PHYSICAL REVIEW B **80**, 115329 (2009)

Solubility study of Yb in *n*-type skutterudites $Yb_xCo_4Sb_{12}$ and their enhanced thermoelectric properties

J. Yang,[1] Q. Hao,[2] H. Wang,[1] Y. C. Lan,[1] Q. Y. He,[1,3] A. Minnich,[2] D. Z. Wang,[1] J. A. Harriman,[1] V. M. Varki,[1]
M. S. Dresselhaus,[4] G. Chen,[2,*,†] and Z. F. Ren[1,*,‡]
[1]*Department of Physics, Boston College, Chestnut Hill, Massachusetts 02467, USA*
[2]*Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA*
[3]*School of Physics and Telecommunication Engineering, South China Normal University, Guangzhou 510631, People's Republic of China*
[4]*Department of Electrical Engineering and Computer Science and Department of Physics,*
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
(Received 18 May 2009; revised manuscript received 21 August 2009; published 29 September 2009)

The solubility of Yb in $Yb_xCo_4Sb_{12}$ was reported to be 0.19 in bulk skutterudites made by melting and slow cooling method. Surprisingly we increased x close to 0.5 by a special sample preparation method: ball mill and hot press. We show that a higher Yb concentration not only increases the power factor due to a higher electron concentration but also reduces the thermal conductivity k because of stronger phonon scattering. In this way, we have achieved a dimensionless thermoelectric figure of merit ZT of about 1.2 at 550 °C in $Yb_{0.35}Co_4Sb_{12}$.

DOI: 10.1103/PhysRevB.80.115329 PACS number(s): 72.15.Jf, 73.50.Lw, 84.60.Rb

I. INTRODUCTION

Co_4Sb_{12}-based skutterudites have been widely studied for their promising thermoelectric properties[1–3] and are regarded as potential candidates for next-generation thermoelectric materials for electrical power generation using either a solar source or waste heat. One of the remarkable features of this material is that the cagelike open structure can be filled with foreign atoms acting as phonon rattlers. The "rattling" of the filled atoms scatters phonons strongly and drastically reduces the thermal conductivity of the skutterudite compounds.[1–3] Various kinds of atoms [Ce,[4] La,[5] Ca,[6] Ba,[7] and Yb (Refs. 8–10)] have been used to fill the cages, thereby resulting in an improved dimensionless thermoelectric figure of merit (ZT). Yb is one of the ideal filler or rattler species.[8–10] Nolas *et al.* reported Yb-filled *n*-type $Yb_{0.19}Co_4Sb_{12}$ with a peak ZT close to 1 at 373 °C,[8] and Geng *et al.* reported $Yb_{0.15}Co_4Sb_{12}$ with ZT of about 0.7 at 400 °C.[9] In the literature for bulk samples, the Yb concentration was limited to 0.19, the so-called bulk solubility, in samples prepared by melting and slow cooling.[3] However, there is one void per each Co_4Sb_{12} formula. So it should be possible to have Yb more than 0.19. Whether a higher Yb concentration can be achieved to further reduce the thermal conductivity is scientifically interesting and technologically important. Recently, a bulk solubility of 0.29 was reported in samples made by melting and fast spin cooling with higher ZT,[10] demonstrating that the bulk solubility issue is not settled in Yb-filled skutterudites and clearly depends on the sample preparation method. Therefore, there is an opportunity to increase Yb into the cage if a suitable sample preparation method could be found. In this paper, we report our success on increasing the bulk solubility close to 0.5 and the good thermoelectric properties obtained by making bulk *n*-type skutterudites with small grains using a ball milling and direct-current-induced hot press (dc hot press) process[11–15] where we chose $x=0.3$, 0.35, 0.4, 0.5, and 1.0 in $Yb_xCo_4Sb_{12}$ to optimize the Yb concentration for maximizing the ZT value. We found that with our process we could increase x up to 0.5 without formation of impurity phases, much higher than the literature bulk solubility value.[8,16] However, when x reaches 1, there is clearly a second phase identified by x-ray diffraction (XRD), which reduces the thermoelectric performance.

