

# LOW THERMAL CONDUCTIVITY **SKUTTERUDITES**

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## ABSTRACT

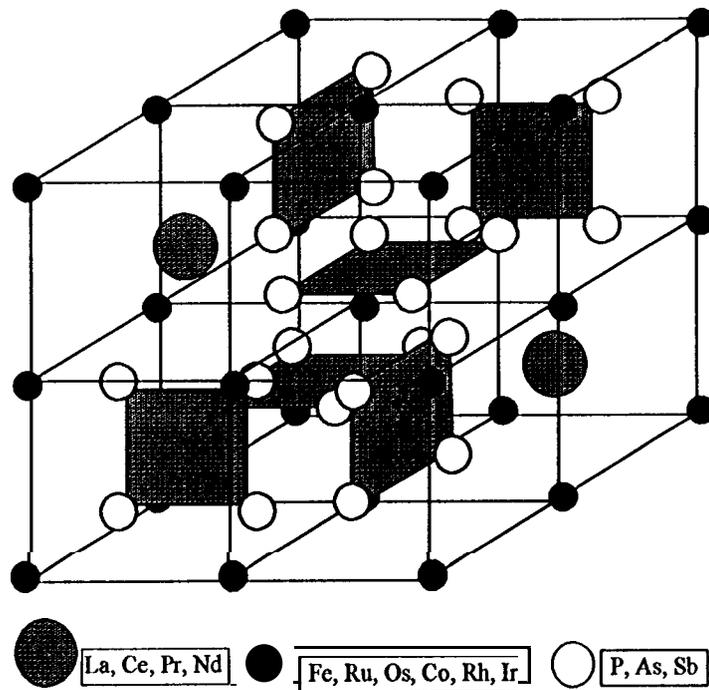
Recent experimental results on semiconductors with the **skutterudite** crystal **structure** show that these materials possess attractive transport properties and have a good potential for achieving ZT **values** substantially larger than for **state-of-the-art** thermoelectric materials. Both n-type and p-type conductivity samples have been obtained, using several preparation techniques. Associated with a low hole effective mass, very high carrier mobilities, low electrical **resistivities** and moderate **Seebeck** coefficients are obtained in p-type **skutterudites**. For a comparable doping level, the carrier mobilities of n-type samples are about an order of magnitude lower than the values achieved on p-type samples. However, the much larger electron effective masses and Seebeck **coefficients make** n-type **skutterudites** promising candidates as well. Unfortunately, the thermal **conductivities** of the binary **skutterudite** compounds are too large, particularly at low temperatures, to be useful for thermoelectric applications.

Several approaches to the reduction of the lattice thermal conductivity **in skutterudites** are being pursued: heavy doping, formation of solid solutions and alloys, study of novel ternary and filled **skutterudite** compounds. All those **approaches** have already resulted in **skutterudite** compositions with substantially lower thermal conductivity values in these materials. Recently, superior thermoelectric properties in the moderate to high temperature range were achieved for compositions combining alloying and “filling” of the skutterudite structure. Experimental results and mechanisms responsible for low thermal conductivity in **skutterudites** are discussed.

## INTRODUCTION

Thermoelectric generators and cooling devices present several advantages compared to other energy conversion technologies: they are reliable, can operate unattended in hostile environments, and are also environmentally friendly. However, their application has been limited up to now because of the relatively low conversion efficiency of traditional thermoelectric materials used in the devices. New more efficient materials are needed. A systematic search for advanced thermoelectric materials was initiated at JPL several years ago and resulted in the discovery of a new **family** of promising **semiconducting** materials with the **skutterudite** crystal structure [1].

The unit cell of the **skutterudite** structure (cubic, space group Im3, prototype **CoAs<sub>3</sub>**) contains square radicals **[As<sub>4</sub>]<sup>4-</sup>**. This anion, located in the center of the smaller cube, is surrounded by 8 **Co<sup>3+</sup>** cations. The unit cell was found to consist of 8 smaller cubes (**octants**) described above but two of them do not have the anions **[As<sub>4</sub>]<sup>4-</sup>** in the center. This is necessary to keep the ratio  $n_{3+}:n_{4-} = 4:3$ . Thus, atypical coordination structure results with **Co<sub>8</sub>[As<sub>4</sub>]<sub>6</sub> = 2Co<sub>4</sub>[As<sub>4</sub>]<sub>3</sub>** composition and 32 atoms per cell, as depicted in Figure 1.



**Figure 1:** Skutterudite crystal structure. The unfilled structure has 32 atoms: a cubic frame with 8 transition metals, 24 pnictogens distributed in six square radicals and located in six of the eight octants, and two empty octants. Two rare earth elements located in the two remaining octants form a completely filled structure.

A low lattice thermal conductivity and a high carrier mobility are desirable for improved figures of merit in new thermoelectric materials. High carrier mobility values are usually found in crystal structures with a high degree of **covalency**. It has been shown that the bonding is predominantly covalent in the **skutterudite** structure and high hole mobility values have been measured on several **skutterudite** compounds: **IrSb<sub>3</sub>**, **RhSb<sub>3</sub>**, **CoSb<sub>3</sub>**, **CoAs<sub>3</sub>**, **RhAs<sub>3</sub>** and **RhP<sub>3</sub>** [2]. The unit cell is relatively large and complex, indicating that low lattice thermal conductivity values might be possible.

For state-of-the-art thermoelectric materials, the number of **isostructural** compounds is limited and the possibilities to optimize their properties for maximum performance at different temperatures of operation are also very limited. This is not the case for the **skutterudite** family of materials, where eleven binary compounds and many solid solutions and related phases are known to exist [2]. These materials cover a large range of decomposition temperatures and bandgaps which offers the possibility to adjust composition and doping level for a specific temperature range of application.

However, the room temperature thermal conductivity of binary skutterudites (100-150 **mWcm<sup>-1</sup>K<sup>-1</sup>**) was found to be too high to result in high ZT values. Substantial reductions in the lattice thermal conductivity must be obtained to achieve values comparable to those of state of the art thermoelectric materials (10-40 **mWcm<sup>-1</sup>K<sup>-1</sup>**).

