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Abstract

New thermoelectric materials with superior properties at high temperatures have been discovered and are part of the large family of Slater-type compounds which have shown a good thermoelectric applications [1-11]. The composition of these materials, called filled Slaterites, is the Slaterite crystal structure and can be written in the formula $M_1M_2P_3Q_4R_5$ (where rare earth Th, U, Ce, Co, Rh, Ir, Pt, P, As, Sb). In these compounds, the octants of the Slaterite structure which are $8Co_8$, $8Pt_8$, $8U_8$, $8Ce_8$, $8P_8$, $8Q_8$, $8R_8$ framework, are filled with a thermoelectric element $P_3Q_4R_5$. Some of these composites ($Co_8P_8Sb_8$) have been prepared by a combination of powder metallurgy techniques and an exceptional thermoelectric properties in a temperature range. At room temperature, $Co_8P_8Sb_8$ as a p-type semiconductor had with a low thermoelectric coefficient, ZT values, consistent with some recent band structure calculations for these compounds [11]. Replacing P_3 with Co_3 and increasing the Co:Ce atomic ratio resulted in the Seebeck coefficient values. The ZT values obtained in p-type conductivity filled Slaterite values higher than $ZT = 3$ is currently being measured. Measurements on bulk samples with a Co:atomic composition and p-type conductivity in a dimensionless figure of merit ZT values of up to 1.650°C.

Introduction

A systematic search for advanced thermoelectric was initiated at JPL several years ago and resulted in the discovery of a new family of promising semiconductor materials with the Slaterite crystal structure. Slaterite structure was originally attributed to the structure from Slaterite (Osoway) with a general formula $M_1M_2P_3Q_4R_5$ (where rare earth Th, U, Ce, Co, Rh, Ir, Pt, P, As, Sb). The unit cell of the Slaterite structure space group $Im\bar{3}m$ (prototype $CoAs_3$) contains eight Co_8 octants. This anion located in the center of the unit cell is surrounded by 8 Co^{2+} cations. The unit cell of $Co_8P_8Sb_8$ consist of 8 smaller cubes (octants) described above, of them do not have the anions $[As_4]^{3-}$ in the center of the unit cell. It is necessary to keep the ratio $Co^{2+}/[As_4]^{3-}$

high to maintain the structure results with $Co_8[As_4]^{3-}$ ZT values comparable to 37 atoms per cell.

As the ZT values of a conductivity and a high carrier mobility are needed for improved figures of merit in new thermoelectric materials, high carrier mobility values are essential for the design of structures with a high degree of conversion. It has been shown that the bonding is necessary to maintain the Slaterite structure [9] and high carrier mobility has been measured recently on several Slaterite compounds: $IrSb_3$, $IrPt$, $IrPtSb_3$, $IrPtSb_3$, $IrPtSb_3$ [12] and $RhPt$ [13]. The unit cell is relatively large of volume is 37 atoms which indicate that a low lattice thermal conductivity might be possible. For state-of-the-art thermoelectric materials, so far as $PbTe$ and Bi_2Te_3 alloys, the number of thermoelectric compounds is limited and the possibilities to optimize their properties for maximum performance at different temperatures of operation are also very limited. Thus, in the case for the Slaterite family of materials, where several binary compounds and several filled Slaterites and ternary phases are known to exist [11]. The Slaterite compounds have range of decomposition temperatures of 1000°C. This offers the possibility to find compounds with a ZT level for a specific application, e.g., engines.

However, the room temperature thermal conductivity of binary Slaterite $Co_8P_8Sb_8$ (150 mW/cm K²) was found to be too high to merit $ZT < 1$ values. Substantial reductions in the lattice thermal conductivity must be obtained to achieve values comparable to those of state of the art thermoelectric materials (10 mW/cm K²). One approach is the reduction of the lattice thermal conductivity of the octants to keep even and characterize filled Slaterite compounds derived from the binary compounds. This requires a thin shell of two empty octants present in the 37 atom unit cell of $Co_8P_8Sb_8$ to reduce electron count to retain conductivity and thermoelectric properties.