II. EXPERIMENT

Pure elements of Co (99.8%, Alfa Aesar), Sb (99.999%, Chengdu Chemphys Chemical Industry, China), and Yb (99.9%, Alfa Aesar) were mixed according to the stoichiometry $Yb_xCo_4Sb_{12}$ and loaded into a stainless steel jar with stainless steel balls and the material was then ball milled. This process is much simpler than the traditional melting and slow crystal growth plus ball milling and hot press.[3,8–10] The as-milled nanopowder was pressed into pellets by the dc hot press method in a graphite die. After cooling down to room temperature, each dc hot pressed pellet was ejected out of the graphite die and was cut into disks and bars and polished for thermoelectric property characterization.

X-ray diffraction (D8, Bruker) analysis with a wavelength of 0.154 nm was performed on both the ball milled powder and the pressed pellets to determine the constituent phases. The freshly fractured surface of the $Yb_xCo_4Sb_{12}$ bulk samples was investigated by scanning electron microscope (SEM) (JEOL 6340F) to determine the grain size. A cross-sectional sample was prepared to check the grain size and the crystallinity using a high-resolution transmission electron microscope (TEM) (JEOL 2010). The four-probe electrical conductivity (σ) and the Seebeck coefficient (S) were measured in a commercial system (ZEM-3, ULVAC-RIKO). The thermal conductivity (k) was measured using a laser flash system (LFA 457, Netzsch).

III. RESULTS AND DISCUSSION

XRD spectra of the ball milled nanopowders (not shown in the paper) indicated that the majority of the powders were not alloyed after ball milling. After the dc hot press, however, the powder was completely transformed into a single