Several approaches were recently considered to reduce the lattice thermal conductivity of these materials. Such reductions have been **observed** in heavily doped n-type binary compounds, solid solutions, ternary compounds, and also filled **skutterudites**. This paper presents recent thermal conductivity experimental data obtained on several **skutterudite** materials and briefly discusses the various **phonon** scattering mechanisms. It is shown that low thermal conductivity

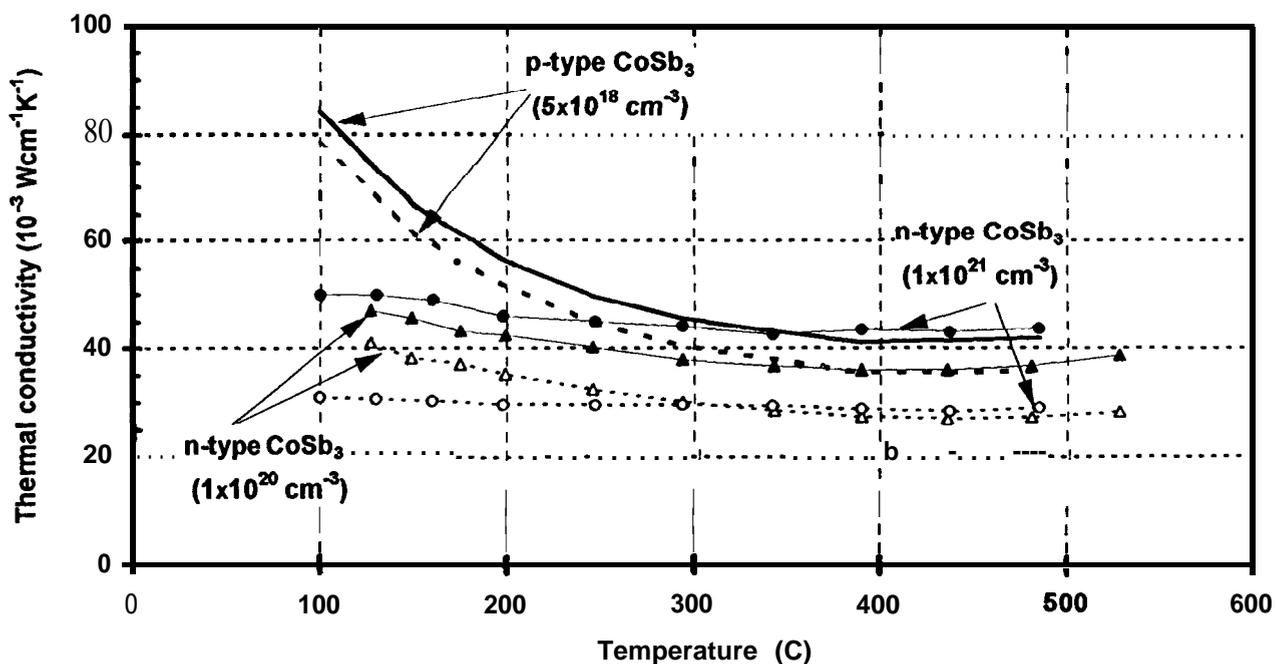
**skutterudites** can be obtained and **high ZT** values are possible, which can lead to a significant improvement in the thermal-to-electric conversion efficiency of thermoelectric devices.

## LATTICE THERMAL CONDUCTIVITY REDUCTION IN SKUTTERUDITES

The dimensionless thermoelectric figure of merit  $ZT$  is inversely proportional to the thermal conductivity. As a consequence, efficient thermoelectric materials have low thermal conductivity values such as **Bi<sub>2</sub>T<sub>3</sub>-alloys** (15 to 20  $\text{mWcm}^{-1}\text{K}^{-1}$ ), **PbTe-alloys** (10 to 20  $\text{mWcm}^{-1}\text{K}^{-1}$ ) and **Si-Ge** alloys (40 to 50  $\text{mWcm}^{-1}\text{K}^{-1}$ ). The contribution of the crystal lattice, through heat conduction by phonons, to the total thermal conductivity can be reduced by effectively scattering the **phonons**. Several scattering mechanisms are of interest to **reduce** the lattice thermal conductivity of **skutterudites**: **electron-phonon** scattering in heavily doped samples, mass and strain fluctuation scattering in solid solutions and alloys, electron charge transfer scattering in mixed-valence ternary compounds, and void filler scattering in filled **skutterudite** compounds [3].

### Heavily Doped CoSb<sub>3</sub>

The thermal conductivity of heavily doped n-type **CoSb<sub>3</sub>** sample was recently measured [4]. The thermal conductivity data are shown in Figure 2. For lightly doped samples, the lattice thermal conductivity at 100°C is about 80  $\text{mWcm}^{-1}\text{K}^{-1}$  but for more heavily doped samples, the value decreases to about 44  $\text{mWcm}^{-1}\text{K}^{-1}$  ( $1 \times 10^{20} \text{ cm}^{-3}$ ) and can be as low as 32  $\text{mWcm}^{-1}\text{K}^{-1}$  ( $1 \times 10^{21} \text{ cm}^{-3}$ ).



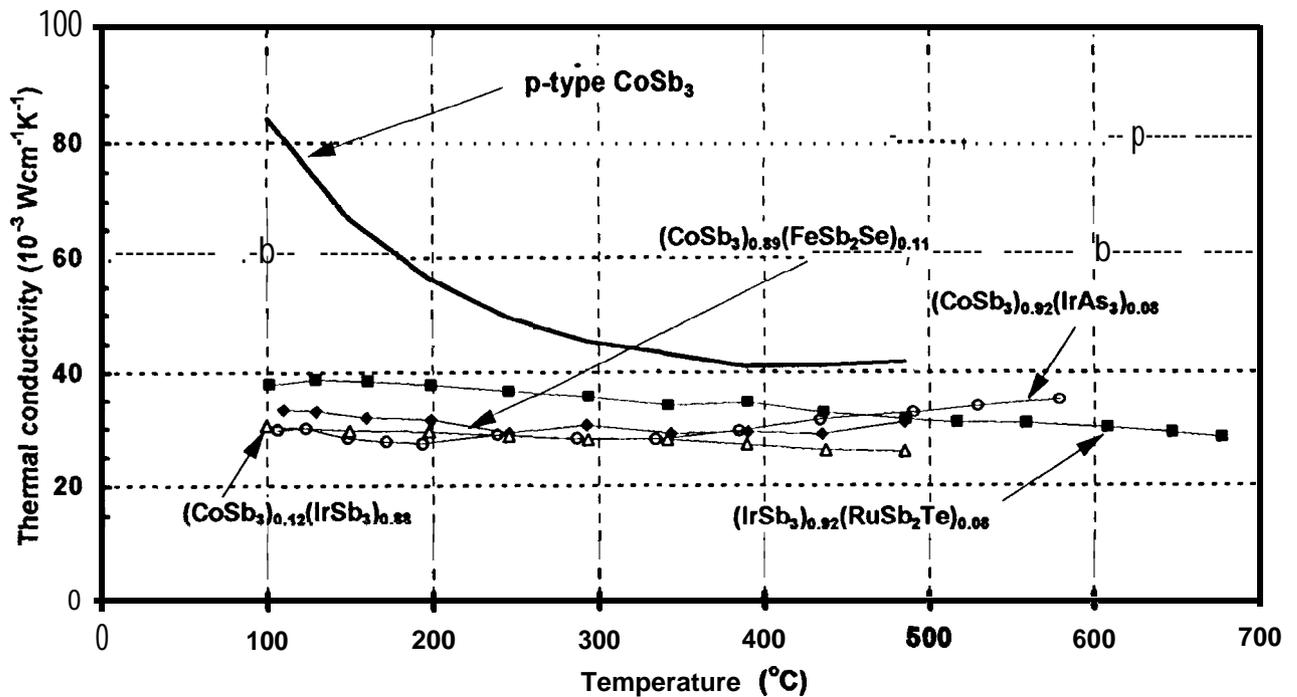
**Figure 2:** Lattice (dotted lines) and total (plain lines) thermal conductivity as a function of temperature for **CoSb<sub>3</sub>** samples with various doping levels.

