Jean Pi...
J-t Propulsion laboratory ...
Don ...
General Motors R...

... ... California, USA
... ... USA

Abstract

New thermoelectric materials with superior properties at high temperatures have been discovered ... properties at high temperatures have been discovered ... materials are part of the large family of skutterudite ... of compounds, which have shown a good ... thermoelectric applications [1–3]. The comp... novel materials, called filled skutterudites, ... the skutterudite crystal structure and can be ... the formula IrT_4X_{12} (t... tate each ... Co, Rh, Ir, Pt; P, As, Sb) In these compou... octants of the skutterudite structure which ar... TPn_3 (TPn_3) framework are filled wit... closed [5,6]. Some of these composite ... CoCo$_3$Sb$_{12}$ have been prepared by a combi... and powder metallurgy techniques and ... exceptional thermoelectric properties in th... temperature range. At room temperature, Co... as a p-type Seebeck coefficient but with a low therm... and surprisingly large Seebeck coefficient. Th... consistent with some recent band structure ca... these compounds [7]. Replacing Fe with Co ... and increasing the CoFe atomic ratio resulted ... in the Seebeck coefficient values. The ... obtaining n-type conductivity filled skutterudite ... values higher than 13 is currently bein... Measurements on bulk samples with a C... atomic composition and p-type conductivity re... dimensionless figure of merit Z values of up to ... 650°C.

Introduction

A systematic search for advanced thermoelectric ... was initiated at JPL several years ago and resul... discovery of a new family of promising ... materials with the skutterudite crystal structure ... skutterudite structure was originally attributed ... from Skutterud (Norway) with a general formula ... As_3 [8]. The unit cell of the skutterudite stru... space group Im3, prototype CoAs$_3$ contains s... $[As_4]^{4-}$. This anion located in the center of the ... is surrounded by 8 Co^{3+} cations. The unit cell ... consist of 8 smaller cubes (octants) described as ... of them do not have the anions $[As_4]^{4-}$ in the cen... skutterudite structure ... $Co^{3+}[As_3]^{3-}$ ... necessary to keep the ratio Co:[As$_4$] ...

... consists ... ... structure ... results with Co$_4$[As$_4$]... X$_{10}$[As$_4$] ... compounds and 32 atoms per cell

... the ... al conductivity and a high carrier ... mobility ... the improved figures of merit in new ... ... High carrier mobility values are ... ... materials with a high degree of ... ... shown that the bonding is ... ... essentially covalent to the skutterudite structure [9] and ... ... Sb have been measured recently on ... compounds, IrSb$_3$, [10], RhSb$_3$, [11]. ... [12] and RhP$_3$ [13]. The unit cell is relatively large ... ... characteristic of a low lattice thermal ... ... possible ... For state-of-the-art ... ... as PtTe and Bi$_2$Te$_3$ alloys, the ... ... compounds is limited and the ... ... thermal properties for maximum ... ... different temperature values of operation are also ... ... in the case for the skutterudite family ... ... binary compounds and several ... ... are known to exist [1] ... ... of decomposition ... ... the possibility to ... ... lead for a specific ...

... the total thermal conductivity of ... binary skutterudite ($\kappa = 100 \, mW cm^{-1} K^{-1}$) was found to be ... ... values and characteristic filled skutterudite ... ... on the binary compounds. This ... ... lattice thermal conductivity must be obtained to ... ... values comparable to those of state of the art ... ... the lattice thermal conductivity of the ... ... lattice thermal conductivity of ... ... and characterize filled skutterudite ...