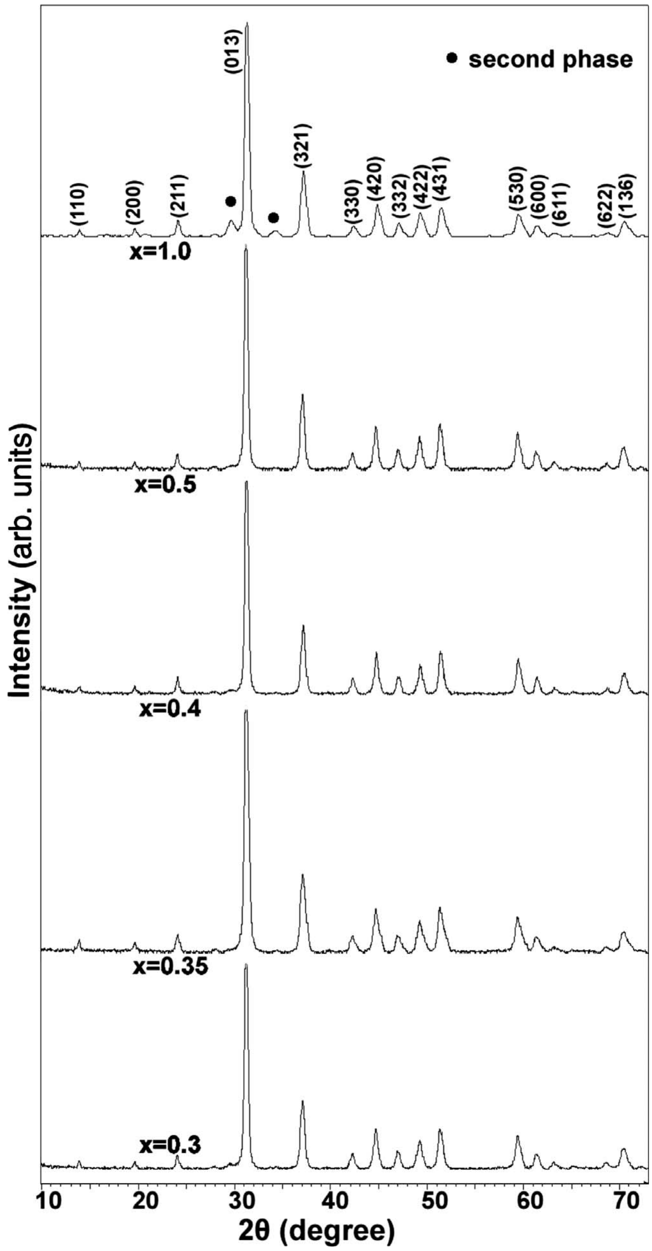

FIG. 1. XRD spectra of dc hot pressed skutterudite $Yb_xCo_4Sb_{12}$ bulk samples with $x=0.3$, 0.35, 0.4, 0.5, and 1.0. The unknown second phase in the sample with $x=1.0$ is clearly marked.

skutterudite phase for x up to 0.5. When $x=1$, an unknown second phase showed up. XRD spectra for all the hot pressed samples of $Yb_xCo_4Sb_{12}$ ($x=0.3$, 0.35, 0.4, 0.5, and 1.0) are shown in Fig. 1. The unknown second phase in the case of $x=1.0$ is clearly marked.

It is worth pointing out that we started with a composition for $x=0.2$ following the literature,[8,9,16] but could only rarely obtain unbroken samples after ejection from the graphite die. Those unbroken $x=0.2$ samples also showed much inferior properties to the ones with $x \geq 0.3$. Here, we show thermoelectric property results on all the compositions with $x > 0.2$.

Figure 2 shows the SEM images at low [Fig. 2(a)] and high [Fig. 2(b)] magnification of the dc hot pressed $Yb_{0.35}Co_4Sb_{12}$ samples that demonstrated the highest ZT among all the compositions studied. The average grain size is about 200–500 nm. There are some big grains as large as about 1 μm, which is probably due to the grain growth from the alloyed portion of the powders[17] during the hot press process. The grain growth from less than 50 to 200–500 nm is significant. With such large grain sizes, we do not expect a strong phonon scattering due to fewer interfaces.[12–15] The clear facets show that the grains are well crystallized. The SEM image also shows that the crystallized grains are closely packed, implying a high volume mass density, consistent with the Archimedean volumetric mass density measurement of around 7.6 g cm^{-3}, which is close to the full theoretical density.

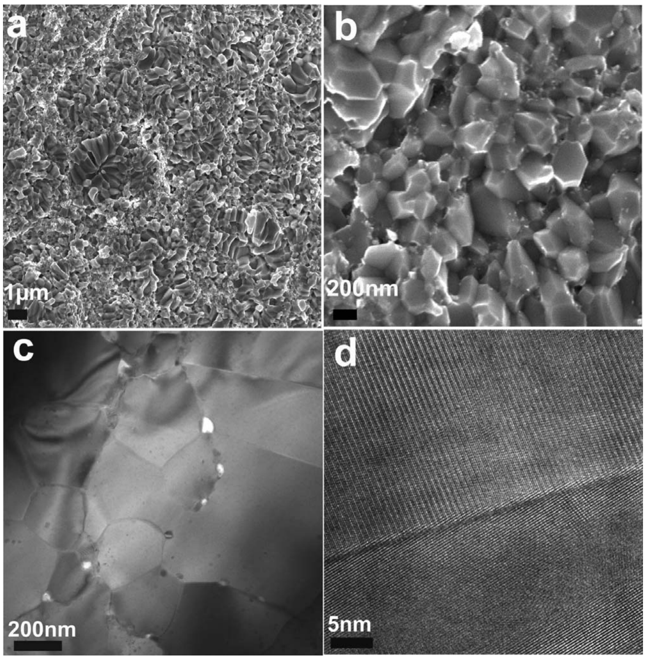

FIG. 2. SEM images at (a) low and (b) high magnification and TEM images at (c) low and (d) high magnification of dc hot pressed skutterudite $Yb_{0.35}Co_4Sb_{12}$ bulk samples, showing the high crystallinity and clean grain boundary with a large angle.