The total thermal conductivity of the most heavily doped sample is actually higher than the one doped at  $1 \times 10^{20} \text{ cm}^{-3}$  because of the large electronic contribution (proportional to the electrical conductivity). The temperature dependence of the lattice thermal conductivity

becomes weaker for more heavily doped samples, indicating that electron-phonon scattering is responsible for the large decrease in lattice thermal conductivity. This is an interesting finding because charge carrier phonon scattering would scatter the phonons with low frequency and if coupled with point defect scattering could result in very low lattice thermal conductivity values. The combination of point **defects** and charge carrier scattering was utilized in **Si-Ge** alloys [5]. Because of lower carrier concentrations, this scattering mechanism has not been identified yet in p-type samples.

### Skutterudite Solid Solutions

All state-of-the-art thermoelectric materials are solid solutions between two or more **isostructural** binary compounds or phases. The mass and strain fluctuations brought **by** point defects in solid solutions is a well known approach to reduce the lattice thermal conductivity. However, point defects not only scatter phonons but also scatter charge carriers, resulting in some decrease in carrier mobility. Thus, improvements in the thermoelectric properties can be obtained if the ratio of the carrier mobility to the lattice thermal conductivity is higher for the solid solutions.

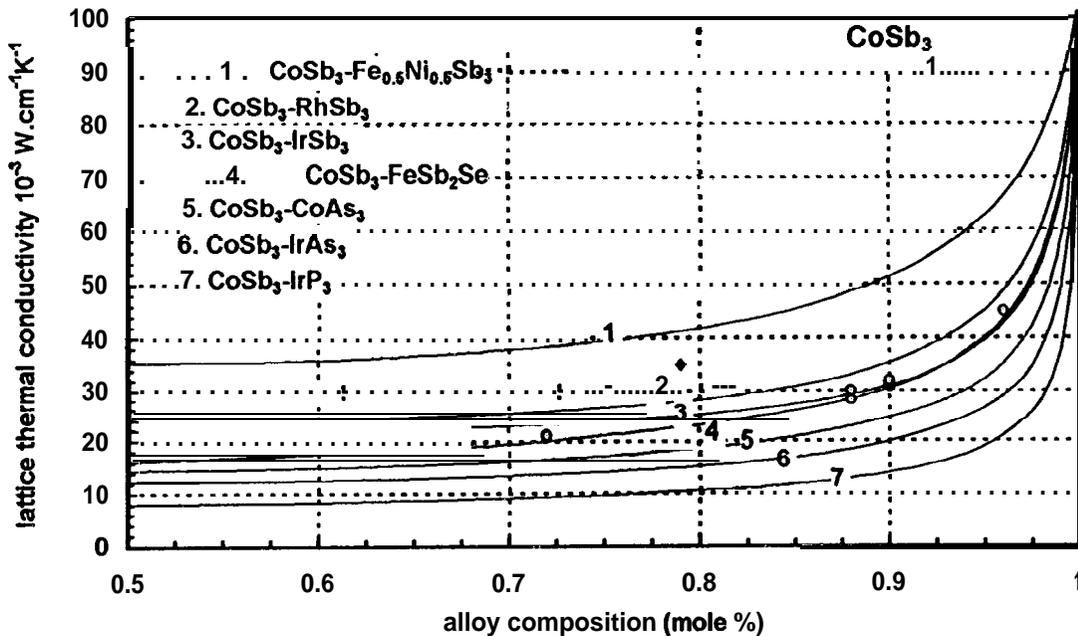


**Figure 3:** Thermal conductivity as a **function** of temperature for **CoSb<sub>3</sub>-** and **IrSb<sub>3</sub>-based** solid solutions. Results are compared to those obtained for lightly doped **CoSb<sub>3</sub>**.

The existence of several solid solutions between skutterudite compounds were reported in the literature [6-9]. More recent studies showed that many more solid solutions can be formed and initial results demonstrated that a reduction in lattice thermal conductivity can be obtained [10]. For example, a room temperature lattice thermal conductivity of  $33\text{mWcm}^{-1}\text{K}^{-1}$  was obtained for a lightly-doped, single phase, homogeneous **and fully** dense p-type **(CoSb<sub>3</sub>)<sub>0.75</sub>(IrSb<sub>3</sub>)<sub>0.25</sub>** solid solution. This represents a **70%** reduction compared to either one of the end members in this system. The corresponding reduction in carrier mobility was only **about 46%**. Results

obtained for  $a(\text{RhSb}_3)_{0.5}(\text{IrSb}_3)_{0.5}$  solid solution showed that its room temperature lattice thermal conductivity was decreased by about 45% [8]. The smaller reduction in this latter sample can be attributed to the fact that the decrease is only due to mass fluctuations in this system and that there is no strain fluctuation (the atomic volumes of Rh and Ir are almost identical). Some of the high temperature experimental results on several lightly doped solid solutions are shown in Figure 3. The results are compared to the experimental data on  $\text{CoSb}_3$  and demonstrate the sharp reduction and near temperature-independent variation of the thermal conductivity of solid solutions.

In order to help selecting the most promising solid solutions systems, the effect of mass and strain fluctuation scattering of phonons was calculated for **skutterudites** using the theory developed by Callaway and VonBaeyer[11]. The calculation requires computing an alloy scattering parameter  $\Gamma$  which is a function of the variations in atomic masses and volumes introduced by the presence of different atoms located on the same sublattice. For compositions where volume fluctuations are becoming important, an adjustable strain parameter used in calculating  $\Gamma$  can be determined by fitting experimental data [10]. The result of the calculations conducted for  $\text{CoSb}_3$ -based solid solutions are shown in Figure 4.



