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THERMOELECTRIC MATERIALS DEVELOPMENT

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TABLE OF CONTENTS

1. Introduction.....	3
2. Background on Skutterudite Materials.....	4
2.1. Binary skutterudite compounds.....	5
2.2. Solid Solutions.....	7
2.3. Ternary and Quaternary Skutterudite Related Phases.....	10
2.4. Filled Skutterudites	12
3. CoSb₃(IrSb₃)-RuSb₂Te Solid Solutions.....	12
4. CeFe_{4-x}Ru_xSb₁₂ Filled Compositions.....	14
5. Conclusions.....	16
6. References	18
7. Appendix A: Methods of physico-chemical analysis.....	20
8. Appendix B: Methods of measurements of transport properties	21
9. List of Tables and Illustrations.....	22

1. Introduction

There has been a lot of interest in thermoelectricity between 1957 and 1963 because of the expectations that a high thermoelectric energy conversion efficiency could be achieved and results transferred to large-scale applications. At that time, the best thermoelectric materials known were bismuth telluride (Bi_2Te_3) and lead telluride (PbTe) and a large number of companies and laboratories were involved in the search for better thermoelectric materials. Later on, $\text{Si}_{1-x}\text{Ge}_x$ alloys were added as a prime material for high-temperature space applications. By optimizing the doping level and the composition of state of the art materials, significant improvements were obtained and maximum ZT values close to 1 were reproducibly achieved.

Numerous new materials were synthesized and their properties investigated. However, the search for materials which combine high electrical conductivity, high Seebeck coefficient and low thermal conductivity did not result in any breakthrough. As a consequence, the search for new thermoelectric materials was significantly reduced in the early 70s and limited to a few laboratories. Supported by the experimental results achieved at that time, one could think of ZT of 1 as a limit common to all materials and that something in the theory could predict such a limitation. However, any attempt to determine such a boundary condition for the dimensionless figure of merit ZT has been unsuccessful so far [1]. More recently, experimental results on TAGS (tellurium-silver-germanium-antimony) alloys [2] and the solid solution $\text{Mg}_2\text{Si}_{0.6}\text{Ge}_{0.4}$ [3, 4] indicated that material with ZT greater than 1 can indeed be found.

The Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California has developed a plan for the improvement of thermoelectric material performance through the development of new semiconductor materials with high thermoelectric figures of merit, ZT. The multi-thrust effort, which began in 1981, has received multiple sponsorship from NASA, DOE, BMDO, DOD, and private industry. The primary objective of the effort is to identify through solid state physics modeling and initial synthesis and property measurement, strong potential candidate materials for improved thermoelectric performance. Support for the effort has been spread over several sponsors who have interest in either power generation or cooling applications.

A systematic search for advanced thermoelectric materials was initiated at JPL several years ago to evaluate candidate materials which includes consideration of the following property attributes:

- Semiconducting properties
- Large Seebeck coefficient
- High carrier mobility and high electrical conductivity
- Low lattice thermal conductivity

- Chemical stability and low vapor pressure

Through this candidate screening process, JPL identified several families of materials as promising candidates for improved thermoelectric materials including the skutterudite family. There are several programs supporting various phases of the effort on these materials.

Earlier results obtained on p- and n-type binary skutterudite compounds under the sponsorship of the Office of Naval Research showed that they possess very attractive electrical properties with power factor values comparable or even greater than those obtained for state-of-the-art thermoelectric materials. However, their thermal conductivity is too large (~ 100 mW/cmK at 300K) to achieve ZT values higher than those obtained for state-of-the-art thermoelectric materials. One of the approaches to lower the thermal conductivity is to form solid solutions to increase point defect scattering of phonons. As part of an ongoing effort to develop skutterudite materials with lower thermal conductivity values, several solid solutions and filled skutterudite materials were investigated under the effort sponsored by DOE. The efforts have primarily focused on: 1) study of existence and properties of solid solutions between the binary compounds CoSb_3 and IrSb_3 , and RuSb_2Te , and 2) $\text{CeFe}_{4-x}\text{Ru}_x\text{Sb}_{12}$ based filled compositions. For the solid solutions, the lattice thermal conductivity reduction was expected to be reduced by the introduction of the Te and Ru atoms while in the case of $\text{CeFe}_{4-x}\text{Ru}_x\text{Sb}_{12}$ filled compositions, the reduction would be caused by the rattling of Ce atoms located in the empty voids of the skutterudite structure and the substitution of Fe for Ru. The details of the sample preparation and characterization of their thermoelectric properties are reported in this report which consists of the following sections:

- Background literature information about skutterudites
- Results and thermoelectric properties of $\text{CoSb}_3(\text{IrSb}_3)$ - RuSb_2Te solid solutions and $\text{CeFe}_{4-x}\text{Ru}_x\text{Sb}_{12}$ based filled compositions
- Conclusions

2. Background on Skutterudite Materials

The skutterudite structure was originally attributed to a mineral from Skutterud (Norway) with a general formula $(\text{Fe}, \text{Co}, \text{Ni}) \text{As}_3$ [5]. The skutterudite structure (cubic space group $Im\bar{3}$, prototype CoAs_3) is illustrated in Figure 1. The unit cell contains square radicals $[\text{As}_4]^{4-}$. This anion located in the center of the smaller cube is surrounded by 8 Co^{3+} cations. The unit cell was found to consist of 8 smaller cubes (octants) described above but two of them do not have the anions $[\text{As}_4]^{4-}$ in the center. This is necessary to keep the ratio $\text{Co}^{3+} : [\text{As}_4]^{4-} = 4:3$. Thus, a typical coordination structure results with $\text{Co}_8[\text{As}_4]_6 = 2\text{Co}_4[\text{As}_4]_3$ composition and 32 atoms per cell.

A low lattice thermal conductivity and a high carrier mobility are desirable for improved thermoelectric properties in new semiconductor 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 [6] and high hole mobility values have been measured on several skutterudite compounds: IrSb₃ [7], RhSb₃ [8] and RhP₃ [9]. The unit cell is relatively large and contains 32 atoms which indicate that low lattice thermal conductivity might be possible. For state-of-the-art thermoelectric materials such as PbTe and Bi₂Te₃ alloys, 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 ten binary compounds and several solid solutions and related phases are known to exist. These materials cover a large range of decomposition temperatures and bandgaps that offers the possibility to adjust composition and doping level for a specific temperature range of application. However, little information was initially available about their thermoelectric properties, and the recent work is briefly reviewed in the following sections.

2.1. Binary skutterudite compounds

Binary skutterudite compounds are formed with all nine possible combinations of the elements Co, Rh, Ir with P, As, Sb. In this structure each metal atom has six bonds to a pnictogen and each of three pnictogens has two bonds to another pnictogen. Thus, each bond has two electrons which is consistent with the fact that they are diamagnetic semiconductors [10]. Some properties of these compounds are summarized in Table 1. The only other binary compounds known to have the same structure are NiP₃ and PdP₃ but they have one more electron valence per formula unit and consequently show metallic conduction [11].

The antimonides CoSb₃, RhSb₃, IrSb₃, and arsenides CoAs₃, RhAs₃ all exhibit semiconducting behavior, with band gap values ranging from 0.63 to 1.18 eV. The phosphide compounds as well as some new ternary skutterudites are expected to have even wider band gaps. Due to the exceptionally high hole mobility values, p-type skutterudites exhibit high electrical conductivity values, ranging from 2 to $5 \times 10^5 \Omega^{-1} \text{m}^{-1}$ for a hole concentration of $1 \times 10^{19} \text{cm}^{-3}$. The room temperature mobility values of p-type skutterudites are 1 to 100 times higher than those for p-type Si and GaAs at similar carrier concentrations. JPL has measured a Hall mobility value close to $8000 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ on a p-type RhSb₃ single crystal with a Hall carrier concentration of about $3.5 \times 10^{18} \text{cm}^{-3}$. This is the highest p-type mobility ever measured at this doping level, which is about 70 times higher than p-type GaAs and still 5 times higher than n-type GaAs. For comparison, p-type Bi₂Te₃ and p-type PbTe have mobility values of 150 and $220 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively, at a carrier concentration of about $3 \times 10^{19} \text{cm}^{-3}$. All skutterudites seem to have these high hole mobility values which make them very promising materials for thermoelectric applications.

Skutterudites with n-type conductivity have been obtained by doping with selected elements such as Ni, Pd, Pt and Te [12, 13]. The electron mobility values of n-type CoSb₃ are comparable to the values obtained for p-type Si and GaAs. Results obtained on CoSb₃, CoAs₃ and IrSb₃, indicate that the electron effective masses are much larger than the hole effective masses. It is interesting to note that these characteristics of skutterudites are the opposite of

those found for Si, Ge and most III-V compounds, where the electron effective mass is significantly smaller than the hole effective mass.