Figure 2(c) shows a low-magnification TEM image of a sample with the same composition $Yb_{0.35}Co_4Sb_{12}$, further indicating that the grain is about several hundred of nanometers in size, consistent with the SEM observation. The high-resolution TEM image shown in Fig. 2(d) confirms the excellent crystallinity and the clean grain boundary with a large angle. The excellent crystallinity and clean grain boundaries are needed for achieving good electrical transport properties, whereas the large angle grain boundary can potentially benefit phonon scattering.

Table I shows the compositions studied and their properties at about 25 °C. Those marked with * are from Nolas *et al.*[8] The lattice thermal conductivity is derived by extracting the electronic thermal conductivity k_e from k. Here, k_e was computed by the Weidemann-Franz law $k_e = L\sigma T$, where σ is the electrical conductivity, T is the absolute temperature, and the Lorenz number is estimated to be 1.8×10^{-8} V^2 K^{-2} for all samples, with uncertainties from factors including the

TABLE I. Room-temperature (25 °C) thermoelectric properties of $Yb_xCo_4Sb_{12}$ with $x=0.3$, 0.35, 0.4, and 0.5 samples. Data marked with * are from Nolas *et al.* (Ref. 8).

Nominal composition	Electrical conductivity (10^5 S m^{-1})	Seebeck coefficient ($\mu V\ K^{-1}$)	Lattice thermal conductivity (W m^{-1} K^{-1})	ZT
$Yb_{0.066}Co_4Sb_{12}{}^*$	0.48	−186	4.79	0.09
$Yb_{0.19}Co_4Sb_{12}{}^*$	1.64	−141	2.92	0.26
$Yb_{0.3}Co_4Sb_{12}$	1.99	−137	1.9	0.38
$Yb_{0.35}Co_4Sb_{12}$	2.13	−130	1.76	0.37
$Yb_{0.4}Co_4Sb_{12}$	2.34	−120	1.66	0.35
$Yb_{0.5}Co_4Sb_{12}$	2.54	−108	1.57	0.30

band-structure change caused by filling Yb. All our samples show a much higher electrical conductivity than those reported[8] presumably due to the large electron doping effect from the high Yb concentration, and the much lower thermal conductivity than literature values, mainly achieved by the stronger phonon scattering resulting from the presence of a large concentration of rattlers causing strong rattling and mass fluctuation effects and the increased interface densities, defined as the grain interfaces per unit volume.[11–15] Therefore, all the compositions studied here have higher ZT values than the reference samples[8] as a result of the enhanced power factor and the reduced thermal conductivity of our samples.

Figure 3 shows the carrier concentrations and Hall mobilities of samples with x up to 0.5 at room temperature as a function of Yb content. The carrier concentration for $Yb_xCo_4Sb_{12}$ shows a linear relation with the Yb filling fraction x. The Hall mobilities drop with higher Yb filling fraction, which could be due to the increased scattering by higher electron concentration. However, the carrier concentration increase is much larger than the carrier mobility decrease, which is why the electrical conductivity increases with Yb content.

The temperature-dependent thermoelectric properties of $Yb_xCo_4Sb_{12}$ are plotted in Fig. 4. In order not to decrease the readability of the multiple curves in Fig. 4, we intentionally did not show the measurement error bars of each property. For our measurement set up, we have a less than 5% error on the electrical conductivity, 7% on the Seebeck coefficient, and 5% on the thermal conductivity. Figure 4(a) shows that the electrical conductivity σ of all samples decreases with an increase in temperature T. Also σ increases with increased Yb content. The negative Seebeck coefficients [Fig. 4(b)] indicate that electrons are the dominant carriers. Samples with different Yb content show a similar T dependence trend for the Seebeck coefficient from room temperature to 550 °C, with the maximum Seebeck coefficient occurring at 550 °C [Fig. 4(b)]. The absolute value of the Seebeck coefficient decreases with increasing x at the same temperature, consistent with the electrical conductivity increase with increasing x. This behavior may be due to the increase in the electron concentration.