**Figure 4:** The calculated lattice thermal conductivity of  $\text{CoSb}_3$ -based solid solutions at 300K as a function of solid solution composition. Experimental data are reported for  $\text{CoSb}_3$ - $\text{IrSb}_3$  (○),  $\text{CoSb}_3$ - $\text{FeSb}_2\text{Se}$  (■) and  $\text{CoSb}_3$ - $\text{Fe}_{0.5}\text{Ni}_{0.5}\text{Sb}_3$  (◆).

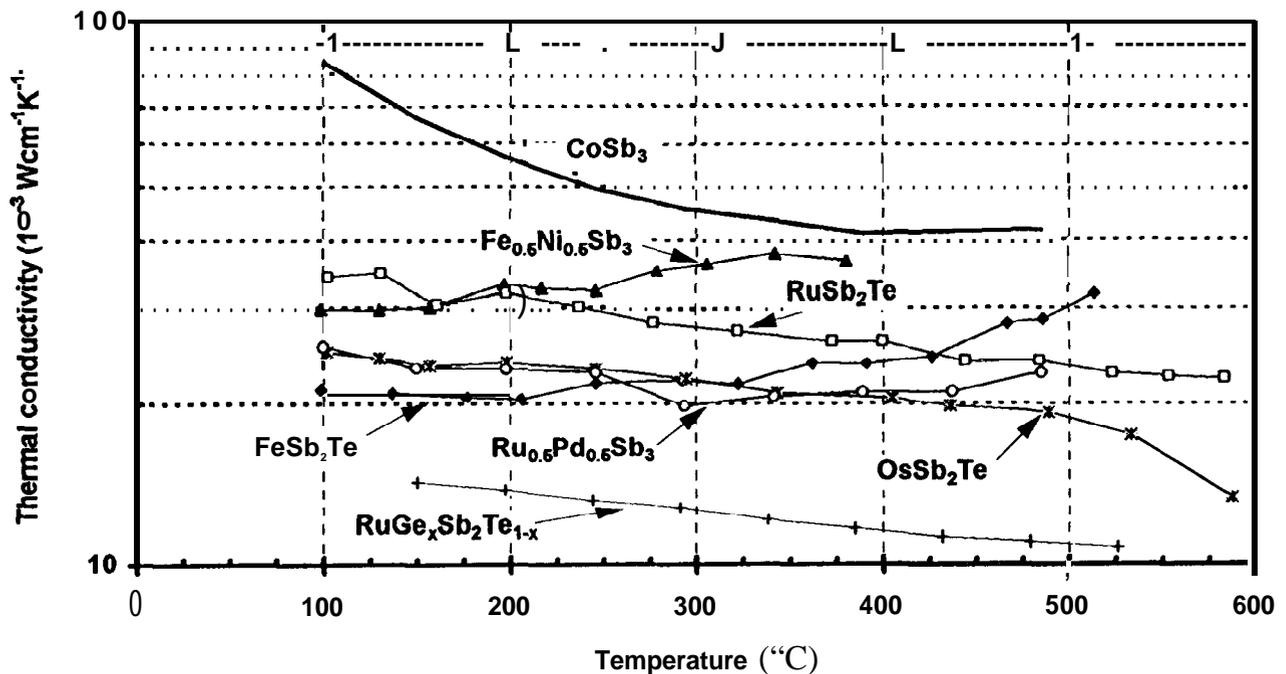
The major findings of these theoretical calculations are that: a) **skutterudite** solid solutions with small mass and volume fluctuations (such as  $\text{CoSb}_3$ - $\text{Fe}_{0.5}\text{Ni}_{0.5}\text{Sb}_3$ ,  $\text{IrSb}_3$ - $\text{RhSb}_3$  and  $\text{IrSb}_3$ - $\text{RuSb}_2\text{Te}$ ) exhibit relatively small decreases in lattice thermal conductivity; b) solid solutions between ternary and binary **skutterudites** do not result in lower thermal conductivity values compared to those obtained for optimum binary **skutterudite** alloys and; c) the lowest thermal conductivity values are achieved for alloys maximizing mass and volume fluctuations, such as  $\text{CoSb}_3$ - $\text{IrP}_3$  with  $8 \text{ mWcm}^{-1}\text{K}^{-1}$  for a 50 mole% concentration.

These calculations show that point defect scattering alone can be a very **efficient** phonon scattering mechanism in some **skutterudite** solid solutions. More work is needed to determine the

volubility limit of some of these solid solutions and efforts are currently underway to prepare samples of the most promising systems and compare the experimental data with the theoretical predictions.

### Ternary Compounds

**Skutterudite** related phases can be formed by substitution by neighboring atoms for the anion or the cation in binary **skutterudite** compounds, the condition being that the valence-electron count remains constant. This is similar to the diamond-like family of semiconductor. The substitution can occur on the anion site or on the cation site. Structurally related **skutterudite** phases can also be formed by partial substitution of the cation and the anion. Nine ternary **skutterudite** related phases have been reported in literature [2]. Based on x-ray **diffraction** analyses, fourteen new compositions were discovered at JPL. A number of **isostructural quaternary** and more complex compositions have also been identified.



**Figure 5:** Thermal conductivity as a function of temperature for several ternary **skutterudite** compounds. Results are compared to those obtained for lightly doped **CoSb<sub>3</sub>**.

The electrical properties of the ternary **skutterudites** can vary substantially from the results obtained on the binary compounds. P-type conductivity samples were obtained for **Ru<sub>0.5</sub>Pd<sub>0.5</sub>Sb<sub>3</sub>**, **FeSb<sub>2</sub>Te** and **RuSb<sub>2</sub>Te**, with typical carrier concentrations of  $1 \times 10^{20} \text{ cm}^{-3}$ ,  $5 \times 10^{20} \text{ cm}^{-3}$ , and  $8 \times 10^{18} \text{ cm}^{-3}$  respectively. N-type conductivity **Fe<sub>0.5</sub>Ni<sub>0.5</sub>Sb<sub>3</sub>** samples were also prepared but characterized by mixed conduction effects near room temperature. These results indicate that significant changes in band structure and doping behavior were brought by changes in the atomic and electronic structure. In particular, fluctuations in the valence of the transition metal atoms could be imposed by the need to conserve the **skutterudite** crystal structure. Understanding and controlling these changes is a key step in designing a **skutterudite** composition with superior thermoelectric properties.

