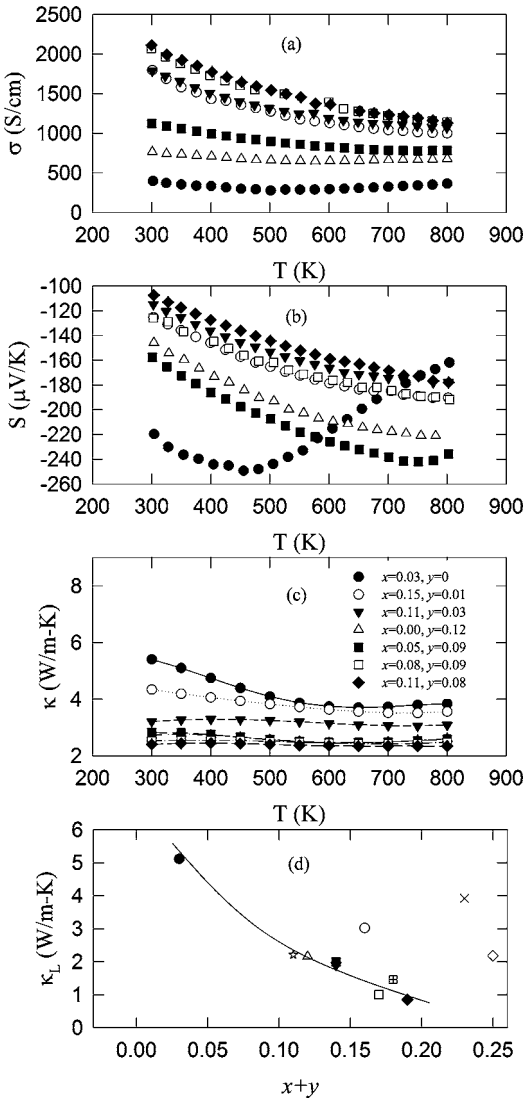

FIG. 1. Temperature dependence of the electrical conductivity (a), thermopower (b), and thermal conductivity (c), and room temperature lattice thermal conductivity as a function of total filling fraction ($x+y$) for $Ba_xYb_yCo_4Sb_{12}$ skutterudites (d). The solid line is to guide eye. The lattice thermal conductivities of $Ba_{0.23}Co_4Sb_{12.10}$ (×), $Ba_{0.07}La_{0.04}Co_4Sb_{12.08}$ (☆), $Ba_{0.12}Ce_{0.06}Co_4Sb_{12.08}$ (⊞), and $Ba_{0.17}Sr_{0.08}Co_4Sb_{12.07}$ (◇) from Ref. 18 are also shown. The solid line emphasizes the monotonic decrease in κ_L with increasing filling fraction ($x+y$).

The electronic contribution to the thermal conductivity (κ_e) is calculated using the Wiedemann–Franz law with the Lorenz number equal to 2.45×10^{-8} V^2/K^2. κ_L is obtained by subtracting κ_e from κ. This assessment of κ_L is only an approximation because one does not precisely know the Lorenz number, nor its temperature dependence for this degenerate semiconducting system. Nevertheless, this approach has the virtue of allowing cross-comparisons of existing κ_L values of skutterudites, as it is a common practice to use the Sommerfeld value for the Lorenz number. Table I lists the room temperature κ_L for all samples studied. κ_L of the Ba-filled skutterudites is quite high, above 5 W/m K, consistent with the literature value.[13] In contrast, κ_L of a pure Yb-filled skutterudites is low, about 2.2 W/m K for $Yb_{0.12}Co_4Sb_{12.11}$. The smaller ionic size of Yb as compared to Ba is expected to be more effective in scattering low frequency phonons that dominate the heat flow in solids.[11,19,20]

The additional reduction in κ_L in $Ba_xYb_yCo_4Sb_{12}$ is a result of the combined influence of the two filler species, Ba and Yb. We found that a low Yb filling fraction in DFS resulted in high κ_L. This is evident for $Ba_{0.15}Yb_{0.01}Co_4Sb_{12.08}$ that had a very low Yb concentration and, consequently, its κ_L was above 3 W/m K at room temperature. All DFS samples show very low κ_L values, lower than those of single element filled at comparable total void filling fractions.[3] Figure 1(d) shows the room temperature κ_L versus ($x+y$) in $Ba_xYb_yCo_4Sb_{12}$. Except for $Ba_{0.15}Yb_{0.01}Co_4Sb_{12.08}$, we observe a monotonic decrease in κ_L with an increasing filling fraction ($x+y$) for all our DFS. κ_L of some other DFS studied in Ref. 18 are also shown in Fig. 1(d). $Ba_xYb_yCo_4Sb_{12}$ have lower κ_L compared to other DFS. As pointed out in Ref. 18, the calculated resonance frequencies for Ba and Yb in $CoSb_3$ are 42 and 93 cm^{-1}, respectively, for modes in the [111] direction and 43 and 94 cm^{-1}, respectively, for modes in the [100] direction, thus differing by a factor of two in both crystallographic directions. This large difference in resonance frequencies broadens the range of normal phonons that undergo scattering, resulting in lower κ_L. There might also be an interplay in phonon scattering between Ba and Yb fillers in $CoSb_3$. This is because the primary interaction between the fillers in the skutterudite structure is Coulombic in nature, as pointed out in Refs. 22 and 23. An additional reduction in κ_L could presumably be achieved in multiple-filled skutterudites by using ions covering an even wider