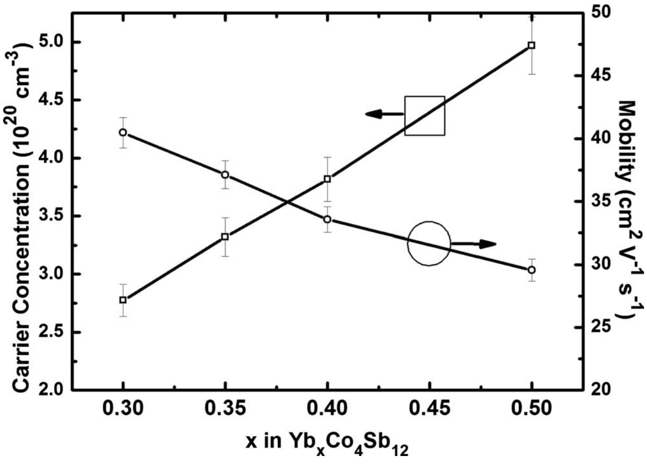

FIG. 3. Room-temperature carrier concentration and Hall mobility of $Yb_xCo_4Sb_{12}$ bulk samples with $x=0.3$, 0.35, 0.4, and 0.5.

The thermal conductivity of the samples is shown in Fig. 4(c). For the samples with $x=0.3$ and 0.35, the thermal conductivity values decrease with increasing T and reach a minimum at 200 °C and then k increases rapidly with increasing T due to bipolar effect. For the samples with $x=0.4$ and 0.5, the thermal conductivity keeps rising all the way from room temperature to 550 °C, which can be attributed to the significant increase in k_e at elevated temperatures. Although higher Yb concentrations increase the electron contribution to the total thermal conductivity, it can significantly decrease the lattice contribution by either the mass fluctuation effect[18] or the rattling effect,[19] so that the total thermal conductivity is much lower than that of the samples without Yb. At the moment, we do not know whether the mass fluctuation effect or the rattling effect is dominant in our samples. However, we do know that the lattice thermal conductivity in the case of $YbCo_4Sb_{12}$ is indeed higher than that of $Yb_{0.35}Co_4Sb_{12}$, which means that the mass fluctuation is a significant factor in $Yb_xCo_4Sb_{12}$ system. Therefore, $Yb_{0.35}Co_4Sb_{12}$ has an optimized lowest thermal conductivity with a minimum of 2.7 W m^{-1} K^{-1}, which leads to the highest observed ZT value among all the samples studied in this work.

Figure 4(d) shows the temperature-dependent ZT from room temperature to 550 °C. ZT increases with temperature and reaches a maximum at around 550 °C. The highest ZT is observed for the $Yb_{0.35}Co_4Sb_{12}$ sample with its maximum value of about 1.2 occurring at 550 °C. This is a high ZT value and comparable to those reported for n-type filled skutterudites made by first ingot formation followed by grinding and hot pressing.[8–10,19–21]

From the commercialization point of view, the combination of ball milling and dc hot pressing probably offers some