... thermal Conductivity in filled Skutterudites

... tubes of materials with a filled skutterudite crystal ... ... was also successfully synthesized (see for example [14] ... ... compositions of these types of compounds can be ... ... by the formula $LaFe_4Pn_{12}$ (Ln = La, Ce, Pr, Nd ... ... T = Fe, Ru, Os; Pn = P, As, Sb). In ... ... the empty octants of the skutterudite

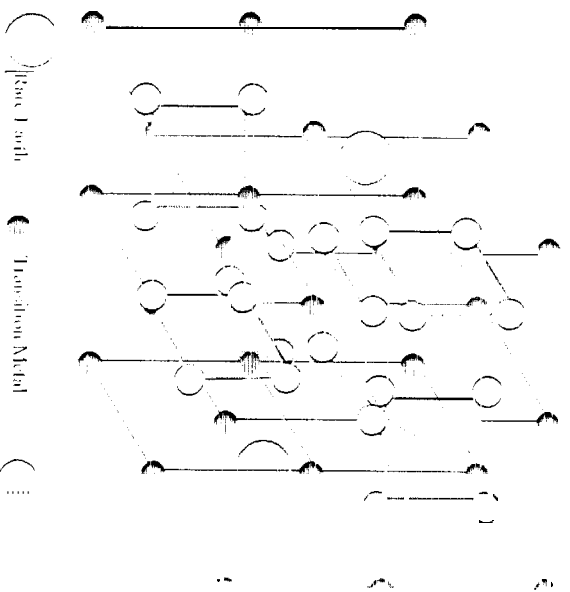structure (see Figure 1) which are formed of the TPn_3 framework are filled with a rare earth...

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

However, the introduction of a filling atom...

○ Pnictide
● Transition Metal
◐ Rare Earth

Experimental Results and Discussion

Table 1 Room temperature properties of Ce-based filled...

Composition		l_a	p	S	λ
$CeFe_4Sb_{12}$		~0.1	1.5	58.7	7.4
$CeFe_3CoSb_{12}$			1.5	0.75	75.8	3.
$CeFe_2Co_2Sb_{12}$			1.9	0.71	75.8	3.
$CeFeCo_3Sb_{12}$			1.7	0.81	10.5	8.7

Figure 2: High temperature variations of the electrical resistivity of filled skutterudite samples
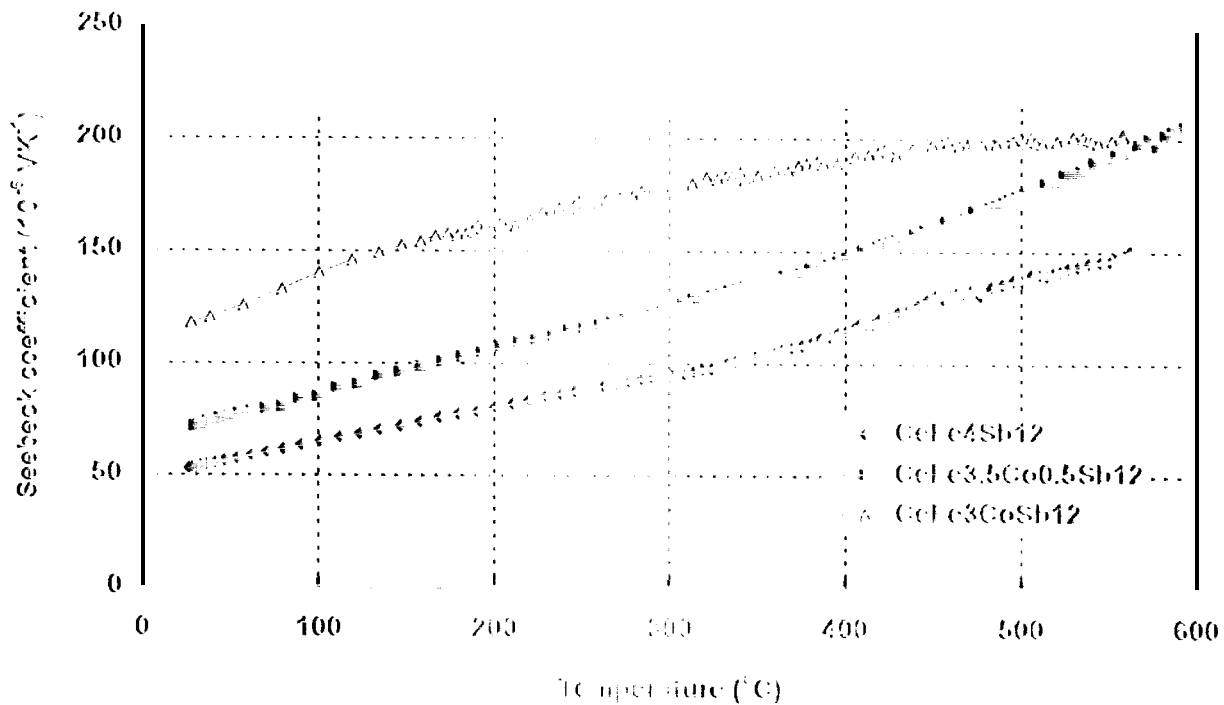
Figure 3: High temperature variations of the Seebeck coefficient of filled skutterudite samples