Table 1: Lattice parameter a , decomposition temperature T_m , band gap E_g , Hall mobility μ_H (at a carrier concentration $1 \times 10^{19} \text{ cm}^{-3}$) and thermal conductivity λ of p-type binary skutterudite compounds

Compound	a (Å)	T_m (°C)	E_g (eV)	$\mu_{H(300K)}$ ($\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$)	λ_{400K} (mW. $\text{cm}^{-1} \cdot \text{K}^{-1}$)
CoP ₃	7.7073	>1000	0.43*	-	-
CoAs ₃	8.2055	960	0.69*	~1300*	120*
CoSb ₃	9.0385	850	0.56*	1200*	89*
RhP ₃	7.9951	> 1200	-	~3000	-
RhAs ₃	8.4507	>1000	0.70*	2400*	130*
RhSb ₃	9.2322	900	0.80*	4300*	97*
IrP ₃	8.0151	> 1100	-	-	-
IrAs ₃	8.4673	> 1200	-	-	-
IrSb ₃	9.2533	1141*	1.18*	1100*	99*
NiP ₃	7.819	> 850	metallic	-	-
PdP ₃	7.705	> 650	metallic	-	-

* JPL findings

Measurement of the temperature dependence of the electrical resistivity, Seebeck coefficient and thermal conductivity of p-type and n-type binary and ternary skutterudite compounds were conducted at JPL. The experimental data show that p-type skutterudites generally exhibit moderate Seebeck coefficient and low electrical resistivity values. Much larger Seebeck coefficient can be achieved for n-type skutterudites (CoSb₃ and IrSb₃), and this is attributed to the much higher effective mass of the electrons. However, due to the lower carrier mobility, the electrical resistivity values are also substantially larger.

The thermal conductivity values of skutterudites were found to be quite reasonable considering the relatively high decomposition temperature and bandgap of this compound (see Table 1). Results indicate that the room temperature thermal conductivity values increase slightly from antimonides to arsenides, and also from Co-based compounds to Ir-based compounds. The thermal conductivity of binary skutterudites is 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 mW.cm⁻¹K⁻¹). Such reductions have been obtained in solid solutions of CoSb₃-IrSb₃ and in several ternary compounds.

2.2. Solid Solutions

Solid solutions should have lower lattice thermal conductivity values than the binary compounds themselves because of the increased point defect scattering. It is also expected that the carrier mobility in these mixed crystals would be lower although they should remain relatively high because of the small difference in electronegativity between the pnictogen elements, for example, 0.01 (As and P). The ratio between mobility and lattice thermal conductivity would be substantially increased in these mixed crystals, resulting in improved thermoelectric properties.

The existence of $\text{CoP}_3\text{-CoAs}_3$ and $\text{CoAs}_3\text{-CoSb}_3$ solid solutions has already been reported in the literature [14]. CoP_3 and CoAs_3 form a complete range of solid solutions which obey the Vegard's rule. For the system $\text{CoAs}_{3-x}\text{Sb}_x$ a miscibility gap in the composition region of $x = 0.4$ to 2.8 was found. Our experimental results have shown that many other skutterudite compounds form solid solutions, at least in some limited range of composition. Thermal conductivity measurements of such mixed crystals conducted at JPL have shown that the thermal conductivity can be very substantially reduced. The study of diluted $\text{CoSb}_3\text{-IrSb}_3$ and $\text{CoAs}_3\text{-CoSb}_3$ solid solution compositions (about 10 mole % alloyed) resulted in thermal conductivity values in the 25 to 45 $\text{mW}\cdot\text{cm}^{-1}\text{K}^{-1}$ range, even at room temperature.

The effect of alloy scattering on the lattice thermal conductivity of skutterudite compounds can be evaluated by using the theoretical work of Callaway et al. [15]. The thermal conductivity of an alloy, λ_{alloy} , can be calculated from the experimental value obtained for the pure compound, λ_{pure} , it is derived from:

$$\lambda_{\text{alloy}} = \frac{\tan^{-1}(u)}{u} \cdot \lambda_{\text{pure}} \quad (1)$$

$$\text{with } u = \sqrt{3G\Gamma\lambda_{\text{pure}}} \quad (2)$$

$$\text{and } G = \frac{\pi^2\theta_D\delta^3}{3hv_s^2} \quad (3)$$

where θ_D is the Debye temperature, δ^3 is the average volume per atom in the crystal, v_s is the average sound velocity, h is the Planck's constant, u is an alloy scattering scaling parameter and Γ is the alloy scattering parameter.

Based on the speed of sound measurements reported earlier, the calculated values for the G parameter for several skutterudites are reported in Table 2. To determine the lattice thermal conductivity of the skutterudite alloys, the alloy scattering parameter Γ must now be calculated. Quaternary skutterudite alloys are considered in the following paragraphs, with the formula $\text{A}_a\text{B}_b\text{C}_c\text{D}_d$. There are only two sublattices present in skutterudites: the sublattice of the transition metal element (such as Co) and the sublattice of the pnictogen element (such as Sb). The mass and volume fluctuations can occur on only one sublattice, such as $\text{Co}_{1-x}\text{Ir}_x\text{Sb}_3$, or

Table 2: Calculation of the G parameter for several skutterudite compounds

	δ (Å)	θ_D (K)	v_s (cm.s ⁻¹)	G (cm K W ⁻¹)	λ (10 ⁻³ W cm ⁻¹ K ⁻¹)
CoSb ₃	2.8470	306.8	2.935x10 ⁵	408.4	103
CoAs ₃	2.5846	425.4	3.695x10 ⁵	267.4	140
IrSb ₃	2.9146	302.7	2.964x10 ⁵	423.8	100
RuSb ₂ Te	2.9211	268.6	2.637x10 ⁵	478.6	32

Fe_xIr_{1-x-y}Ni_ySb₃ alloys or both sublattices, such as Co_{1-x}Ir_xSb_{3-y}As_y. The scattering parameter for each atom located on one of these sublattices can be written as:

For the mass fluctuation term:

$$\Gamma_A^M = \sum_i f_i^A \left(1 - \frac{M_i}{\bar{M}_A} \right)^2 \quad (4)$$

where the average mass of the atoms on the A site is $\bar{M}_A = \sum_i f_i^A M_i$, f_i^A representing the relative proportion of each atom on a particular site ($\sum_i f_i^A = 1$).

For the volume fluctuation term:

$$\Gamma_A^V = \sum_i f_i^A \epsilon_A \left(1 - \frac{r_i}{\bar{r}_A} \right)^2 \quad (5)$$

where the average radius of the atoms on the A site is $\bar{r}_A = \sum_i f_i^A r_i$

The parameters ϵ_A , ϵ_B , ϵ_C , and ϵ_D , are adjustable strain parameters, with values typically of the order of 10 to 100. For skutterudite alloys, only two different values of the strain parameters ϵ_i , are considered, one for the transition metal site, ϵ_{tm} , and one for the pnictogen site, ϵ_{pn} .

The total average mass for the alloy is:

$$M = \sum_i p_i \bar{M}_i \quad (6)$$

with the atomic proportion of the A atoms in the compound is $p_A = \frac{a}{a+b+c+d}$

The total alloy scattering parameter is determined by:

$$\Gamma = \sum_i p_i \left(\left[\frac{\bar{M}_i}{\bar{M}} \right] \Gamma_i^M + \Gamma_i^V \right) \quad (7)$$

Tables 3 and 4 list the atomic mass, radius and charge of the cations and anions used in the calculations.

Table 3: Atomic mass and radius for the transition metal site, using cation radii

Element	Fe	Ru	Os	Co	Rh	Ir	Ni	Pd	Pt
Ion charge	2+	2+	2+	3+	3+	3+	4+	4+	4+
Mass (g)	55.847	101.07	190.2	58.9332	102.9055	192.22	58.70	106.4	195.09
Radius (Å)	1.14	1.26	1.25	1.07	1.19	1.19	1.15	1.26	1.28

Table 4: Atomic mass and radius for the pnictogen site, using anion radii

Element	Si	Ge	Sn	P	As	Sb	S	Se	Te
Ion charge	2-	2-	2-	1-	1-	1-	0	0	0
Mass (g)	28.0855	72.59	118.69	30.97376	74.9216	121.75	32.06	78.96	127.60
Radius (Å)	1.18	1.22	1.41	1.14	1.26	1.45	1.10	1.23	1.43

Experimental thermal conductivity data was obtained on a number of skutterudite alloys. The lattice thermal conductivity values, reported in Table 5, were calculated using the Wiedemann-Franz law (based on electrical resistivity and Seebeck coefficient measurements). Some of the values were increased to account for sample porosity (in particular in the CoSb_3 - IrSb_3 system).