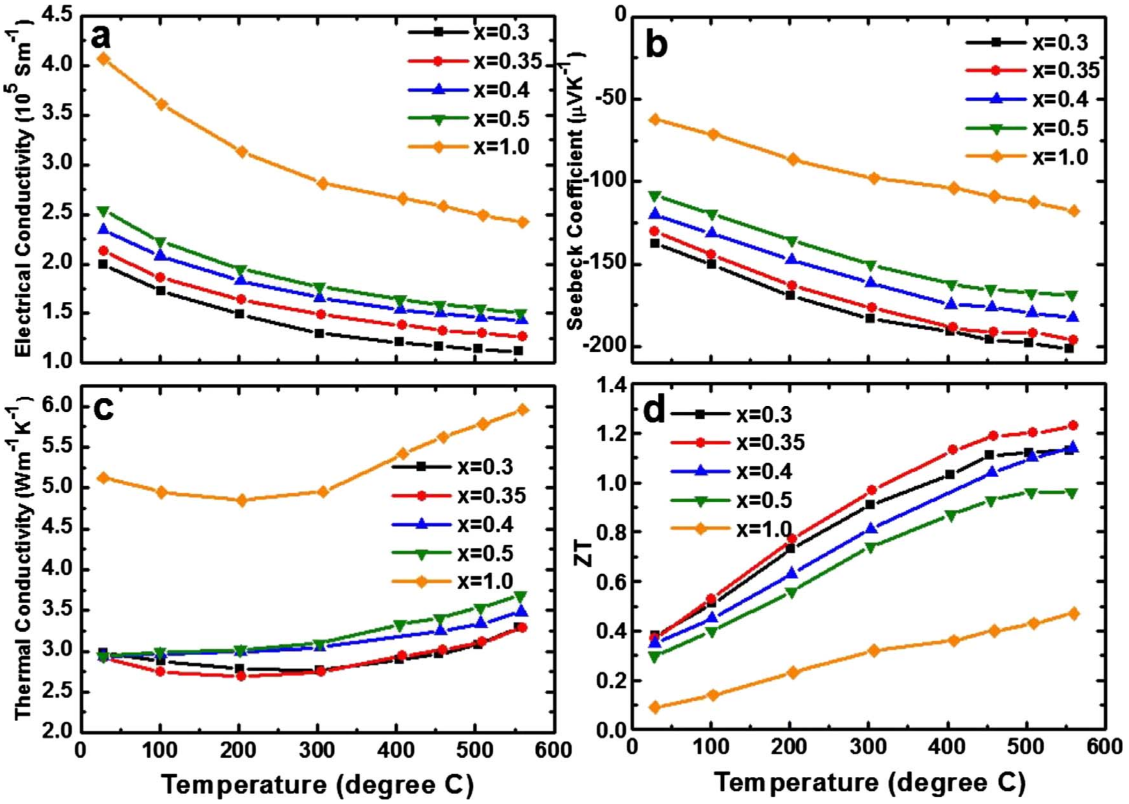

FIG. 4. (Color online) Temperature-dependent (a) electrical conductivity, (b) Seebeck coefficient, (c) thermal conductivity, and (d) ZT of dc hot pressed skutterudite $Yb_xCo_4Sb_{12}$ bulk samples with $x=0.3$, 0.35, 0.4, 0.5, and 1.0.

advantages in the sense that large quantities of powders could be ball milled and large quantities of bulk samples could be pressed in a short time. From the research point of view of studying other rattlers, the combination of ball milling and dc hot press is better in the sense that it is very fast to switch from one rattler to another and from one composition to another, since the traditional procedure of melting and slow crystal growth[3,8–10] takes a lot of effort and a long time.

Further investigation is needed into decreasing the thermal conductivity by preserving the grain size of the original powders, which is smaller than 50 nm. We note that the grain size of 200–500 nm (Fig. 2) is relatively large, which is why the thermal conductivity is still high. If the grain size can be reduced to 10–50 nm, then phonon scattering will be much stronger by the increased interfaces[12–15] so a much lower thermal conductivity can probably be expected. With a much lower thermal conductivity, a much higher ZT should be achievable in this system.

IV. CONCLUSION

In summary, we have discovered that the bulk solubility of Yb in $Yb_xCo_4Sb_{12}$ depends on sample preparation method. A ball milling and dc hot press process could increase x beyond 0.3 and close to 0.5 in bulk samples of n-type skutterudite $Yb_xCo_4Sb_{12}$. The increased Yb concentration in our samples not only enhanced the power factor due to a better electron doping effect but also decreased the thermal conductivity due to a stronger rattling effect. In addition, the increased grain boundary density per unit volume due to the small grains in our bulk skutterudite materials may have also helped to enhance the phonon scattering and thus to reduce the thermal conductivity in some extent, but the grain size is not yet small enough to get a much lower thermal conductivity. The composition $Yb_{0.35}Co_4Sb_{12}$ was found to be optimal for achieving a peak ZT value of about 1.2 at 550 °C even though single skutterudite phase was obtained for $x=0.5$.

ACKNOWLEDGMENTS

The work was sponsored by DOE Contract Nos. DE-FG02-00ER45805 (Z.F.R.), DE-FG02-02ER45977 (G.C.), and DE-FG02-08ER46516 (M.S.D., G.C., and Z.F.R.).