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 5×10^{21} cm^{-3} and low carrier mobilities) with a low electrical resistivity, which increases slightly with temperature. The CeFe$_4$Sb$_{12}$ and CeFe$_{3.5}$Co$_{0.5}$Sb$_{12}$ samples even show a small decrease at temperatures close to 600°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 106 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 [...] an [...] carriers possess large effective masses resulting in a low attributed to the fact that these materials beh[...] to mobility but unusually high Seebeck coefficient [5,7]. heavy fermions systems the hybridization between [...] the transition metal (Fe or Co here) creates a s[...]

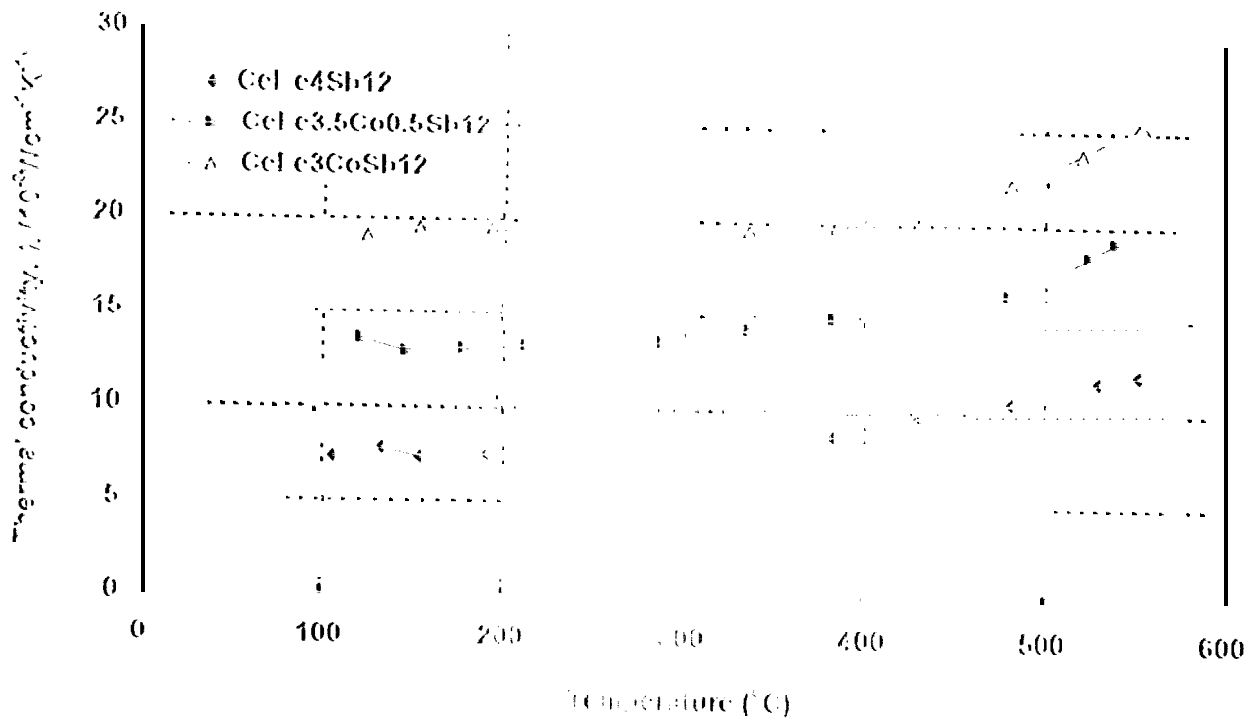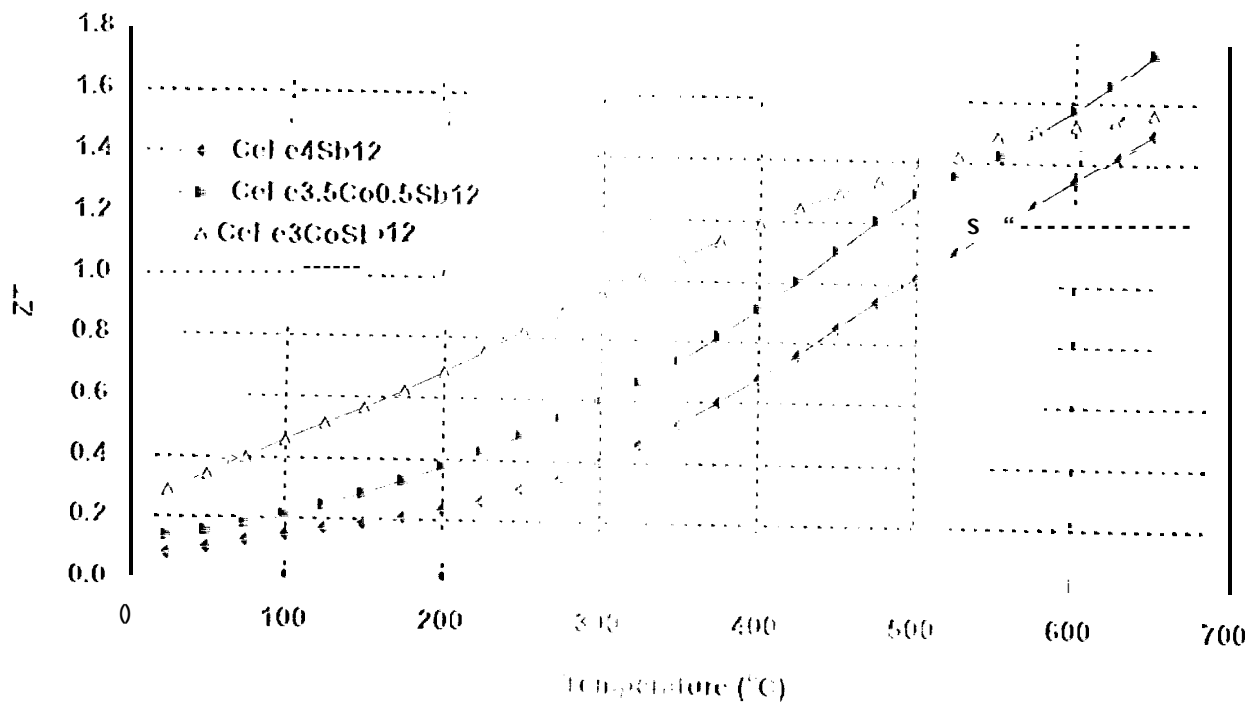Figure 4: High temperature variations of the thermal conductivity of filled skutterudite samples

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 [...] of the art p-type thermoelectric materials.

The thermal conductivity of these materials is low, [...] very low, depending on the composition. The $CeFe_4Sb_{12}$ [...] has a very low thermal conductivity of about [...] at room temperature and increasing up to 12.5 mW [...] 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" [...] very high carrier concentration very effectively [...] phonons, and results in an extremely low lattice thermal conductivity.