Table 5: Lattice thermal conductivity values for some skutterudite alloys at 300K

Skutterudite Alloys	$\lambda_{\text{lattice}} (10^{-3} \text{ W cm}^{-1} \text{ K}^{-1})$
$(\text{CoSb}_3)_{0.96}-(\text{IrSb}_3)_{0.04}$	45
$(\text{CoSb}_3)_{0.90}-(\text{IrSb}_3)_{0.10}$	32
$(\text{CoSb}_3)_{0.88}-(\text{IrSb}_3)_{0.12}$	29
$(\text{CoAs}_3)_{0.98}-(\text{CoSb}_3)_{0.02}$	57
$(\text{CoSb}_3)_{0.92}-(\text{IrAs}_3)_{0.08}$	22

The strain parameter value for the transition metal site is obtained by considering experimental data obtained on several CoSb_3 -rich CoSb_3 - IrSb_3 alloys. The best match between experimental and calculated values was achieved for a value of $\epsilon_{\text{m}} = 398$. The strain parameter value for the pnictogen site is obtained by considering experimental data on CoSb_3 - CoAs_3 and CoSb_3 - IrAs_3 samples. Because the CoSb_3 - CoAs_3 and CoSb_3 - IrSb_3 samples show mixed

conduction effects at room temperature, only an upper limit to the lattice thermal conductivity of these alloys could be determined.

The variations of the thermal conductivity of CoSb_3 - and IrSb_3 -based alloys could now be estimated. The results from our calculations are reported in Figure 2. The lowest thermal conductivity values are achieved for alloys maximizing mass and volume fluctuations, such as $\text{CoSb}_3\text{-IrP}_3$ with $8 \times 10^{-3} \text{ W cm}^{-1}\text{K}^{-1}$ for a 50 mole% alloy. These calculations do not take into account the effect of phonon scattering by charge carriers. This additional scattering is very much apparent in heavily doped n-type samples of CoSb_3 which have substantially lower thermal conductivity values than expected.

These calculations must be further tested against additional experimental data but they suggest that low thermal conductivity values can be obtained for skutterudite solid solutions. Considering the relatively low thermal conductivity of the ternary compound RuSb_2Te ($\sim 32 \text{ mW/cmK}$ at 300K (see Table 5), the study of solid solutions between this compound and the binary compounds CoSb_3 and IrSb_3 is of interest. By lowering the lattice thermal conductivity while preserving some of the good electrical properties of the binary compounds IrSb_3 and CoSb_3 , one can expect to achieve relatively high thermoelectric figures of merit. The results of the investigations of the existence and properties of $\text{CoSb}_3(\text{IrSb}_3)\text{-RuSb}_2\text{Te}$ solid solutions are reported in section 3.0 of this report.

2.3. Ternary and Quaternary Skutterudite Related Phases

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. The substitution can occur on the anion site ($\text{CoAs}_3 \rightarrow \text{CoGe}_{1.5}\text{Se}_{1.5}$) or on the cation site ($\text{CoSb}_3 \rightarrow \text{Fe}_{0.5}\text{Ni}_{0.5}\text{Sb}_3$). Structurally related skutterudite phases can also be formed by partial substitution of the cation and the anion ($\text{IrSb}_3 \rightarrow \text{PtSn}_{1.2}\text{Sb}_{1.8}$).

Nine ternary skutterudite related phases have been reported in literature [14,16-20] and are reported in Table 6. However, almost no information about thermal and electrical properties of such phases is available in the literature. This type of skutterudites offer a promising approach to high ZT values. It is expected that the lattice thermal conductivity of these phases would be substantially lower than for the binary compounds due to atomic mass and atomic volume fluctuations. Also the electronic and/or magnetic disorder due to the presence of various transition metal elements of mixed valence could also contribute to the reduction in lattice thermal conductivity. Regarding the electrical properties, it is expected that while the high p-type mobility characteristic of skutterudites be mostly conserved throughout the different cation/anion substitutions, changes in band structure are very likely. This could lead to very different band gap and Seebeck coefficient values, an altered doping behavior and temperature range of application.

Our first results on six such ternary phases (five of them are new compositions) confirmed these predictions. $\text{Fe}_{0.5}\text{Ni}_{0.5}\text{Sb}_3$ and FeSb_2Te are two new ternary phases derived from CoSb_3 , and the calculated band gap values, 0.16 and 0.27 eV respectively, are much smaller than the 0.56 eV value for CoSb_3 . Similar results are obtained for $\text{Ru}_{0.5}\text{Pd}_{0.5}\text{Sb}_3$ (0.6 eV), which is derived from RhSb_3 (0.8 eV). The lower band gap values are consistent with the lower decomposition temperatures.

Our experimental results indicated that the thermal conductivity is greatly reduced in these materials, with room temperature values ranging from 7 to 30 $\text{mW}\cdot\text{cm}^{-1}\cdot\text{K}^{-1}$. The low thermal conductivity values of these three 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 such as electron exchange scattering of phonons. Moreover, the possibility of forming solid solutions between these ternary compounds and the high mobility binary compounds offers an excellent opportunity of finding a very low thermal conductivity material with good electrical properties.

Table 6: Known skutterudite related phases

Compound	a (Å)	T _m (°C)	E _g (eV)	$\lambda_{400\text{K}}$ (mW/cmK)	Reference
$\text{CoGe}_{1.5}\text{S}_{1.5}$	8.017	1000	-	-	[17]
$\text{CoGe}_{1.5}\text{Se}_{1.5}$	8.299	800	-	-	[17]
$\text{RhGe}_{1.5}\text{S}_{1.5}$	8.2746	> 800	-	-	[18]
$\text{IrGe}_{1.5}\text{S}_{1.5}$	8.297	> 800	-	-	[18]
$\text{IrGe}_{1.5}\text{Se}_{1.5}$	8.5591	> 800	-	-	[18]
$\text{IrSn}_{1.5}\text{S}_{1.5}$	8.7059	> 800	-	-	[18]
$\text{Fe}_{0.5}\text{Ni}_{0.5}\text{Sb}_3$	9.0904	729 *	~0.16*	30*	[19]
$\text{Ru}_{0.5}\text{Pd}_{0.5}\text{Sb}_3$	9.296*	647 *	~0.60*	14*	[20]
$\text{Fe}_{0.5}\text{Ni}_{0.5}\text{As}_3$	8.256	-	-	-	[16]
FeSb_2Se	-	-	-	-	
FeSb_2Te	9.113*	556*	~0.27*	23*	
RuSb_2Se	9.257*	-	-	-	
RuSb_2Te	9.268*	810*	-	28*	
$\text{PtSn}_{1.2}\text{Sb}_{1.8}$	9.390	-	-	-	[21]

* JPL findings

2.4. Filled Skutterudites

A large number of these materials have already been synthesized (see for example [22-25]). The composition of these types of compounds can be represented by the formula $\text{LnT}_4\text{Pn}_{12}$ (Ln = rare earth, Th; T = Fe, Ru, Os; Pn = P, As, Sb). In these compounds, the empty octants of the skutterudite structure (see Figure 1) which are formed in the TPn_3 ($\sim \text{T}_4\text{Pn}_{12}$) framework are filled with a rare earth element. Because the T_4Pn_{12} groups using Fe, Ru or Os are electron-deficient relative (by 4 e^-) 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 semi-metals.

Studies conducted on $\text{CeFe}_4\text{Sb}_{12}$ -based compositions under the sponsorship of the Office of Naval Research showed that these materials indeed behave as semi metals but possess excellent thermoelectric properties in the 400 to 700°C temperature range. A maximum ZT value of 1.4 was obtained at 600°C for a composition $\text{Ce}_{0.9}\text{Fe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$. The major reason for these good properties is the dramatic decrease in lattice thermal conductivity due to the rattling of the Ce inside of the empty voids of the skutterudite crystal structure. The lattice thermal conductivity for $\text{CeFe}_4\text{Sb}_{12}$ -based compositions is about 10 times lower than for the binary compound CoSb_3 and IrSb_3 . It was therefore of interest to study similar filled compositions such as $\text{CeRu}_4\text{Sb}_{12}$ based compositions.

Two major benefits can be obtained from substituting Ru for Fe: 1) Ru is heavier than Fe and one can expect, in addition to the rattling of the rare-earth atoms, a stronger point defect scattering in Ru-containing compositions, which in turn would result in lower lattice thermal conductivity; 2) $\text{CeRu}_4\text{Sb}_{12}$ is most likely more refractory than $\text{CeFe}_4\text{Sb}_{12}$ and might be optimum at higher temperatures to accommodate DOE needs for high performance TE materials at relatively high temperatures. The investigation of such compositions for thermoelectric applications has therefore been started and the results of the synthesis and property measurements of the samples fabricated are included in this report.