[*] Author to whom correspondence should be addressed.

[†] gchen2@mit.edu

[‡] renzh@bc.edu

[1] B. C. Sales, D. Mandrus, and R. K. Williams, Science **272**, 1325 (1996).

[2] G. S. Nolas, J. L. Cohn, and G. A. Slack, Phys. Rev. B **58**, 164 (1998).

[3] T. M. Tritt, *Semiconductors and Semimetals* (Academic, San Diego, CA, 2001), Vol. 69, pp. 139–253.

[4] B. 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] V. Keppens, D. Mandrus, B. C. Sales, B. C. Chakoumakos, P. Dai, R. Coldea, M. B. Maple, D. A. Gajewski, E. J. Freeman, and S. Bennington, Nature (London) **395**, 876 (1998).

[6] M. Puyet, B. Lenoir, A. Dauscher, M. Dehmas, C. Stiewe, and E. Muller, J. Appl. Phys. **95**, 4852 (2004).

[7] 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).

[8] G. S. Nolas, M. Kaeser, R. T. Littleton IV, and T. M. Tritt, Appl. Phys. Lett. **77**, 1855 (2000).

[9] H. Y. Geng, S. Ochi, and J. Q. Guo, Appl. Phys. Lett. **91**, 022106 (2007).

[10] H. Li, X. F. Tang, Q. J. Zhang, and C. Uher, Appl. Phys. Lett. **93**, 252109 (2008).

[11] M. S. Dresselhaus, G. Chen, M. Y. Tang, R. G. Yang, H. Lee, D. Z. Wang, Z. F. Ren, J. P. Fleurial, and P. Gogna, Adv. Mater. **19**, 1043 (2007).

[12] B. Poudel, Q. Hao, Y. Ma, Y. C. Lan, A. Minnich, B. Yu, X. Yan, D. Z. Wang, A. Muto, D. Vashaee, X. Y. Chen, J. M. Liu, M. S. Dresselhaus, G. Chen, and Z. F. Ren, Science **320**, 634 (2008).

[13] Y. Ma, Q. Hao, B. Poudel, Y. C. Lan, B. Yu, D. Z. Wang, G. Chen, and Z. F. Ren, Nano Lett. **8**, 2580 (2008).

[14] X. W. Wang, H. Lee, Y. C. Lan, G. H. Zhu, G. Joshi, D. Z. Wang, J. Yang, A. J. Muto, M. Y. Tang, J. Klatsky, S. Song, M. S. Dresselhaus, G. Chen, and Z. F. Ren, Appl. Phys. Lett. **93**, 193121 (2008).

[15] G. Joshi, H. Lee, Y. C. Lan, X. W. Wang, G. H. Zhu, D. Z. Wang, R. W. Gould, D. C. Cuff, M. Y. Tang, M. S. Dresselhaus, G. Chen, and Z. F. Ren, Nano Lett. **8**, 4670 (2008).

[16] X. Shi, W. Zhang, L. D. Chen, and J. Yang, Phys. Rev. Lett. **95**, 185503 (2005).

[17] Q. Y. He, Q. Hao, X. W. Wang, J. Yang, Y. C. Lan, X. Yan, B. Yu, Y. Ma, B. Poudel, G. Joshi, D. Z. Wang, G. Chen, and Z. F. Ren, J. Nanosci. Nanotechnol. **8**, 4003 (2008).

[18] G. P. Meisner, D. T. Morelli, S. Hu, J. Yang, and C. Uher, Phys. Rev. Lett. **80**, 3551 (1998).

[19] B. C. Sales, B. C. Chakoumakos, and D. Mandrus, Phys. Rev. B **61**, 2475 (2000).

[20] H. Li, X. F. Tang, X. L. Su, and Q. J. Zhang, Appl. Phys. Lett. **92**, 202114 (2008).

[21] X. Shi, H. Kong, C.-P. Li, C. Uher, J. Yang, J. R. Salvador, H. Wang, L. Chen, and W. Zhang, Appl. Phys. Lett. **92**, 182101 (2008).