The experimental data on the high temperature thermal conductivity of five ternary compounds, **FeSb<sub>2</sub>Te**, **RuSb<sub>2</sub>Te**, **OsSb<sub>2</sub>Te**, **Fe<sub>0.5</sub>Ni<sub>0.5</sub>Sb<sub>3</sub>** and **Ru<sub>0.5</sub>Pd<sub>0.5</sub>Sb<sub>3</sub>** are plotted in Figure 5

[3, 12]. The results are compared to the data on lightly doped **CoSb<sub>3</sub>**. The lattice contribution to the thermal conductivity is greatly reduced in these materials, with room temperature values ranging from 15 to 30 **mW.cm<sup>-1</sup>K<sup>-1</sup>**. The low thermal conductivity values of these compounds, while very encouraging, are nevertheless a bit surprising considering that the atomic mass and volume differences introduced by the substituting anion/cation are fairly small. This indicates that additional mechanisms must be involved.

A possible explanation for the unusually **high** phonon scattering rate could be that transition metal elements have mixed valence states and electrons are **transferred** between the different ions, thus scattering the phonons in **this** process [3, 13]. In a study of the thermal conductivity of **Fe<sub>3</sub>O<sub>4</sub>**, Slack [14] has shown that the phonon scattering caused by interaction of the phonons by local disorder in the magnetic lattice was significant. The binary compound **CoSb<sub>3</sub>** can be described by its ionic formula: **Co<sup>3+</sup>Sb<sub>3</sub><sup>-1</sup>**. For example, when considering the **stoichiometric Ru<sub>0.5</sub>Pd<sub>0.5</sub>Sb<sub>3</sub>** composition, it is assumed that the valence state of Ru, Pd, and **Sb** would be **Ru<sup>2+</sup>**, **Pd<sup>4+</sup>**, and **Sb<sup>-1</sup>**, respectively. Systematic **shifts** from the **stoichiometric Ru<sub>0.5</sub>Pd<sub>0.5</sub>Sb<sub>3</sub>** were revealed by microprobe analysis [12]. Results indicate that the Ru:Pd atomic ratio can vary substantially from the expected 1:1 value and that there is a significant number of vacancies on the transition metal **sublattice**. To compensate for the Pd deficit and excess **Sb** in the samples, the Ru must adopt a mixed valence state, *i.e.*, **Ru<sup>2+</sup>** and **Ru<sup>4+</sup>**. Such valence fluctuations were recently **confirmed** by x-ray absorption near-edge structure analysis [13].

In addition to **Ru<sub>0.5</sub>Pd<sub>0.5</sub>Sb<sub>3</sub>**, other ternary **skutterudites** such as **RuSb<sub>2</sub>Te** also show significant stoichiometric deviations. Experimental data for **Fe<sub>0.5</sub>Ni<sub>0.5</sub>Sb<sub>3</sub>**, **Ru<sub>0.5</sub>Pd<sub>0.5</sub>Sb<sub>3</sub>**, **FeSb<sub>2</sub>Te**, **RuSb<sub>2</sub>Te**, **OsSb<sub>2</sub>Te** and **RuGe<sub>x</sub>Sb<sub>2</sub>Te<sub>1-x</sub>** samples prepared at JPL are presented in Table 1. Based on electron microprobe analysis, we have recalculated each composition to conform to the **T<sup>3+</sup>X<sub>3</sub><sup>-1</sup> stoichiometry**, adding vacancies to the metal **sublattice** when needed. The valence ratio *v* of the mixed valence transition metal (for example **[Ru<sup>2+</sup>]/[Ru<sup>4+</sup>]**) was then determined from the ionic formula. The lattice thermal conductivity calculated from the measured thermal conductivity at room temperature using the **Wiedmann-Franz** law is also reported in this table.

Table 1: Valence Fluctuations in Low Thermal Conductivity Ternary **Skutterudites**, where *v* is the valence ratio (e.g. **[Ru<sup>2+</sup>]/[Ru<sup>4+</sup>]**) and **λ<sub>L</sub>** is the lattice thermal conductivity in 10<sup>3</sup> **W/cmK**.

Compound	Composition (at%)	Ionic Formula	<i>v</i>	<b>λ<sub>L</sub></b>
<b>Fe<sub>0.5</sub>Ni<sub>0.5</sub>Sb<sub>3</sub></b>	<b>Fe<sub>12.8</sub>Ni<sub>11.9</sub>Sb<sub>75.2</sub></b>	<b>Fe<sup>2+</sup><sub>0.51</sub>Ni<sup>4+</sup><sub>0.49</sub>Sb<sup>-1</sup><sub>3</sub></b>	--	29
<b>Ru<sub>0.5</sub>Pd<sub>0.5</sub>Sb<sub>3</sub></b>	<b>Ru<sub>12.3</sub>Pd<sub>10.6</sub>Sb<sub>77.1</sub></b>	<b>[]0.11Ru<sup>2+</sup>0.28Ru<sup>4+</sup>0.20Pd<sup>4+</sup>0.41Sb<sup>-1</sup><sub>3</sub></b>	1.4	15
<b>FeSb<sub>2</sub>Te</b>	<b>Fe<sub>25.1</sub>Sb<sub>52.0</sub>Te<sub>22.9</sub></b>	<b>Fe<sup>2+</sup><sub>0.91</sub>Fe<sup>3+</sup><sub>0.09</sub>Sb<sup>-1</sup><sub>2.1</sub>Te<sup>0</sup><sub>0.9</sub></b>	10.4	23
<b>RuSb<sub>2</sub>Te</b>	<b>Ru<sub>22.4</sub>Sb<sub>49.7</sub>Te<sub>25.3</sub></b>	<b>[]0.10Ru<sup>2+</sup>0.79Ru<sup>4+</sup>0.11Sb<sup>-1</sup>1.98Te<sup>0</sup><sub>1.02</sub></b>	7.2	28
<b>OsSb<sub>2</sub>Te</b>	<b>Os<sub>24.6</sub>Sb<sub>50.5</sub>Te<sub>24.9</sub></b>	<b>[]0.02Os<sup>2+</sup>0.98Os<sup>4+</sup>0.02Sb<sup>-1</sup>2.03Te<sup>0</sup><sub>0.97</sub></b>	32.3	25
<b>RuGe<sub>x</sub>Sb<sub>2</sub>Te<sub>1-x</sub></b>	<b>Ru<sub>24.0</sub>Ge<sub>4.7</sub>Sb<sub>50.6</sub>Te<sub>20.7</sub></b>	<b>[]0.05Ru<sup>2+</sup>0.75Ru<sup>4+</sup>0.2Ge<sup>-2</sup>0.18Sb<sup>-1</sup>2.0Te<sup>0</sup><sub>0.82</sub></b>	3.7	14