The $CeFe_{3.5}Co_{0.5}Sb_{12}$ and $CeFe_3CoSb_{12}$ samples also [...] low thermal conductivity values with a temperature dependence identical to that of $CeFe_4Sb_{12}$. 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 $CeFe_3CoSb_{12}$ 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 [...] fluctuations. As discussed above, the introduction of [...] Te 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 very 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 state of the art 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 those materials to be useful at lower temperature for cooling applications, the Seebeck coefficient must be increased which requires a lower doping level. For example, it might be achieved by increasing the Co to Fe atomic ratio ($CeFe_{4-x}Co_xSb_{12}$ with $1<x<4$) or combining Co with [...] Se. Replacing Co by Ir in the filled skutterudites would certainly result in higher decomposition temperature, allowing their use in power generation applications at temperatures close to 1000°C. In addition, the heavier and larger Ir atom will introduce additional scattering of the phonons, resulting in a decrease in lattice thermal conductivity.

Acknowledgments

References

[1] J.-P. Fleurial, T. Caillat, and A. Borshchevsky, *Proc. XIV Intl. Conf. Thermoelectrics*, St. Petersburg, Russia, June 27-30, 231 (1995).

[2] T. Caillat, A. Borshchevsky, and J.-P. Fleurial, J.-P., *Proc. XIII Intl. Conf. on Thermoelectrics*, AIP Press No. 316, 58-61, Kansas City, MO (1994).

[3] T. Caillat, A. Borshchevsky, and J.-P. Fleurial, J.-P., *Proc. XIII Intl. Conf. on Thermoelectrics*, AIP Press No. 316, 31-34, Kansas City, MO (1994).

[4] T. Caillat, A. Borshchevsky, and J.-P. Fleurial, *Proc. XIII Intl. Conf. on Thermoelectrics*, AIP Press No. 316, 499-11, Kansas City, MO (1994).

[5] D.T. Morelli and G.P. Meisner, J. Applied Physics 77, 3777 (1995).

[6] G.S. Nolas, G.A. Slack, T.M. Tritt and D.T. Morelli, *Proc. XIV Intl. Conf. on Thermoelectrics*, St. Petersburg, Russia, June 27-30, 236 (1995).

[7] L. Nordstrom and D. Singh, Phys. Rev. B. 53 (3) 1103 (1996).

[8] Oftedal I., Z. Kristallogr., 66, 517 (1928).

[9] A. Kjekshus, D. G. Nicholson, T. Rakke, *Acta Chem. Scand.*, 27, 4 (1973).

[10] T. Caillat, A. Borshchevsky, J. P. Fleurial, in K. R. Rao (ed.) *Proc. XI Int. Conf. Thermoelectrics*, Arlington, TX, The University of Texas, Arlington, 98 (1993).

[11] T. Caillat, J.-P. Fleurial, and A. Borshchevsky, J. Cryst. Growth 4201 (1995).

[12] D.T. Morelli, T. Caillat, J.-P. Fleurial, A. Borshchevsky, J.W. Vandersande, B. Chen and C. Uher, Phys. Rev. B 51, 9622 (1995).

[13] J. P. Odile, S. Soled, C. A. Castro, A. Wold, *Inorganic Chemistry*, 17, 2, 283 (1978).

[14] G. P. Meisner, M. S. Torikachvili, K. N. Yang, M. B. Maple, R. P. Guertin, J. Appl. Phys., 57, 1, 3073 (1985).

[15] D. Jung, M. H. Whangbo, S. Alvarez, *Inorganic Chemistry*, 29, 2252 (1990).

[16] F. Grandjean, A. Gérard, D. J. Braun, W. Jeitschko, J. Phys. Chem. Solids, 45, 879, 877 (1984).

[17] N. T. Stetson, S. M. Kauzlarich, H. Hope, *Journal of Solid State Chemistry*, 91, 140 (1991).

[18] W. Jeitschko and D. Braun, Acta Cryst. B33, 3401 (1977).