3. $\text{CoSb}_3(\text{IrSb}_3)\text{-RuSb}_2\text{Te}$ Solid Solutions

Several room temperature properties for RuSb_2Te samples, $\text{IrSb}_3\text{-RuSb}_2\text{Te}$, and $\text{CoSb}_3\text{-RuSb}_2\text{Te}$ samples are listed in Tables 7, 8, and 9, respectively. Also listed in these tables are the synthesis conditions and results of x-ray and microprobe analysis. The x-ray patterns of the reacted powders are shown in Figures 3 through 23.

The calculated lattice constants are listed in Tables 7, 8, and 9. The results show that there is a full range of solid solutions between IrSb_3 and RuSb_2Te . The relatively small difference between the lattice constant of IrSb_3 (9.2533Å) and RuSb_2Te (9.268Å) is consistent with this finding. The lattice constant variation as a function of the IrSb_3 percentage in RuSb_2Te is shown in Figure 24.

The formation of a full range of solid solutions was confirmed by the results of microprobe analysis which showed single phase samples only. In contrast, both x-ray analysis and microprobe results systematically showed the presence of two phases for $(\text{CoSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ samples. One phase has a composition close to CoSb_3 whereas the other phase is close to a RuSb_2Te composition. The relatively large difference between the lattice constant of CoSb_3 (9.0309 Å) and RuSb_2Te (9.268 Å) is consistent with this finding. Microprobe samples showed that CoSb_3 -rich alloys predominantly correspond to a Te-doped CoSb_3 phase with isolated RuSb_2Te inclusions.

The room temperature properties of $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloys are summarized in Table 8. Although several attempts were made to obtain n-type samples by doping with various amount of Pt and/or Te, the samples always showed p-type conductivity. The reason for this is still unclear. N-type IrSb_3 can be obtained by doping with Pt. Results obtained on the ternary compound RuSb_2Te showed that only p-type samples could be obtained which might be due to a mixed valence state of the metal atoms in this compound (Ru^{2+} and Ru^{4+}). The ratio between the two ions would change in the doped samples, compensating for the additional carriers donated by the dopants. It is possible that a similar mechanism occurs in $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloys. The variations of the electrical resistivity, Hall mobility, Seebeck coefficient, power factor, and thermal conductivity are shown in Figures 25 through 29. The electrical resistivity values are relatively high with moderate Seebeck coefficient values, resulting in relatively low power factor values with a maximum of $10 \mu\text{W}/\text{cmK}^2$ at about 600K. The room temperature thermal conductivity values are much lower than those obtained for IrSb_3 and range between 30 and 35 mW/cmK depending on the composition. The thermal conductivity of sample OX6 is much lower but this sample had a very poor density (see Table 8). This sample had however relatively good electrical properties and has the highest ZT value obtained for p-type samples (Figure 30). The maximum ZT value is about 0.6 in the 400 to 700 K temperature range. Because of the difficulties in controlling the doping level for p-type samples, it appears that further improvement in ZT values are unlikely for $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloys.

The room temperature thermoelectric properties of $(\text{CoSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ samples are summarized in Table 9. All samples have n-type conductivity. As we mentioned before, these samples are mostly Te and/or Pd doped n-type CoSb_3 . The carrier concentration of the samples is ranging between 1 and $2.5 \times 10^{20} \text{ cm}^{-3}$ with carrier mobility values between 17 and 30 cm^2/Vs . At these doping levels, the Seebeck coefficient values are relatively large, as high as - 220 $\mu\text{V}/\text{K}$. The high temperature properties of the samples are shown in Figures 25 through 29. The electrical resistivity increases with increasing temperature up to about 700K where the onset of mixed conduction effects (holes and electrons) is observed. This effect is also seen in the variations of the Hall mobility as a function of the temperature (see Figure 26). The Seebeck coefficient variations are shown in Figure 27. The values are large and almost temperature independent. The calculated power factor values are shown in Figure 28. They are comparable to those obtained for state-of-the-art thermoelectric materials and maximum values of $40 \mu\text{W}/\text{cmK}^2$ were obtained in the 300 to 800 K temperature range for sample OX46. The results of the thermal conductivity

measurements are shown in Figure 29. The room temperature thermal conductivity values range between 30 and 48 mW/cmK. Considering that, based on the samples composition, there is little point defect scattering of the phonons, the significant decrease in the thermal conductivity at room temperature compared to CoSb_3 ($\sim 100 \text{ mW/cmK}$) is due to scattering of the phonons by electrons in these heavily doped samples. The variation in the composition and carrier composition of the samples explain the variations in the experimental thermal conductivity data. A maximum ZT value of 0.9 was obtained at 880K. The values are compared to values obtained for state-of-the-art thermoelectric materials (Figure 30). The values for heavily doped n-type CoSb_3 samples are comparable to those obtained for PbTe-based alloys in the 500 to 750K temperature range. There is however a sharp decrease in the ZT values above 750K for PbTe alloys due to the onset of mixed conduction. For heavily doped n-type CoSb_3 samples, the ZT values keeps increasing up to about 900K.

The increase in the ZT values compared to undoped CoSb_3 can be attributed to the reduction in lattice thermal conductivity due to electron-phonon scattering. These results suggest that even higher ZT values can be expected for heavily doped n-type alloys in which electron-phonon and point defect scattering could be combined. In addition, n-type alloys look more promising than p-type due to the larger effective mass of the electrons, resulting in much larger Seebeck coefficient values.

4. $\text{CeFe}_{4-x}\text{Ru}_x\text{Sb}_{12}$ Filled Compositions

Recent studies have focused on Fe-based filled skutterudites, investigating the electronic band structure of $\text{CeFe}_4\text{P}_{12}$ and $\text{CeFe}_4\text{Sb}_{12}$ [26] and the transport properties of $\text{LaFe}_{4-x}\text{Co}_x\text{Sb}_{12}$ and $\text{CeFe}_{4-x}\text{Co}_x\text{Sb}_{12}$ compositions [27-29]. These materials are particularly attractive because of the dramatic reductions in the lattice thermal conductivity due to the “rattling” of the filling atom in the two empty octants present in the skutterudite structure [30]. As briefly discussed in the Technical Background section, the valence electron count (VEC) in filled skutterudites such as $\text{CeFe}_4\text{Sb}_{12}$ is only 71, instead of 72 in semiconducting CoSb_3 , resulting in metallic behavior. This is because Ce brings only three electrons (Ce is trivalent near room temperature in filled skutterudites [29]) to compensate for the four electron deficit due to the presence of Fe (Fe^{2+} instead of Co^{3+}). The study of the $\text{CeFe}_{4-x}\text{Co}_x\text{Sb}_{12}$ compositions was thus driven by the expectation of returning to a semiconducting CoSb_3 -like behavior. However, this is not the case for $\text{CeFe}_{4-x}\text{Ru}_x\text{Sb}_{12}$ compositions studied here, since Ru is isoelectronic with Fe. The existence of $\text{CeRu}_4\text{Sb}_{12}$ was previously reported [31] and the formation of a complete set of solid solutions is expected to form between $\text{CeFe}_4\text{Sb}_{12}$ and $\text{CeRu}_4\text{Sb}_{12}$.

Five $\text{CeFe}_{4-x}\text{Ru}_x\text{Sb}_{12}$ compositions were prepared with $x = 0.5, 1.0, 1.45$ and 4.0 . All preparation conditions and characterization data near room temperature are reported in Table 10. The x-ray diffraction patterns obtained for the reacted powders of samples DX500 ($\text{CeRu}_4\text{Sb}_{12}$), DX501 ($\text{CeFe}_{3.5}\text{Ru}_{0.5}\text{Sb}_{12}$), DX502 ($\text{CeFe}_{3.0}\text{Ru}_{1.0}\text{Sb}_{12}$) and DX503 ($\text{CeFe}_{2.55}\text{Ru}_{1.45}\text{Sb}_{12}$) are shown

in Figures 31 to 34, respectively. Two samples of $\text{CeRu}_4\text{Sb}_{12}$ were prepared (DX500 and M2379) and both show the presence of the targeted phase, $\text{CeRu}_4\text{Sb}_{12}$, as seen in Figure 31. However, RuSb_2 and some CeSb_2 secondary phases were detected. The presence of these phases is due to the fact that, unlike in the Ce-Fe system where all the Fe can be reacted with Ce by forming a mixture of CeFe_2 and $\text{Ce}_2\text{Fe}_{17}$ compounds, the reaction of Ce with Ru in the 1:4 atomic ratio leads to the formation of CeRu_2 and free Ru [32]. Subsequent reaction with Sb powder of the free Ru means that the thermally stable RuSb_2 compound can form. Samples DX501 and DX502 were found to be single phase, while sample DX503 presented two major skutterudite phases, one close in composition to $\text{CeFe}_{3.0}\text{Ru}_{1.0}\text{Sb}_{12}$ and one much richer in Ru, close to $\text{CeFe}_{0.8}\text{Ru}_{3.2}\text{Sb}_{12}$. Based on electron microprobe results, the variations in Ce atomic filling and the variations in lattice parameter as a function of Fe substitution by Ru for the series of $\text{CeFe}_{4-x}\text{Ru}_x\text{Sb}_{12}$ samples have been plotted in Figure 35. It can be seen that the lattice parameter variations follow quite closely Vegard's law (simple interpolation between values for $\text{CeFe}_4\text{Sb}_{12}$ and $\text{CeRu}_4\text{Sb}_{12}$). And as expected from the fact that Fe and Ru are isoelectronic, all compositions remain fully filled.