From Table 1, it **can** be seen that **Ru<sub>0.5</sub>Pd<sub>0.5</sub>Sb<sub>3</sub>** and **RuGe<sub>x</sub>Sb<sub>2</sub>Te<sub>1-x</sub>** possess high concentrations of **Ru<sup>4+</sup>** (and vacancies), resulting in *v* values approaching 1, for which the scattering rate of phonons by the electron exchange mechanism is maximized. Those two compositions have the lowest lattice thermal conductivity values. For **FeSb<sub>2</sub>Te**, **RuSb<sub>2</sub>Te** and

**OsSb<sub>2</sub>Te**, the  $\nu$  values are much larger than 1, but the lattice thermal **conductivities** are still much lower than the values obtained for **CoSb<sub>3</sub>**, **RhSb<sub>3</sub>** and **IrSb<sub>3</sub>**. However, as is the case in some **arsenopyrites** [15], short-range disorder on the **pnictogen sublattice could** also lead to substantial valence fluctuations for the transition metals (and thus lower **values** of  $\nu$ ) trying to compensate for localized variations in the **Sb:Te** atomic ratio of 2. It is also likely that the substitution of Te by **Ge** in **RuSb<sub>2</sub>Te** imposes a much higher **Ru<sup>4+</sup>** concentration, which results in a 50% decrease in lattice thermal conductivity. As to **Fe<sub>0.5</sub>Ni<sub>0.5</sub>Sb<sub>3</sub>**, it is likely that Fe and Ni are of valence 2+ and 4+ respectively since the valence of Fe in the corresponding **arsenopyrite**, **Fe<sub>0.5</sub>Ni<sub>0.5</sub>Sb<sub>2</sub>**, was determined as close to 2+[15]. However the presence of some small amount of **Fe<sup>3+</sup>** and **Ni<sup>3+</sup>** could also result in strong electron exchange scattering of the phonons and explain the low lattice thermal conductivity.

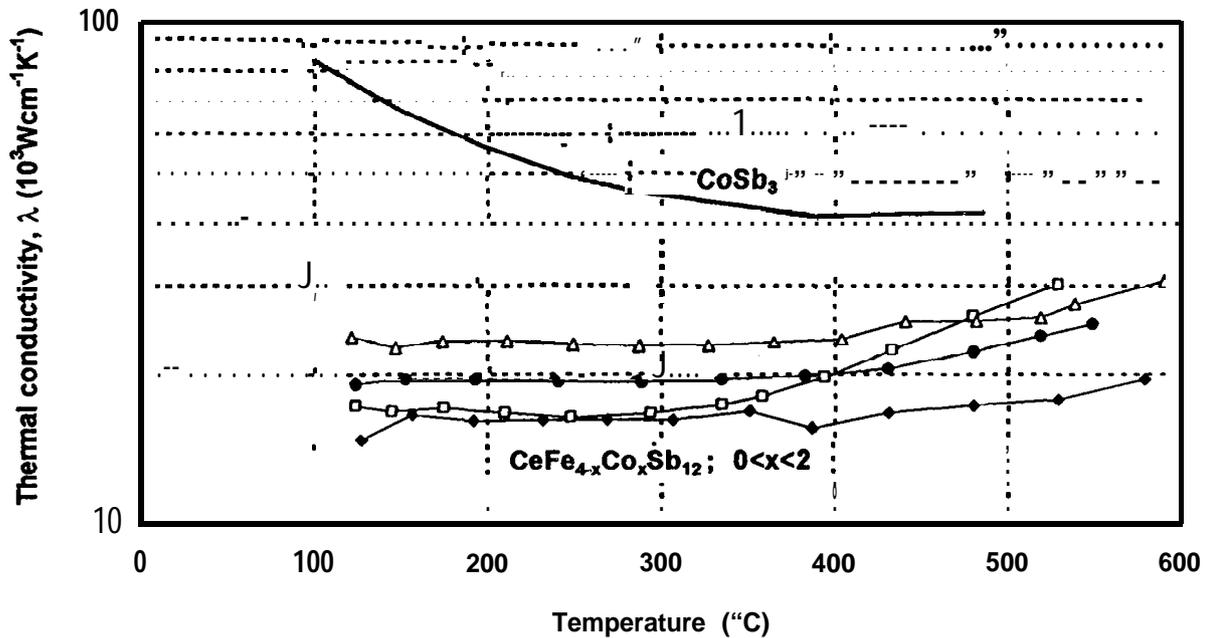
Although ternary compounds have rather low thermal conductivity values, it is difficult to control their electrical properties. When doping ternary **skutterudites**, and supposing that the electron exchange mechanism is indeed present, changes in carrier concentration are not easy to achieve because dopants can be compensated by small fluctuations in the overall valence of the transition metals.

### Filled Skutterudites

Finally, the last approach which is now under consideration for reducing the lattice thermal conductivity of **skutterudite** materials is to fill the voids present in the **skutterudite** structure with rare earth elements (see Figure 1). Slack first suggested that the “rattling” of the rare earth element would produce a significant **phonon** scattering and reduce the thermal conductivity, but with minimal decrease in carrier mobility [16]. A large number of materials with **filled skutterudite** crystal structure has already been synthesized [17]. The composition of these types of compounds can be represented by the formula **LnT<sub>4</sub>Pn<sub>12</sub>** (**Ln** = **La**, Ce, Pr, Nd, Sm, Eu, Gd, Th and U; **T** = Fe, Ru, Os; **Pn** = P, As, **Sb**). In these compounds, the empty **octants** of the **skutterudite** structure which are formed in the T<sub>4</sub>Pn<sub>12</sub> framework are **filled** with a rare earth element. Because the T<sub>4</sub>Pn<sub>12</sub> groups using Fe, Ru or Os are electron-deficient (by 4 e<sup>-</sup>) relative to the **skutterudite** electronic structure (using **Co**, **Rh** or **Ir**), the introduction of the rare earth atom compensates this deficiency by adding free electrons. However, the number of valence electrons given up by the rare earth atoms is generally insufficient: for example, **La** has a 3+ oxidation state, **Ce** can be 3+ or 4+. This means that most of these compounds behave as metals, or very heavily doped p-type **semimetals**.

To conserve the excellent **semiconducting** behavior of the unfilled binary **skutterudites**, it is necessary to introduce a “compensating” atom for the addition of the “filling” atom into the structure. The ratio of compensating atoms to filling atoms is determined exclusively 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 **octants** of the 32 atoms **CoSb<sub>3</sub>** unit cell, 6 atoms of Fe (each providing one acceptor per atom) will have to be substituted for Co: **CoSb<sub>3</sub>** (or **Co<sub>8</sub>Sb<sub>24</sub>**) will become **Ce<sub>2</sub>Fe<sub>6</sub>Co<sub>2</sub>Sb<sub>24</sub>** (or **CeFe<sub>3</sub>CoSb<sub>12</sub>**). This composition is very close to the compound **CeFe<sub>4</sub>Sb<sub>12</sub>** whose existence was previously reported. The same approach can be applied with other atoms. Moreover, the doping level and conductivity type might be controlled by changing the compensating to filling atomic ratio. Also, the introduction of compensating atoms can bring a substantial increase in phonon scattering (mass and volume differences) and carrier scattering (ionized impurity, disorder) rates. Experimental evidence of this enhanced **phonon** scattering has since been published in the literature [18-23]. It also has been demonstrated that **Ce** is nearly trivalent at temperatures higher than 100K [23].