Low Thermal Conductivity in Filled Slaterite anions

In a previous paper, we have synthesized a filled Slaterite crystal structure which has been synthesized (see for example [14-16]). The composition of these types of compounds can be predicted by the formula $M_1M_2P_3Q_4R_5$ (where rare earth Th, U, Ce, Co, Rh, Ir, Pt, P, As, Sb). In these compounds, the empty octants of the Slaterite

structure (see Figure 1) which are formed in the $\text{La}_2\text{Pb}_3\text{O}_7$ framework, are filled with a rare earth ion. Because the LaPb_3 groups using Fe, Ru or Os (rare earth deficient (dy, f-c) relative to the skutterudite structure (using Co, Rh or Ir), the introduction of the rare earth atom compensates this deficiency. The filling of electrons. However, the number of valence electrons is not up by the rare earth atom; is generally 2 electrons (for example La has a 3+ oxidation state, Ce^{3+} , Pr^{3+} , Sm^{2+}). This means that most of these compounds have a net gain or very heavily doped p-type semimetals.

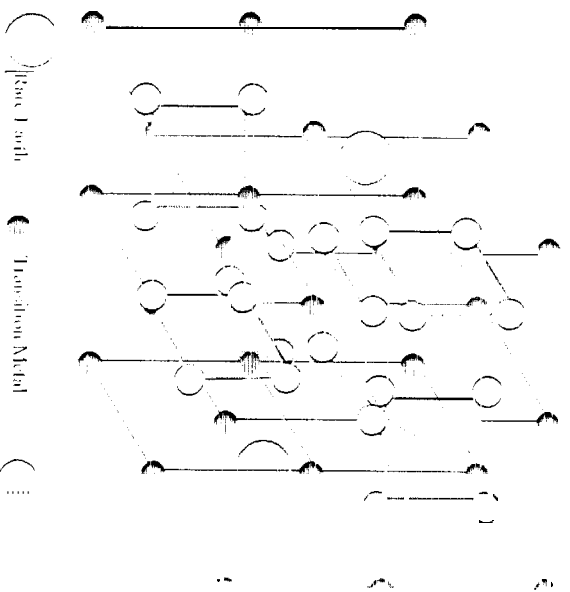


Figure 1. Schematic of the filled skutterudite unit cell of the novel thermoelectric materials. La and Ce: 8 transition metal atoms; Fe, Ru, Os, Co, Rh, Ir: 24 pnicogen atoms; P, As, Sb (substitution by S possible); 2 rare earth atoms filling the vacant octahedral sites in the skutterudite structure; La, Ce, Pr, Nd, Sm, Eu (if possible).

However, the introduction of a filling atom skutterudite structure is expected to substantially reduce the thermal conductivity of the original binary with minimal decrease in carrier mobility. The La atom would 'rattle' within its octahedral cage and fill phonons quite effectively. Also because it is an empty octahedron, its contribution to the electrical conductivity would be minimal though the increased phonon scattering rate should somewhat impact the carrier scattering rate (carrier-phonon interaction). Recent experimental results on filled skutterudite samples have confirmed that the room temperature conductivity values are much lower in these $\text{LaCo}_4\text{Sb}_{12}$, CeSb_4 , or IrSb_4 , even taking into account the higher carrier concentration of the samples [3,6].

To conserve the excellent semiconducting behavior of the unfilled binary skutterudites, it is necessary to fill the 'compensating' atom for the addition of the fill

into the structure. The ratio of compensating atoms to filling atoms is also varied extensively from the number of valence electrons of the filling atom. Thus, if Ce (the most stable valence number is +3) is introduced into the two empty octahedra of the 31 atoms CeSb_4 unit cell, 6 atoms of Fe (each providing one valence electron) will have to be substituted for Co (CoSb_4 for CeSb_4) will become $\text{CeFe}_6\text{Co}_5\text{Sb}_{14}$ (on $\text{Ce}(\text{CeSb}_3)_2$). This composition is very close to the compound $\text{CeFe}_6\text{Sb}_{14}$ whose existence was previously reported. The same approach can be applied to replacing Sb by Co, resulting in $\text{CeCo}_6\text{Fe}_6\text{Sb}_8$, or both Co and Sb by Fe and Co resulting in $\text{CeCo}_6\text{Sb}_8\text{Fe}_6$. Moreover, the doping level and carrier density might be controlled by changing the compensating to filling atomic ratio. It is important to note that because compensating atoms need to be introduced in pairs, they could also bring a substantial increase in phonon scattering (mass and volume differences) and carrier scattering (ionized impurity disorder) rates.