The high temperature electrical and thermal transport properties of the $\text{CeFe}_{4-x}\text{Ru}_x\text{Sb}_{12}$ filled skutterudite samples have been measured from 25 up to 700°C. The temperature dependence of the electrical resistivity, Hall mobility, Seebeck coefficient, power factor, thermal conductivity, lattice thermal conductivity and ZT are reported in Figures 36 to 42, respectively. Data for pure $\text{CeFe}_4\text{Sb}_{12}$ (sample OX501) have also been reported on these figures for comparison purpose.

The results in Figures 36 and 37 show that the $\text{CeFe}_{4-x}\text{Ru}_x\text{Sb}_{12}$ compositions have a similar semimetallic behavior to that of pure $\text{CeFe}_4\text{Sb}_{12}$: very high carrier concentration of about $3 \times 10^{21} \text{ cm}^{-3}$, low carrier mobilities of $5\text{-}10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, with a low electrical resistivity of $0.5 \times 10^{-3} \Omega\text{cm}$, which increases slightly with temperature. However, the samples containing Ru display a departure from metallic behavior at the lowest temperatures (80-150K temperature range). This increase in resistivity with decreasing temperatures shows that the opening of a band gap occurs and that the resistivity follows an activated energy temperature dependence. No such behavior is observed for pure $\text{CeFe}_4\text{Sb}_{12}$, suggesting that $\text{CeRu}_4\text{Sb}_{12}$ is a more semiconducting filled skutterudite. It undoubtedly would be interesting to perform first principle electronic band structure calculations on this material [33].

As observed before for pure $\text{CeFe}_4\text{Sb}_{12}$, the magnitude of the Seebeck coefficient values in Figure 38 is quite large considering the very high carrier concentration levels, $75 \mu\text{VK}^{-1}$ at 25°C and increasing steadily with temperature. For p-type semiconducting CoSb_3 samples with similar doping levels one would expect Seebeck values to be close to $10 \mu\text{VK}^{-1}$. This is attributed to the fact that these materials behave similarly to heavy fermions systems: the hybridization between Ce and the transition metal (Fe or Ru here) creates a small bandgap and carriers possess large effective masses resulting in a low mobility but unusually high Seebeck coefficient [26,34]. Low temperature measurements conducted on sample DX502 ($\text{CeFe}_{3.0}\text{Ru}_{1.0}\text{Sb}_{12}$) show an anomalous increase in Seebeck values in the 20 to 60K temperature range. In spite of the metallic

behavior of the samples, the combination of relative high Seebeck values and low electrical resistivities resulted in large power factor values at elevated temperatures, as seen in Figure 39.

Figures 40 and 41 plot the thermal conductivity and the lattice thermal conductivity of the filled skutterudite samples as a function of temperature and inverse temperature respectively. It can be seen in Figure 40 that values obtained for $\text{CeFe}_{4-x}\text{Ru}_x\text{Sb}_{12}$ compositions are much lower than those obtained for CoSb_3 . The $\text{CeFe}_{3.5}\text{Ru}_{0.5}\text{Sb}_{12}$ 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 $35 \times 10^{-3} \text{ Wcm}^{-1}\text{K}^{-1}$ at 700°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 $10 \times 10^{-3} \text{ Wcm}^{-1}\text{K}^{-1}$. This confirms that the combination of the "rattling" atom and very high carrier concentration ($3 \times 10^{21} \text{ cm}^{-3}$) very effectively scatter the phonons, and results in an extremely low lattice thermal conductivity. Similar low thermal conductivity values have also been obtained on IrSb_3 -based filled skutterudite compositions [35,36]. Another interesting result from Figures 40 and 41 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 already scatter phonons in a wide frequency domain. Other filled skutterudite composition must be prepared and characterized to test this interpretation.

The combination of the low electrical resistivity, moderate Seebeck coefficient and low thermal conductivity resulted in high ZT values at temperatures above 400°C for the $\text{CeFe}_{4-x}\text{Ru}_x\text{Sb}_{12}$ compositions (Figure 42), with values close to 1.0 at 600°C . A maximum ZT value of 1.4 has been achieved to date at a temperature of 600°C [26]. High ZT values have also been reported on similar compositions filled with La instead of Ce [27]. However, because of the semimetallic behavior of the $\text{CeFe}_{4-x}\text{Ru}_x\text{Sb}_{12}$ compositions it is difficult to control carrier concentration, obtain n-type conductivity samples and optimize the thermoelectric properties at various temperatures. To do so requires the preparation of semiconducting filled skutterudites with good carrier mobility values.

5. Conclusions

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. ZT values significantly greater than those obtained for state-of-the-art thermoelectric alloys can be achieved if the lattice thermal conductivity can be reduced close to its theoretical minimum value, λ_{min} . The detailed studies of lattice thermal conductivity reduction in a variety of skutterudite phases show that values close to λ_{min} appear to be possible. In particular, JPL work under ONR and DOE sponsorship have shown that significant reduction in lattice thermal conductivity can be obtained when phonons are scattered by charge carriers, electrons transferred between mixed valence atoms, void fillers and point defects.

As part of an ongoing effort to develop skutterudite materials with lower thermal conductivity values, the existence and thermoelectric properties of solid solutions between the binary compounds CoSb_3 and IrSb_3 and the ternary compound RuSb_2Te were investigated. It was found that there is a full range of solid solutions between IrSb_3 and RuSb_2Te but almost no miscibility between CoSb_3 and RuSb_2Te . A strong electron-phonon scattering was revealed by thermal conductivity measurements on heavily doped n-type CoSb_3 , reducing the thermal conductivity by about 60% at room temperature compared to lightly doped CoSb_3 . As a result of this thermal conductivity reduction ZT values of 0.9 were obtained at 900K for n-type heavily doped CoSb_3 samples. The ZT values obtained for p-type $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloys are lower with a maximum of 0.6. It was found that it is difficult to control the doping level of these p-type alloys and n-type $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ samples could not be prepared. This might be due to valence fluctuations of the Ru atoms which would compensate for the additional carriers given by the dopants. N-type alloys appear to be more promising and, provided that samples in which phonons are scattered by both point defects and charge carriers, ZT values much higher than those obtained for state-of-the-art thermoelectric materials could be obtained.

A series of filled $\text{CeFe}_{4-x}\text{Ru}_x\text{Sb}_{12}$ skutterudite compositions have been successfully synthesized and as expected, Ru-containing compositions are more refractory than the pure $\text{CeFe}_4\text{Sb}_{12}$ filled compound. Transport property measurements conducted in the 4-1000K range determined that while $\text{CeFe}_{4-x}\text{Ru}_x\text{Sb}_{12}$ samples show some onset of semiconducting behavior at low temperatures, high temperature properties are nearly identical to those of pure $\text{CeFe}_4\text{Sb}_{12}$. This is in particular surprising considering the lattice thermal conductivity since one expected the substitution of Fe by Ru to result in further reduction of this property. It appears that the Fe/Ru site point defect does not add up to the already existing void filling, valence fluctuations and electron-phonon scattering mechanisms for the $\text{CeFe}_{4-x}\text{Ru}_x\text{Sb}_{12}$ skutterudite compositions. However, more recent results have shown that for some combinations of elements, such as in $\text{Ce}_t\text{Co}_4\text{Sb}_{12-x}\text{Ge}_x$, point defect scattering can be detected and result in much lower thermal conductivity values. All these mechanisms have not yet been combined in one skutterudite phase but calculations suggest that lattice thermal conductivity close to the "minimum" lattice thermal conductivity λ_{min} are achievable near room temperature. This minimum lattice thermal conductivity, which corresponds to "maximum" phonon scattering rates, has been calculated at $2.5 \text{ mW.cm}^{-1}\text{K}^{-1}$ for skutterudite antimonides, about 4 to 5 times lower than that of pure $\text{CeFe}_4\text{Sb}_{12}$ but 45 times lower than that of lightly doped p-type CoSb_3 . Based on such results, filled skutterudite compositions such as p-type $\text{CeFe}_{4-x}\text{Ru}_x\text{Sb}_{12-y}\text{Ge}_y$ seem to be very attractive for high temperature applications and should be investigated. For n-type thermoelements, heavily doped lightly filled CoSb_3 -based alloys are most promising.