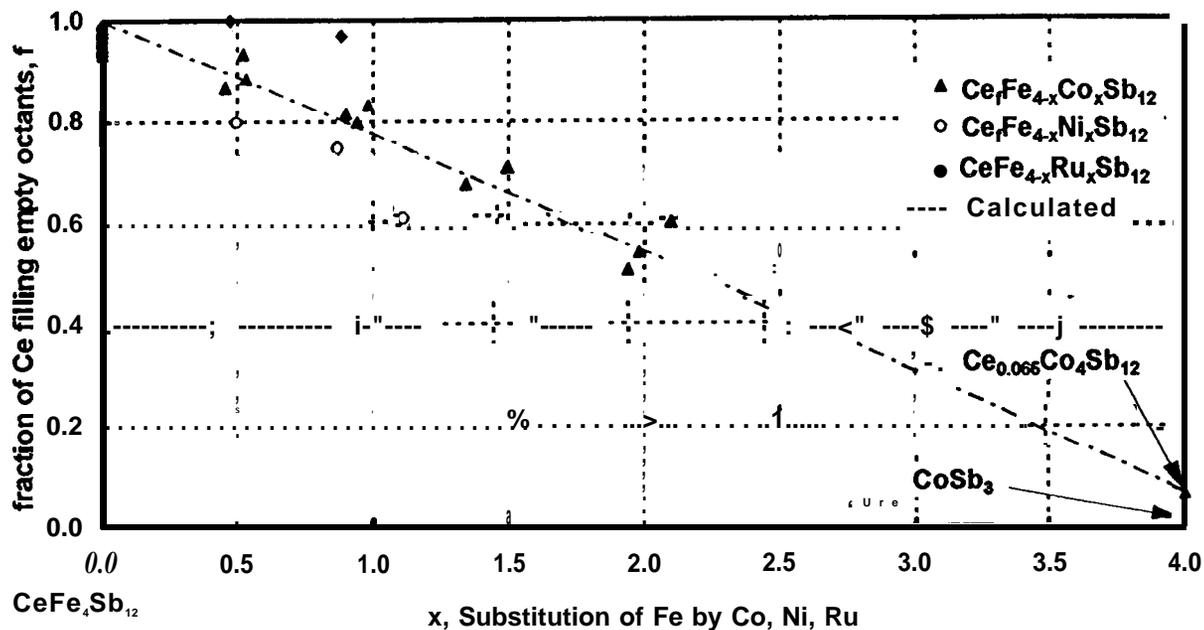
This approach seems to be particularly promising in light of recent results obtained on p-type  $\text{CeFe}_{4-x}\text{Co}_x\text{Sb}_{12}$  materials [21-23]. The high temperature thermal conductivity data of some of these compositions are shown in Figure 6. The thermal conductivity of those materials is much lower than for  $\text{CoSb}_3$ . The  $\text{CeFe}_4\text{Sb}_{12}$  sample has a room temperature thermal conductivity of about  $24 \times 10^{-3} \text{Wcm}^{-1}\text{K}^{-1}$  at room temperature and increasing up to  $27 \times 10^{-3} \text{Wcm}^{-1}\text{K}^{-1}$  at  $575^\circ\text{C}$ . Based on the low electrical resistivity value ( $0.5 \times 10^{-3} \Omega\text{cm}$ ), the lattice contribution to the thermal conductivity was estimated at  $12 \times 10^{-3} \text{Wcm}^{-1}\text{K}^{-1}$ . This demonstrates that the combination of the “rattling” atom and very high carrier concentration ( $5 \times 10^{21} \text{cm}^{-3}$ ) very effectively scatter the phonons, and results in an extremely low lattice thermal conductivity. However, it is difficult to quantify the two scattering mechanisms, void-filling and electron-phonon. Experiments on a series of  $\text{CeFe}_{4-x}\text{Co}_x\text{Sb}_{12}$  samples have shown that the amount of Ce filling decreases with increasing substitution of Fe by Co. Despite this reduction, a decrease in carrier concentration and increase in electrical resistivity and Seebeck coefficient was observed with increasing Co content, indicative of a more semiconducting behavior [23].



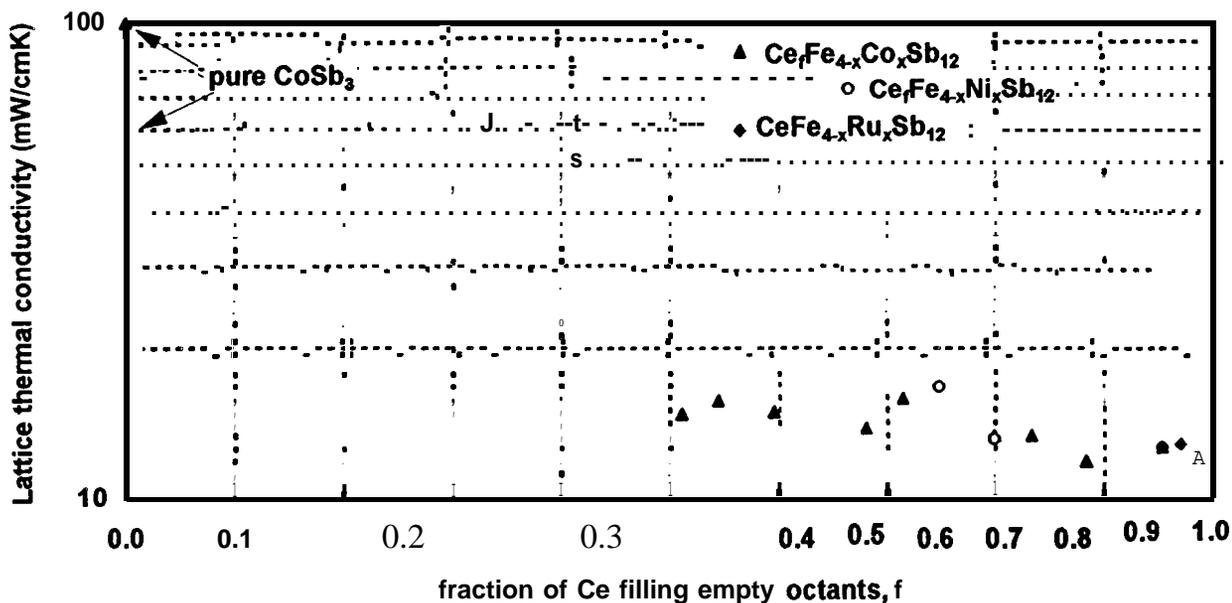
**Figure 6:** Thermal conductivity as a function of temperature for several  $\text{CoSb}_3$ -based filled skutterudite compositions. Results are compared to those obtained for lightly doped  $\text{CoSb}_3$ .