Experimental details and Discussion

The filled skutterudite compositions based on $\text{CeFe}_6\text{Sb}_{14}$ were prepared by a combination of melting and powder X-ray diffraction. X-ray diffraction analysis indicated that the samples were mostly filled skutterudites with the presence of some CeSb_3 and CeSb_4 . After synthesis, mass density measurements showed that the geometrical density of the cylindrical pellets (about 10 mm long and 6.3 mm in diameter) were close to 98% of the theoretical values calculated from the experimentally determined lattice parameter (see Table 1). The electron microprobe analysis of the samples confirmed the previous X-ray diffraction results indicating the presence of only about 5% in volume of FeSb_3 and CeSb_4 in the $\text{CeFe}_6\text{Sb}_{14}$, $\text{CeFe}_6\text{Co}_6\text{Sb}_{14}$, and $\text{CeCo}_6\text{Fe}_6\text{Sb}_{14}$ samples. The compositions of the filled skutterudite phase in these samples were found to be very close to the nominal stoichiometric concentrations.

The Hall effect, magnetoresistance and thermal transport measurements of the filled skutterudite samples were measured at 300 K up to 600 K. The room temperature results are given in Table 1.

Table 1. Room temperature properties of Ce-based filled (a) and Co based samples where a is the lattice parameter (Å), cc is the unit cell concentration, ρ (cm $^{-2}$), μ_H is the Hall mobility (cm 2 /Vs), ρ is the electrical resistivity (m Ω cm), S is the Seebeck coefficient (mV/K) and Z is the thermal conductivity (mW/mK).

Composition	a	ρ_a	ρ	S	Z
$\text{CeCe}_6\text{Sb}_{14}$	11.1	1.5	0.75	58.7	7.4
$\text{CeCe}_6\text{Co}_6\text{Sb}_{14}$	1.1×10^{-3}	1.5	0.71	75.8	3
$\text{CeCo}_6\text{Fe}_6\text{Sb}_{14}$	1.10	1.7	0.81	106.3	8.7

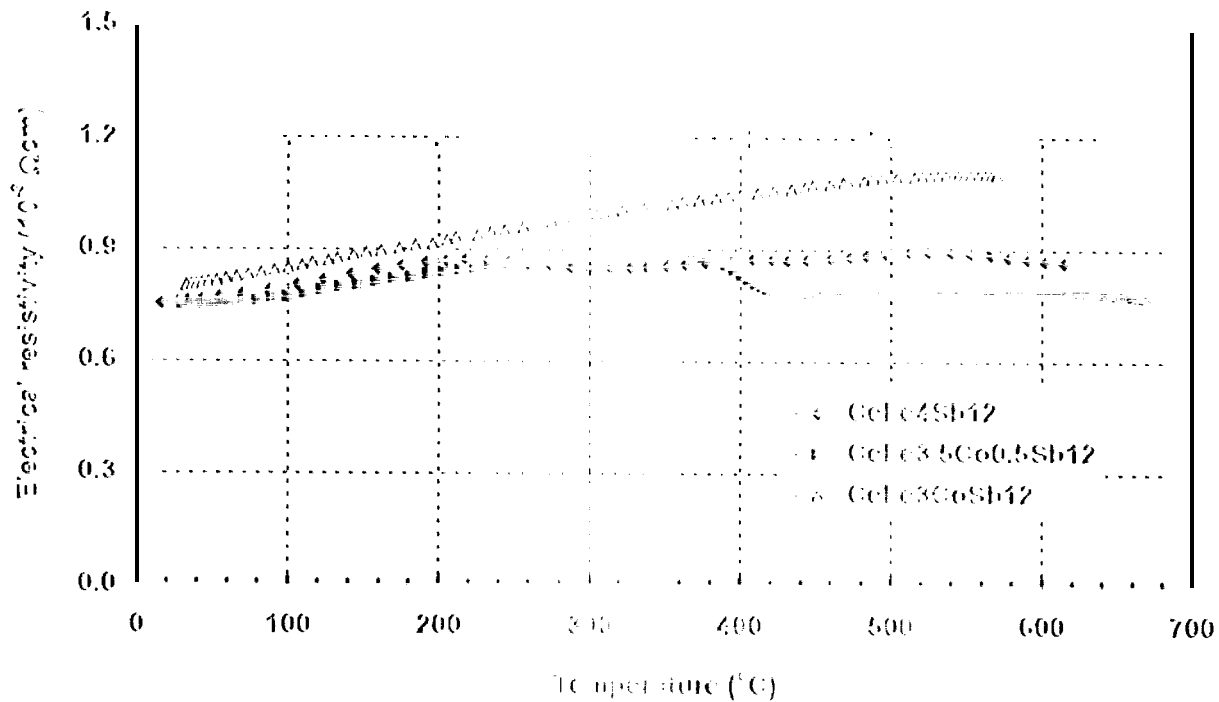


Figure 2: High temperature variations of the electrical resistivity of filled skutterudite samples