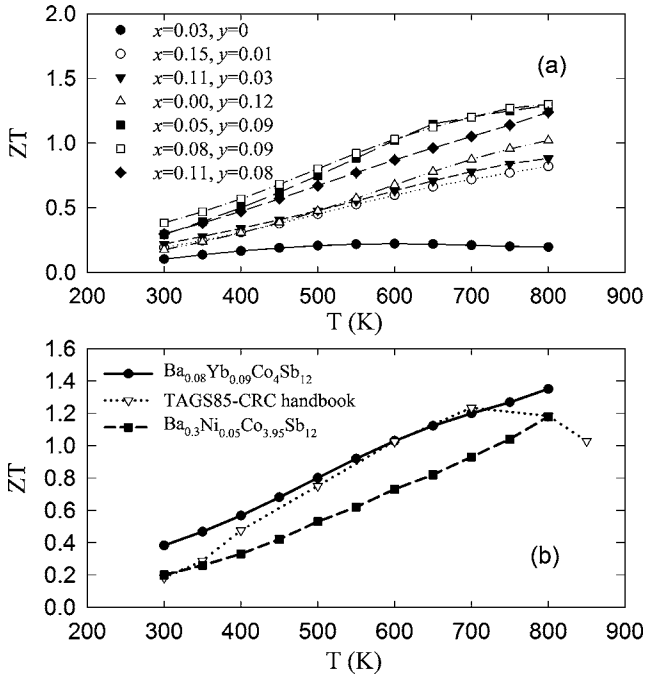

FIG. 2. (a) Temperature dependence of *ZT* for $Ba_xYb_yCo_4Sb_{12}$ DFS. (b) Temperature dependence of the *ZT* for $Ba_{0.08}Yb_{0.09}Co_4Sb_{12.12}$, $Ba_xNi_{0.05}Co_{3.95}Sb_{12}$ (Ref. 24), and $(AgSbTe_2)_{0.85}(GeTe)_{0.15}$ (Ref. 25).

range of resonant frequencies or stronger correlations among the various filler ions.

Figure 2(a) displays *ZT* for $Ba_xYb_yCo_4Sb_{12}$ between 300 and 800 K based on the measured σ, *S*, and κ. Because $Ba_xYb_yCo_4Sb_{12}$ have much lower κ and high power factor, their *ZT*s are markedly improved by means of Ba and Yb double filling. The *ZT* of $Ba_{0.08}Yb_{0.09}Co_4Sb_{12.12}$, which is 0.4 at room temperature, increases to 1.0 at 600 K and reaches 1.36 at 800 K, higher than that of pure Ba-filled skutterudites (1.1 at 850 K) (Ref. 13) and that measured for Yb-filled skutterudites (1.0 at 700 K).[21] Figure 2(b) shows the best experimentally determined *ZT*s reported so far in *n*-type skutterudites[24] and *p*-type $(AgSbTe_2)_{1-x}(GeTe)_x$ solid solutions (an exceptional high efficiency thermoelectric material in the intermediate temperature range).[25] The *ZT* values in our best sample ($Ba_{0.08}Yb_{0.09}Co_4Sb_{12.12}$) are almost 0.2 higher than those of *n*-type skutterudite $Ba_xNi_{0.05}Co_{3.95}Sb_{12}$ (Ref. 24) over the entire temperature range investigated. Also, the *ZT* of our sample is twice as large as optimized $(AgSbTe_2)_{0.15}(GeTe)_{0.85}$ (Ref. 25) at room temperature and 0.2 higher near 800 K. This indicates that $Ba_{0.08}Yb_{0.09}Co_4Sb_{12.12}$ is an excellent *n*-type material for use in intermediate temperature thermoelectric generators.

Our findings suggest that an even greater reduction in κ and increased *ZT* might be achieved by filling multiple (chemically distinct) ions into the voids of the skutterudite structure, especially if they cover a broad range of resonant frequencies. We expect that doping multiple resonant scattering centers into other cagelike structures, such as clathrates, will be equally effective in reducing κ_L.