We can rewrite those compositions with the following formula,  $\text{Ce}_f\text{Fe}_{4-x}\text{Co}_x\text{Sb}_{12}$ , where  $f$  represent the fraction of Ce filling ( $f=1$  represents complete filling). In addition to Co, substitution of Fe by Ni and Ru has also been investigated recently. The variations of the filling fraction  $f$  as a function of  $x$  have been plotted in Figure 7 for the three different ranges of compositions. When Fe is totally replaced by Co, only a very small amount of Ce remains in the sample ( $f=0.065$ ) while completely filled  $\text{CeRu}_4\text{Sb}_{12}$  can be prepared ( $f=1$ ). This is attributed to the fact that Ru and Fe are isoelectronic. The dotted line was calculated based on a  $\text{CeFe}_4\text{Sb}_{12}$ - $\text{Ce}_{0.065}\text{Co}_4\text{Sb}_{12}$  range of “solid solution” compositions.  $\text{Ce}_f\text{Fe}_{4-x}\text{Ni}_x\text{Sb}_{12}$  compositions with  $x > 1.5$  have not yet been synthesized, but it is clear that at equivalent concentrations, Ni substitution results in less Ce filling than Co substitution. However, because Ni donates two electrons instead of only one for Co when replacing Fe, the decrease in carrier concentration and

corresponding change in properties with increasing  $x$  is much stronger for  $\text{Ce}_f\text{Fe}_{4-x}\text{Ni}_x\text{Sb}_{12}$ . A more detailed study of the transport properties of these samples will be given elsewhere.



**Figure 7:** Ce filling fraction ( $f$ ) for  $\text{Ce}_f\text{Fe}_{4-x}\text{M}_x\text{Sb}_{12}$  samples as a function of Fe substitution by M ( $x$ ) with M = Co, Ni and Ru. No decrease in Ce filling is observed for  $\text{Ce}_f\text{Fe}_{4-x}\text{Ru}_x\text{Sb}_{12}$  samples.



**Figure 8:** Room temperature lattice thermal conductivity as a function of the Ce filling fraction ( $f$ ) for  $\text{Ce}_f\text{Fe}_{4-x}\text{M}_x\text{Sb}_{12}$  compositions with M = Co, Ni or Ru. Results for lightly doped p-type and heavily doped n-type  $\text{CoSb}_3$  samples are also reported at  $f = 0$ .

The lattice thermal conductivity  $\lambda_L$  of  $\text{Ce}_f\text{Fe}_{4-x}\text{M}_x\text{Sb}_{12}$  samples, where M = Co, Ni or Ru, was calculated from the total thermal conductivity using the **Wiedman-Franz** law. Calculations show that the lattice thermal conductivity increases slowly with increasing Co or Ni content, but is **left**

unchanged for Ru substitution, even for  $x = 0.9$ . The room temperature values of  $\lambda_L$  is plotted as a function of the Ce filling fraction  $f$  in Figure 8. The weak dependence of  $\lambda_L(f)$  for samples of  $\text{Ce}_f\text{Fe}_{4-x}\text{Co}_x\text{Sb}_{12}$  suggests that void filling phonon scattering could be effective even at low values off. It also appears that because of the very high carrier concentrations, electron-phonon scattering accounts for most of the variations in  $\lambda_L$ . Indeed, atypical carrier concentration value of  $5 \times 10^{21} \text{ cm}^{-3}$  is obtained for  $\text{CeFe}_4\text{Sb}_{12}$  at 300K, while a carrier concentration of  $4 \times 10^{20} \text{ cm}^{-3}$  was measured for both  $\text{Ce}_{0.51}\text{Fe}_{2.1}\text{Co}_{1.9}\text{Sb}_{12}$  and  $\text{Ce}_{0.75}\text{Fe}_{3.1}\text{Ni}_{0.9}\text{Sb}_{12}$  compositions. The Co-based sample has 51% of its voids filled with Ce while the Ni-based sample has 75% of filled voids, but their lattice thermal conductivity is nearly identical, 16 to  $17 \times 10^{-3} \text{ W cm}^{-1} \text{ K}^{-1}$ , to be compared with a value of  $12 \times 10^{-3} \text{ W cm}^{-1} \text{ K}^{-1}$  for  $\text{CeFe}_4\text{Sb}_{12}$ .

Another interesting result is the fact that no decrease in lattice thermal conductivity was observed when Ru was substituted for Fe. It seems that the point defects generated by a Ru atom on the Fe site do not contribute any further to the overall scattering rate, possibly because void fillers (Ce) already scatter phonons in a wide frequency domain.

The combination of the low electrical resistivity, moderate Seebeck coefficient and low thermal conductivity resulted in high ZT values at temperatures above  $400^\circ\text{C}$ . A maximum ZT value of 1.4 has been achieved to date at a temperature of  $600^\circ\text{C}$  [21]. If current data is extrapolated to higher temperatures, it appears that even higher ZT would be obtained, provided that those materials were determined to remain stable. High ZT values at lower temperatures, as well as n-type conductivity samples might be obtained by controlling the composition and doping levels to increase the Seebeck coefficient and achieve a more semiconducting behavior. For example, this might be achieved by increasing the Co (or Ni) to Fe atomic ratio, or combining substitutions of both Fe and Sb, or filling the voids with a tetravalent atom.

## CONCLUSION

The properties of binary skutterudite compounds are very attractive for thermoelectric applications. However, their lattice thermal conductivity values are too high, in particular at low temperatures. Several approaches to significantly reduce the thermal conductivity of skutterudites have been identified: heavy doping, solid solution formation, valence fluctuations, and void filling. Ultimately, a combination of these approaches should be employed to reach a lattice thermal conductivity close to the theoretical minimum. Recent results have shown that high ZT values substantially larger than 1.0 can be achieved for some skutterudite solid solutions and filled compositions. Efforts are currently underway to pursue these various approaches, both experimentally and theoretically, and demonstrate that they can lead to a significant improvement in the thermal-to-electric conversion efficiency of thermoelectric devices.

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