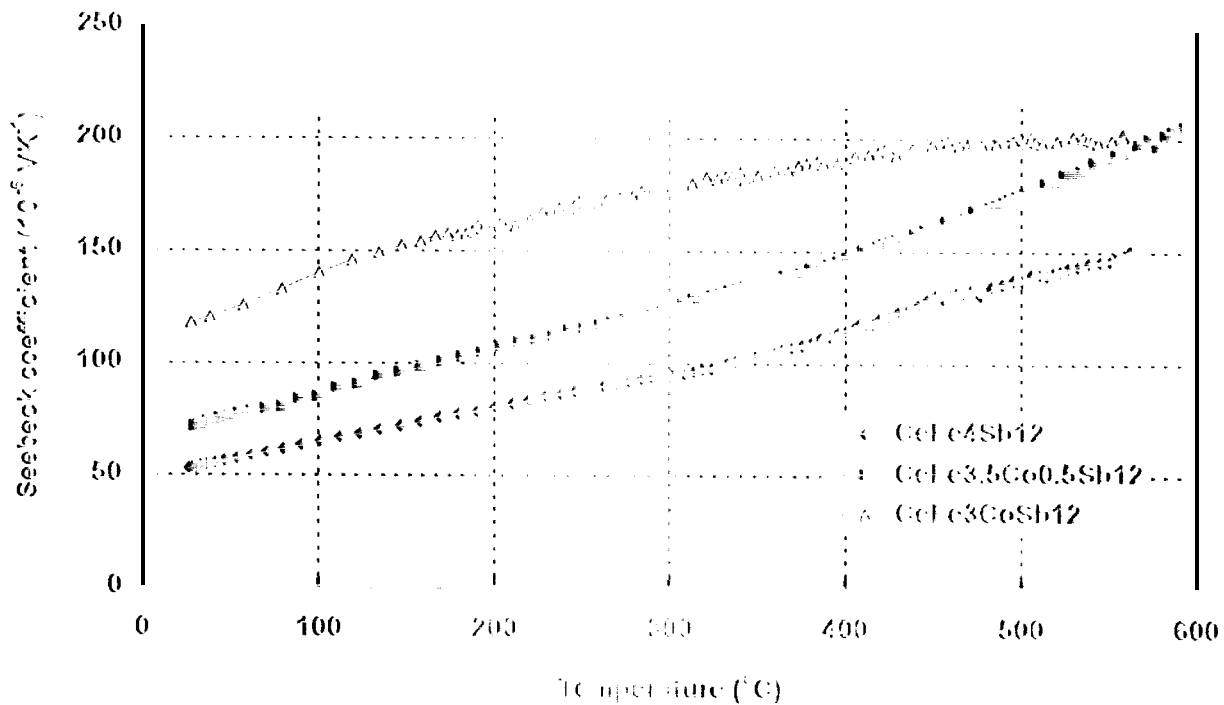


Figure 3: High temperature variations of the Seebeck coefficient of filled skutterudite samples

The temperature dependence of the electrical resistivity, Seebeck coefficient and thermal conductivity are reported in Figures 2, 3 and 4, respectively. The results show that these materials have a semi-metallic behavior (very high carrier concentration of about $5 \times 10^{21} \text{ cm}^{-3}$ and low carrier mobilities) with a low electrical resistivity, which increases slightly with temperature. The CeTe₃Sb₁₂ and

CeTe_{3.5}Co_{0.5}Sb₁₂ samples even show a small decrease at temperatures close to 400°C. The reason for this is not yet understood. However, what is most surprising is the magnitude of the Seebeck coefficients, ranging from 55 to 206 μV/K at 25°C and increasing steadily with temperature. These values are comparable to those obtained for other p-type binary skutterudites except that here the carrier

concentration is two orders of magnitude higher than in conventional materials, attributed to the fact that these materials belong to the class of heavy fermions systems, the hybridization between the f orbitals of the transition metal (Fe or Co here) creates a small density of states and carriers possess large effective masses resulting in a low mobility but unusually high Seebeck coefficient [5,7].