6. References

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7. Appendix A: Methods of physico-chemical analysis

Samples were investigated using an optical microscope with and without light polarization or Nomarski contrast to observe their quality and homogeneity. Microprobe analyses (MPA) were performed on selected samples to determine their atomic composition using a JEOL JXA-733 electron superprobe operating at 20 kV of accelerating potential and 25×10^{-9} A of probe current. Pure elements were used as standards and x-ray intensity measurements of peak and background were conducted by wavelength dispersive spectrometry. Mass densities were calculated from the experimental weight and dimensions of the samples. A Siemens D-500 diffractometer produced diffractometry patterns at room temperature. Small additions of Pt or Si powders were made to some samples as an internal standard.

8. Appendix B: Methods of measurements of transport properties

The longitudinal and shear wave velocities of sound were measured on some samples to determine the speed of sound using normal incidence transducers. The measurement technique used a frequency of 5 Mhz. Multiple reflections were used to increase the signal accuracy. The Debye temperature of the samples was calculated from these experimental results.

The electrical and thermal transport properties of the samples investigated in this program were measured in different apparatuses. The electrical resistivity and the Hall coefficient were measured in the 25-600°C temperature range by the Van der Pauw method [37] using tungsten probes located on the top surface of the sample as close as possible to the sample's edge (typically a 1 mm thick, 6.35 mm diameter slice). The low temperature electrical resistivity and Van der Pauw measurements (80 to 380K) were conducted using thin gold wires soldered to the edges of the top surface of the samples. The 25-600°C Seebeck coefficient measurement was conducted by creating a variable temperature difference across the sample and measuring the corresponding linear variation of its thermoelectric voltage [38]. Large samples are usually measured by this technique but samples as thin as 1 mm can also be accommodated. A static ΔT technique was used for the low temperature Seebeck measurement (4 to 300K). The 25-600°C thermal diffusivity and the heat capacity of selected samples was measured by our flash diffusivity technique [39]. The heat capacity determination is a delicate measurement, but provided a careful calibration of the system (heat input from the flash lamp) is conducted on a graphite sample, we have found that reasonably good data can be obtained.

9. List of Tables and Illustrations

TABLES

1. Lattice parameter a , decomposition temperature T_m , band gap E_g , Hall mobility m_H (at a carrier concentration $1 \times 10^{19} \text{ cm}^{-3}$) and thermal conductivity κ of p-type binary skutterudite compounds
2. Calculation of the G parameter for several skutterudite compounds
3. Atomic mass and radius for the transition metal site, using cation radii
4. Atomic mass and radius for the pnictogen site, using anion radii
5. Lattice thermal conductivity values for some skutterudite alloys at 300K
6. Known skutterudite related phases
7. Room temperature properties of RuSb_2Te samples
8. Room temperature properties of $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloys
9. Room temperature properties of $(\text{CoSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloys
10. Room temperature properties of $\text{CeRu}_4\text{Sb}_{12}$ - based alloys

FIGURES

1. Illustration of the skutterudite crystal structure
2. Calculated lattice thermal conductivity for CoSb_3 -based solid solutions
3. X-ray diffraction pattern for $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloy OX5
4. X-ray diffraction pattern for $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloy OX5-2
5. X-ray diffraction pattern for $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloy OX5-3
6. X-ray diffraction pattern for $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloy OX6
7. X-ray diffraction pattern for $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloy OX6-2
8. X-ray diffraction pattern for $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloy OX6-3
9. X-ray diffraction pattern for $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloy OX13
10. X-ray diffraction pattern for $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloy OX16
11. X-ray diffraction pattern for $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloy OX17
12. X-ray diffraction pattern for $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloy OX23

13. X-ray diffraction pattern for $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloy OX24
14. X-ray diffraction pattern for $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloy OX41
15. X-ray diffraction pattern for $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloy DX1
16. X-ray diffraction pattern for $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloy DX2
17. X-ray diffraction pattern for $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloy DX4
18. X-ray diffraction pattern for $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloy DX6
19. X-ray diffraction pattern for $(\text{CoSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloy OX25
20. X-ray diffraction pattern for $(\text{CoSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloy OX26
21. X-ray diffraction pattern for $(\text{CoSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloy OX46
22. X-ray diffraction pattern for $(\text{CoSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloy DX3
23. X-ray diffraction pattern for $(\text{CoSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloy DX5
24. Lattice constant as a function of x for $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloys
25. Electrical resistivity as a function of temperature for $(\text{CoSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ and $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloys
26. Hall mobility as a function of temperature for $(\text{CoSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ and $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloys
27. Seebeck coefficient as a function of temperature for $(\text{CoSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ and $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloys
28. Power factor as a function of temperature for $(\text{CoSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ and $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloys
29. Thermal conductivity as a function of temperature for $(\text{CoSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ and $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloys
30. ZT values as a function of temperature for selected $(\text{CoSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ and $(\text{IrSb}_3)_{1-x}(\text{RuSb}_2\text{Te})_{1-x}$ alloys
31. X-ray diffraction pattern for sample DX500
32. X-ray diffraction pattern for sample DX501
33. X-ray diffraction pattern for sample DX502
34. X-ray diffraction pattern for sample DX503
35. Fraction of Ce filling empty octants as a function Fe substituted in $\text{Ce}_f\text{Fe}_{4-x}\text{Ru}_x\text{Sb}_{12}$ samples
36. Electrical resistivity as a function of temperature for $\text{Ce}_f\text{Fe}_{4-x}\text{Ru}_x\text{Sb}_{12}$ samples

- 37. Hall mobility as a function of temperature for $\text{Ce}_f\text{Fe}_{4-x}\text{Ru}_x\text{Sb}_{12}$ samples
- 38. Seebeck coefficient as a function of temperature for $\text{Ce}_f\text{Fe}_{4-x}\text{Ru}_x\text{Sb}_{12}$ samples
- 39. Power factor as a function of temperature for $\text{Ce}_f\text{Fe}_{4-x}\text{Ru}_x\text{Sb}_{12}$ samples
- 40. Thermal conductivity as a function of temperature for $\text{Ce}_f\text{Fe}_{4-x}\text{Ru}_x\text{Sb}_{12}$ samples
- 41. Lattice thermal conductivity as a function of temperature for $\text{Ce}_f\text{Fe}_{4-x}\text{Ru}_x\text{Sb}_{12}$ samples
- 42. ZT values as a function of temperature for $\text{Ce}_f\text{Fe}_{4-x}\text{Ru}_x\text{Sb}_{12}$ samples

Ox series RuSb ₂ Te - based compositions	Sample Label	Melting Point (C)	lattice A	ApB g	d _{geo} g.cm ⁻³	d _{me} g.cm ⁻³	d _{calc} g.cm ⁻³	N _A at.cm ⁻³	C _p (D) J/g.K	E _g eV	CC ₃₀₀ cm ⁻³	μ ₃₀₀ cm ² /Vs	P ₃₀₀ mΩ.cm	S ₃₀₀ μV/K	λ ₃₀₀ mW/cmK	preparation method	comments
CoSb ₂		850	9.0385	108.05			7.621	4.33E+22	0.235	0.550	3.71E+18	1746.0	0.96	130.0	104		
RhSb ₂		900	9.2322	117.04			7.893	4.07E+22	0.213	0.800	2.36E+18	7724.6	0.34	60.0	107		
IrSb ₂		1128	9.2533	139.37			9.335	4.04E+22	0.179	1.180	1.82E+19	1477.0	0.29	70.0	110		
Ru ₂ Sb ₃ Te ₃	OX 27 1-OX27 3-OX27	810	9.26811	118.04	7.796	7.796	7.869	4.02E+22	0.211	1.195				134.1	22.7	mixed+CP+annealed 600C/120h+X-ray+DTA+HP700C/2h +MPA homogeneous RuSb ₂ Te: Ru _{20.5} Sb _{31.5} Te _{28.5}	very clean skutterudite X-ray
Ru ₂ Sb ₃ Te ₃ Sb-rich, Te-poor RuSb ₂ Te	OX 51 1-OX51 2-OX51		9.28291	117.68	7.977	8.151	7.807	4.00E+22	0.212				1.82	16.7	28.1	mixed+CP+annealed 600C/120h+X-ray+HP700C/2h/950lbs+MPA slightly Sb-rich Te-poor single phase Ru _{22.2} Sb _{34.1} Te _{34.2} lost a lot of the excess antimony during hot-pressing (scales)	clean kutterudite Xray with traces of RuSb ₂