J.R.S. and J.Y. would like to thank Dr. J. F. Herbst and Dr. M. W. Verbrugge for continuous support and encouragement. The work is supported by GM and by DOE under corporate agreement DE-FC26-04NT42278 by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies as part of the High Temperature Materials Laboratory User Program at Oak Ridge National Laboratory managed by the UT-Battelle LLC, for the Department of Energy under contract DE-AC05000OR22725. W.Z. and L.C. thank the financial support from National Basic Research Program of China (973-program) under Project No. 2007CB607503.

[1] G. A. Slack, *CRC Handbook of Thermoelectrics*, edited by D. M. Rowe (CRC Press, Boca Raton, 1995) p. 407.
[2] T. M. Tritt and M. A. Subramanian, MRS Bull. **31**, 188 (2006), and references therein.
[3] C. Uher, in *Recent Trends in Thermoelectric Materials Research I, Semiconductors and Semimetals*, edited by T. M. Tritt (Academic, San Diego, 2001), Vol. 69, pp. 139–253, and references therein.
[4] D. T. Morelli and G. P. Meisner, J. Appl. Phys. **77**, 3777 (1995).
[5] B. C. Sales, D. Mandrus, and R. K. Williams, Science **272**, 1325 (1996).
[6] B. Chen, J. Xu, C. Uher, D. T. Morelli, G. P. Meisner, J. Fleurial, T. Caillat, and A. Borshchevsky, Phys. Rev. B **55**, 1476 (1997).
[7] V. L. Kuznetsov, L. A. Kuznetsova, and D. M. Rowe, J. Phys.: Condens. Matter **15**, 5035 (2003).
[8] G. S. Nolas, J. L. Cohn, and G. A. Slack, Phys. Rev. B **58**, 164 (1998).
[9] G. A. Lamberton, Jr., S. Bhattacharya, R. T. Littleton IV, M. A. Kaeser, R. H. Tedstrom, T. M. Tritt, J. Yang, and G. S. Nolas, Appl. Phys. Lett. **80**, 598 (2002).
[10] D. T. Morelli, G. P. Meisner, B. Chen, S. Hu, and C. Uher, Phys. Rev. B **56**, 7376 (1997).
[11] J. Yang, D. T. Morelli, G. P. Meisner, W. Chen, J. S. Dyck, and C. Uher, Phys. Rev. B **67**, 165207 (2003).
[12] Y. Z. Pei, L. D. Chen, W. Zhang, X. Shi, S. Q. Bai, X. Y. Zhao, Z. G. Mei, and X. Y. Li, Appl. Phys. Lett. **89**, 221107 (2006).
[13] L. D. Chen, T. Kawahara, X. F. Tang, T. Goto, T. Hirai, J. S. Dyck, W. Chen, and C. Uher, J. Appl. Phys. **90**, 1864 (2001).
[14] M. Puyet, B. Lenoir, A. Dauscher, P. Pécheur, C. Bellouard, J. Tobola, and J. Hejtmanek, Phys. Rev. B **73**, 035126 (2006).
[15] M. Puyet, B. Lenoir, A. Dauscher, M. Dehmas, C. Stiewe, and E. Müller, J. Appl. Phys. **95**, 4852 (2004).
[16] V. Keppens, D. Mandrus, B. C. Sales, B. C. Chakoumakos, P. Day, R. Coldea, M. B. Maple, D. A. Gajewski, E. J. Freeman, and S. Bennington, Nature (London) **395**, 876 (1998).
[17] G. J. Long, R. P. Hermann, F. Grandjean, E. E. Alp, W. Sturhahn, C. E. Johnson, D. E. Brown, O. Leupold, and R. Rüffer, Phys. Rev. B **71**, 140302(R) (2005).
[18] J. Yang, W. Zhang, S. Q. Bai, Z. Mei, and L. D. Chen, Appl. Phys. Lett. **90**, 192111 (2007).
[19] G. S. Nolas, H. Takizawa, T. Endo, H. Sellinschegg, and D. C. Johnson, Appl. Phys. Lett. **77**, 52 (2000).
[20] N. R. Dilley, E. D. Bauer, M. B. Maple, and B. C. Sales, J. Appl. Phys. **88**, 1948 (2000).
[21] H. Anno, K. Ashida, K. Matsubara, G. S. Nolas, K. Akai, M. Matsuura, and J. Nagao, *MRS Symposium Proceedings* Vol. 691 (Materials Research Society, Warrendale, PA, 2002), pp. 49–54.
[22] X. Shi, W. Zhang, L. D. Chen, and J. Yang, Phys. Rev. Lett. **95**, 185503 (2005).
[23] X. Shi, W. Zhang, L. D. Chen, J. Yang, and C. Uher, Phys. Rev. B **75**, 235208 (2007).
[24] J. S. Dyck, W. Chen, C. Uher, L. Chen, X. F. Tang, and T. Hirai, J. Appl. Phys. **91**, 3698 (2002).
[25] E. A. Skrabek and D. S. Trimmer, in *CRC Handbook of Thermoelectrics*, edited by D. M. Rowe (CRC Press, Boca Raton, 1995) p. 267.