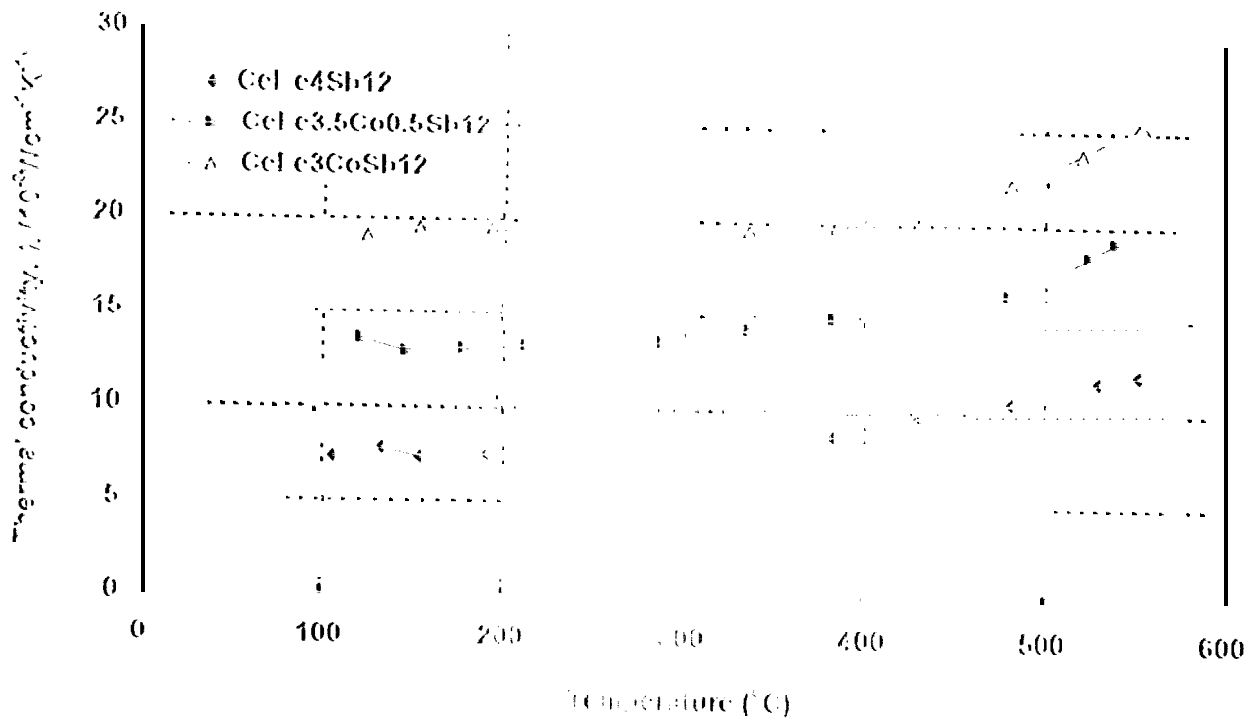


Figure 4: High-temperature variations of the thermoelectric figure of merit of filled skutterudite samples