TABLE : 7

OX series RuSb ₂ Te - IrSb ₂ compositions	Sample Label	Melting Point (C)	lattice A	ApB g	d _{geo} g.cm ⁻³	d _{me} g.cm ⁻³	d _{teo} g.cm ⁻³	N _{at} at.cm ⁻³	C _p (D) J/g.K	E _g eV	ρ ₃₀₀ cm ⁻³	μ ₃₀₀ cm ² /Vs	P ₃₀₀ mΩ.cm	S ₃₀₀ μV/K	λ ₃₀₀ mW/cm.K	preparation method	comments	
CoSb ₃		850	9.0385	106.05		7.621	4.33E+22	0.235	0.550		3.71E+18	1746.0	0.96	130.0	104			
RhSb ₃		900	9.2322	117.04		7.893	4.07E+22	0.213	0.800		2.36E+18	7724.6	0.34	60.0	107			
IrSb ₃		1128	9.2533	139.37		9.335	4.04E+22	0.179	1.180		1.82E+19	1477.0	0.29	70.0	110			
Ru ₄ Ir ₇ Sb ₂₂ Te ₂ (IrSb ₃) _{10.75} (RuSb ₂ Te) _{10.25}	OX5 1-OX5 2-OX5	?	9.2644	134.08	7.516	8.333	8.948	4.02E+22	0.186		2.79E+19 2.08E+19	108.8 125.1	2.06 2.40	66.4 67.3		26.1	mixed+CP+annealed 600C/120h+X-ray+HP 900C/900lbs/2h+MPA clean skutterudite X-ray	bit of Ru(Sb ₂ Te) ₂ phase mostly skutterudite phase (but only 12 mol% RuSb ₂ Te)
Ru ₄ Ir ₇ Sb ₂₂ Te ₂ (IrSb ₃) _{10.75} (RuSb ₂ Te) _{10.25}	OX5 #2	?	9.2607	134.08	7.003	8.611	8.959	4.03E+22	0.186					48.7			mixed+CP+annealed 600C/130h+X-ray+HP 950C/1000lbs/2h messed up during hot-pressing	clean skutterudite Xray HP temperature too high
Ru ₄ Ir ₇ Sb ₂₂ Te _{2.02} (IrSb ₃) _{10.75} (RuSb ₂ Te) _{10.25}	OX5 #3 1-OX53	?	9.26718	134.09	9.018	8.940	8.941	4.02E+22	0.186		2.47E+19	73.0	3.46	2.5	measure?		mixed+CP+annealed 600C/120h+Xray+HP 750C/1000lbs/2h+MPA (IrSb ₃) _{10.25} (RuSb ₂ Te) _{10.75} + 10% arsenopyrite second phase	clean skutterudite Xray HP temperature too high?
Ru ₄ Ir ₇ Sb ₂₀ Te ₄ (IrSb ₃) _{10.5} (RuSb ₂ Te) _{10.5}	OX6 1-OX6 2-OX6		9.26625	128.78	8.206	8.266	8.590	4.02E+22	0.194		1.36E+19 3.22E+19	50.4 42.3	9.11 4.58	50.2 27.5		4.6	mixed+CP+annealed 600C/120h+X-ray+HP 800C/900lbs/2h+MPA very porous	some Ru(Sb ₂ Te) ₂ phase some skutterudite phase (but only 14 mol% RuSb ₂ Te)
Ru ₄ Ir ₇ Sb ₂₀ Te ₄ (IrSb ₃) _{10.5} (RuSb ₂ Te) _{10.5}	OX6 #2		9.26718	128.78			8.587	4.02E+22	0.194								mixed+CP+annealed 600C/130h+X-ray+HP 950C/1000lbs/2h messed up during hot-pressing	clean skutterudite Xray HP temperature too high
Ru ₄ Ir ₇ Sb ₂₀ Te _{4.33} (IrSb ₃) _{10.5} (RuSb ₂ Te) _{10.5}	OX6 #3 1-OX63		9.26718	128.81	8.645	8.778	8.589	4.02E+22	0.194		1.56E+19	108.3	3.71	62.3			mixed+CP+annealed 600C/120h+Xray+HP 700C/1000lbs/2h (IrSb ₃) _{10.25} (RuSb ₂ Te) _{10.75} + 40% arsenopyrite second phase	clean skutterudite Xray HP temperature too high?
Ru ₄ Ir ₅ Sb ₁₈ Te ₆ (IrSb ₃) _{10.25} (RuSb ₂ Te) _{10.75}	OX 13		9.26811	123.37	7.190	7.440	8.224	4.02E+22	0.202								mixed+CP+annealed 600C/120h+X-ray+HP 950C/1000lbs/2h+MPA melted at HP, MPA shows only arsenopyrites	very clean Xray HP temperature too high
Ru ₄ Ir ₅ Sb ₁₈ Te _{2.15} Te-rich (IrSb ₃) _{10.25} (RuSb ₂ Te) _{10.25}	OX 16	846	9.2700	134.16	8.863	8.885	8.938	4.02E+22	0.186		2.24E+19	68.9	4.05	65.5			mixed+CP+ann. 600C/144h+Xray+DTA+HP750C/1000lbs/2h+MPA (IrSb ₃) _{10.25} (RuSb ₂ Te) _{10.75} + 25% arsenopyrite second phase	very clean skutterudite X-ray why HP of 750!!!!
Ru ₄ Ir ₅ Sb ₁₈ Te _{4.15} Te-rich (IrSb ₃) _{10.5} (RuSb ₂ Te) _{10.5}	OX 17	811	9.26625	128.83	8.530	8.516	8.593	4.02E+22	0.194		1.47E+19	79.4	5.36	86.5			mixed+CP+ann. 600C/144h+Xray+DTA+HP700C/1000lbs/2h+MPA RuSb ₂₂ Te _{0.9} + (IrSb ₃) _{10.25} (RuSb ₂ Te) _{10.75} + (IrSb ₃) _{10.25} (RuSb ₂ Te) _{10.75}	very clean skutterudite X-ray HP temperature too high?
Ru ₄ Ir ₅ Sb ₁₈ Te _{10.22} Te-rich (IrSb ₃) _{10.125} (RuSb ₂ Te) _{10.125}	OX 23 1-OX23 2-OX23		9.26255	136.72	8.934	9.091	9.130	4.03E+22	0.182		3.24E+19	102.6	1.88		34		mixed+CP+annealed 600C/120h+Xray+HP750C/1000lbs/2h+MPA matrix (IrSb ₃) _{10.25} (RuSb ₂ Te) _{10.75} small inclusion (IrSb ₃) _{10.25} (RuSb ₂ Te) _{10.75}	very clean skutterudite X-ray slice (1.096 mm) cylinder (3.527 mm)
Ru ₄ Ir ₅ Sb ₁₇ Te _{7.22} Te-rich (IrSb ₃) _{10.125} (RuSb ₂ Te) _{10.875}	OX 24 1-OX24 2-OX24		9.27736	120.72	7.993	8.041	8.023	4.01E+22	0.207		1.40E+19 1.56E+19	87.9 61.7	6.58 6.49				mixed+CP+annealed 600C/120h+Xray 1/4 of phase (IrSb ₃) _{10.25} (RuSb ₂ Te) _{10.75}	very clean skutterudite X-ray +RuSb ₂ Te
Ru ₄ Ir ₅ Sb ₁₇ Te _{7.22} Te-rich (IrSb ₃) _{10.125} (RuSb ₂ Te) _{10.875}	OX 41		9.26718	120.72	7.991	7.953	8.050	4.02E+22	0.207		1.12E+19	104.9	5.33	118.7			mixed+CP+annealed 600C/120h+X-ray+HP700C/2h/950lbs+MPA RuSb ₂₂ Te _{0.9} + (IrSb ₃) _{10.25} (RuSb ₂ Te) _{10.75}	very clean skutterudite X-ray HP temperature too high?
Ru ₄ Ir ₇ Sb ₂₂ Te ₉ Pt _{0.44} 0.12at% Pt-doped, (IrSb ₃) _{10.875} (RuSb ₂ Te) _{10.125}	DX1 1-DX1 3-DX1		9.25978	136.77	9.011		9.142	4.03E+22	0.182		1.60E+19 2.33E+19	204.5 175.2	1.91 1.53	68.3	44.3		mixed+CP+annealed 600C/120h+X-ray+HP700C/2h/950lbs MPA shows 3 phases: 80%Ru ₄ Ir ₇ Sb ₂₂ Te ₉ Pt _{0.44} Te _{0.8} + 15% Ru ₄ Ir ₁₈ Pt _{0.5} Sb ₇₀ Te _{9.2} + 5% arsenopyrite	very clean skutterudite X-ray
Ru ₄ Ir ₇ Sb ₂₂ Te ₉ Pt _{0.16} 0.5at% Pt-doped, (IrSb ₃) _{10.125} (RuSb ₂ Te) _{10.875}	DX2		9.2700	117.15	7.895		7.804	4.02E+22	0.213				8.35	129.1	29.5		mixed+CP+annealed 600C/120h+X-ray+HP600C/2h/950lbs+ MPA MPA inconsistent with composition!!	very clean skutterudite X-ray maybe traces of RuSbTe
Ru ₄ Ir ₇ Sb ₂₂ Te ₉ Pt _{0.8} Pt-doped Te-rich (IrSb ₃) _{10.875} (RuSb ₂ Te) _{10.25}	DX4 1-DX4 3-DX4		9.2598	135.57	8.845		9.062	4.03E+22	0.184		5.05E+18 4.72E+18	109.2 107.7	11.35 12.29	135.0	33.4		mixed+CP+600C/120h+Xray+HP 600C/950lbs/2h+MPA MPA shows 3 phases: 80%Ru ₄ Ir ₇ Sb ₂₂ Te ₉ Pt _{0.8} Te _{0.2} + 15% Ru ₂₂ Ir ₇ Pt _{0.5} Sb ₇₀ Te _{9.2} + 5% PtSb ₂	very clean skutterudite X-ray
Ru ₄ Ir ₇ Sb ₂₂ Te ₉ Pt _{0.8} Pt-doped Te-rich (IrSb ₃) _{10.875} (RuSb ₂ Te) _{10.125}	DX6 1-DX6 3-DX6		9.2616	137.81	9.148		9.205	4.03E+22	0.181				39.60	224.1			mixed+CP+600C/120h+Xray+HP 600C/950lbs/4h+MPA MPA shows 3 phases: 90%Ir ₂₂ Pt _{0.5} Sb ₇₀ Te _{9.2} + 5% Ru ₂₂ Ir ₇ Pt _{0.5} Sb ₇₀ Te _{9.2} + 5% PtSb ₂	very clean skutterudite X-ray traces of RuTe ₂ ?