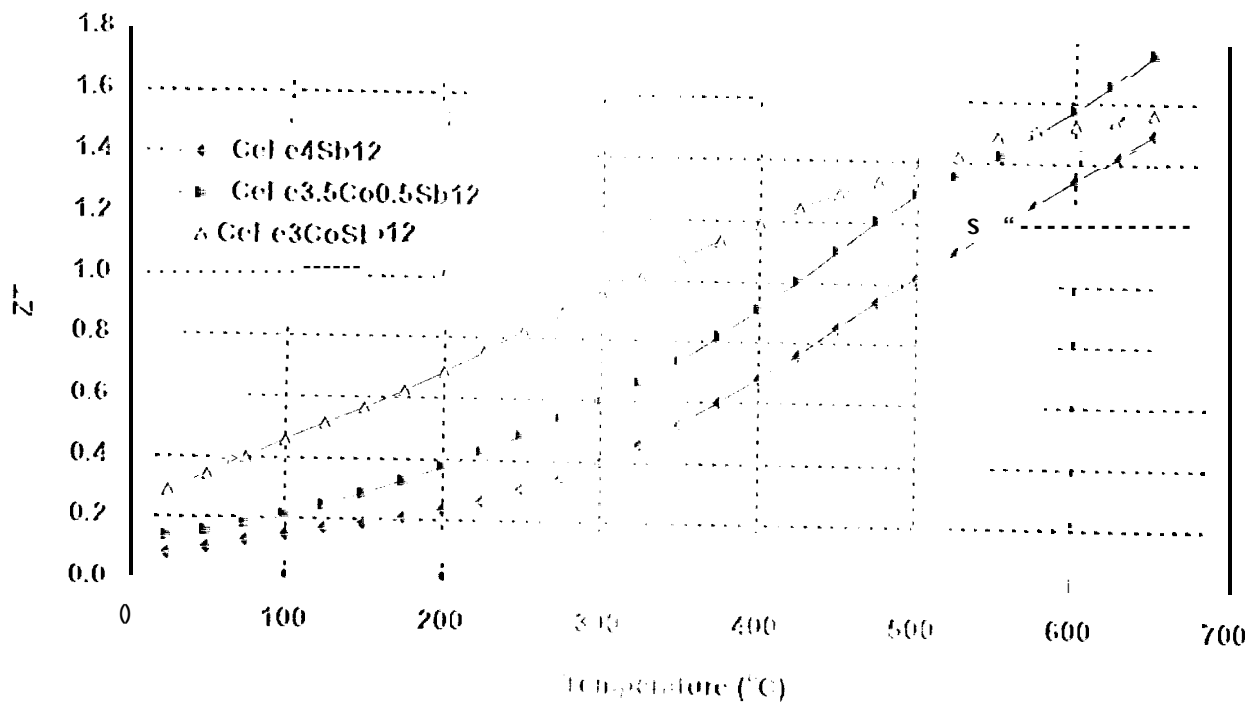


Figure 5: Dimensionless figure of merit ZT as a function of temperature for filled skutterudite samples with different compositions. Results are compared with those for conventional state-of-the-art p-type thermoelectric materials.

The thermal conductivity of those materials is by a very low, depending on the composition. The CeFe_3Sb_5 sample has a very low thermal conductivity of about 2 mW/cm²K at room temperature and increasing up to 12.5 mW/cm²K at 550°C. Such low values indicate that nearly all of the thermal conductivity is from an electronic contribution. This demonstrates that the combination of the rattling ions and a very high carrier concentration very effectively scatter the phonons, and results in an extremely low lattice thermal conductivity.

The $\text{CeFe}_{4-x}\text{Co}_x\text{Sb}_5$ and $\text{CeFe}_3\text{CoSb}_5$ samples also show low thermal conductivity values with a temperature dependence identical to that of CeFe_3Sb_5 . It is quite interesting to note that both the room temperature Seebeck coefficient and thermal conductivity increase in magnitude as the amount of Co is increased from 0 at.% to 6 at.%. This suggests that the introduction of Co alters the strength of the Ce-Fe interactions. However, even for the $\text{CeFe}_3\text{CoSb}_5$ composition (with 6 at.% of Co), the carrier concentration is still very high, indicating that the compensation effects between Fe and Co might be neutralized by the local fluctuations. As discussed above, the introduction of H instead of Co might lead to very different results.

The combination of the low electrical resistivity, moderate Seebeck coefficient and low thermal conductivity result in high ZT values at temperatures above 350°C. A maximum ZT value of 1.8 has been achieved to date at a temperature of 650°C. However, it appears that ZT keeps on increasing with temperature for those filled skutterudite samples as expected from the metallic behavior of the electrical properties. This means that if those materials were determined to remain stable at higher temperatures, even higher ZT would be obtained. The results displayed in Figure 5, are much higher than for any other set of filled materials (p-type or n-type).

High ZT values in lower or higher temperature ranges as well as n-type conductivity samples might be obtained by controlling the composition and doping levels. For many materials to be useful at lower temperatures for cooling applications, the Seebeck coefficient must be increased, which requires a lower doping level. For example, this might be achieved by increasing the Co to Fe atomic ratio ($\text{CeFe}_{4-x}\text{Co}_x\text{Sb}_5$ with $1.5 < x < 4$) or combining Co with H or Se. Replacing Co by H in the filled skutterudites would certainly result in higher decomposition temperatures, allowing their use in power generation applications at temperatures close to 1000°C. In addition, the larger and larger H atom will introduce additional scattering of the phonons, resulting in a decrease in lattice thermal conductivity.

Acknowledgments

Part of the work described in this paper was carried out at the Jet Propulsion Laboratory/California Institute of Technology, under contract with the National Aeronautics and Space Administration

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