TABLE : 8

OX series RuSb ₂ Te - CoSb ₂ compositions	Sample Label	Melting Point (C)	lattice A	ApB g	d _{geo} g.cm ⁻³	d _{me} g.cm ⁻³	d _{calc} g.cm ⁻³	N _A at.cm ⁻³	C _V (D) J/g.K	E _g eV	ρ ₃₀₀ cm ⁻¹	μ ₃₀₀ cm ² /Vs	ρ ₃₀₀ mΩ.cm	S ₃₀₀ μV/K	λ ₃₀₀ mW/cmK	preparation method	comments
CoSb ₂		850	9.0385	108.05			7.621	4.33E+22	0.235	0.550	3.71E+18	1746.0	0.96	130.0	104		
RhSb ₂		900	9.2322	117.04			7.893	4.07E+22	0.213	0.800	2.38E+18	7724.6	0.34	60.0	107		
IrSb ₂		1128	9.2533	139.37			9.335	4.04E+22	0.179	1.180	1.82E+19	1477.0	0.29	70.0	110		
Ru _{0.99} Co _{0.01} Sb _{2.01} Te _{0.99} Te-rich (CoSb ₂) _{0.995} (RuSb ₂ Te) _{0.995}	OX 25 1-OX25 3-OX25		9.05085 9.28533	107.56	7.290		7.699	4.32E+22	0.232				2.02 1.97E+20 2.38E+20	-175.3 -11.9 -8.2	26.6 2.65 3.21	mixed+CP+600C/120h+Xray+CP+600C/120h+Xray+HP 650C/950bs/2h+MPA (CoSb ₂) _{0.995} (RuSb ₂ Te) _{0.995} and (CoSb ₂) _{0.995} (RuSb ₂ Te) _{0.995} MPA: 90% Ru _{0.99} Co _{0.01} Sb _{2.01} Te _{0.99} + 10% related arsenopyrite	two phase skutterudite X-ray
Ru _{0.99} Co _{0.01} Sb _{1.99} Te _{0.99} Te-rich (CoSb ₂) _{0.995} (RuSb ₂ Te) _{0.995} Te-rich (CoSb ₂) _{0.995} (RuSb ₂ Te) _{0.995}	OX 26 1-OX26 3-OX26		9.04973 9.28718	116.56	7.760		8.346	4.32E+22	0.214				6.20 1.32E+19 1.31E+19	80.8 65.6 67.2	37.6 7.20 7.11	mixed+CP+600C/120h+Xray+CP+600C/120h+Xray+HP 600C/950bs/2h+MPA (CoSb ₂) _{0.995} (RuSb ₂ Te) _{0.995} and (CoSb ₂) _{0.995} (RuSb ₂ Te) _{0.995} MPA: 80% Ru _{0.99} Co _{0.01} Sb _{1.99} Te _{0.99} + 10% of 2.2%Te-doped CoSb ₂	two phase skutterudite X-ray
Ru _{0.99} Co _{0.01} Sb _{2.01} Te _{0.99} (CoSb ₂) _{0.995} (RuSb ₂ Te) _{0.995}	OX 46 1-OX46 3-OX46		9.0451	106.85	7.512	7.534	7.648	4.32E+22	0.234				0.91 1.50E+20 1.55E+20	-189.7 -32.6 -33.5	45 1.28 1.20	mixed+CP+annealed 600C/120h+Xray+HP550C/2h/950bs+MPA shows Te-doped (0.9%) CoSb ₃ plus ~5% second phases of arsenopyrite phases (RuSb ₂ Te ₂ , CoSb ₂ Te ₂)	very clean skutterudite X-ray single phase
Ru _{0.99} Co _{0.01} Sb _{2.01} Te _{0.99} (CoSb ₂) _{0.995} (RuSb ₂ Te) _{0.995} add Fe _{0.01} Pd _{0.01} Sb _{2.01} Te _{0.99}	DX3 DX3-1 1-DX3-1 3-DX3-1		9.04788 9.06638	106.65 107.34			7.641 7.644	4.32E+22 4.29E+22	0.234 0.232							10g mixed+CP+600C/120h+Xray 2.5g DX3 +add+CP+600C/120h+Xray+HP 550C/950bs/2h+MPA MPA shows mixture of Fe _{0.01} Co _{0.01} Pd _{0.01} Sb _{2.01} Te _{0.99} and Ru _{0.99} Co _{0.01} Pd _{0.01} Sb _{2.01} Te _{0.99} + inclusions of Fe _{0.01} Ru _{0.99} Pd _{0.01} Sb _{2.01} Te _{0.99}	clean skutterudite X-ray trace of RuSb ₂ Te-rich alloy clean skutterudite X-ray trace of RuSb ₂ Te-rich alloy
Ru _{0.99} Co _{0.01} Pd _{0.01} Sb _{2.01} Te _{0.99} Pd-doped, Te-rich (CoSb ₂) _{0.995} (RuSb ₂ Te) _{0.995}	DX5 1-DX5 1-DX5 (b) 3-DX5 4-DX5 5-DX5		9.0460	108.67	7.410		7.647	4.32E+22	0.234				1.29 1.68E+20 1.34E+20 1.68E+20 1.44E+20 1.52E+20	-188.1 -22.5 -27.6 -26.9 -30.5 -29.7	40.1 1.66 1.69 1.38 1.42 1.38	mixed+CP+600C/120h+Xray+HP 550C/950bs/4h+MPA (in progress) analyze at MPA to check Co/Sb ratio MPA: Ru _{0.99} Co _{0.01} Pd _{0.01} Sb _{2.01} Te _{0.99} + 7-8% RuSb ₂ Te-based inclusions MPA: Ru _{0.99} Co _{0.01} Pd _{0.01} Sb _{2.01} Te _{0.99} + 7-8% RuSb ₂ Te-based inclusions	clean skutterudite X-ray trace of RuSb ₂ Te-rich alloy trace of RuSb ₂ Te-rich alloy Co>25.5 at% ???

Table 10: Filled Skutterudites $\text{CeFe}_{1-x}\text{Ru}_x\text{Sb}_{12}$

Filled Skutterudites	Sample Label	Melting Point (C)	lattice A	$\langle M \rangle$ g	d_{exp} g.cm ⁻³	$d_{\text{calc}}/d_{\text{theo}}$ %	d_{theo} g.cm ⁻³	N_A at.cm ⁻³	C_p (D) J/g.K	E_{gap} eV	ρ_{300} cm ⁻³	μ_{300} cm ² /Vs	ρ_{300} mΩ.cm	S_{300} μV/K	λ_{300} mW/cmK	preparation method	comments
CoSb_3		850	9.0395	106.05			7.621	4.33E+22	0.235	0.55	3.71E+18	1746.0	0.96	130.0	104	LSPS/HP	
$\text{CeFe}_x\text{Sb}_{12}$ (was OX81)	OX501		9.1460	107.32	7.816	98.8	7.907	4.18E+22	0.232				0.51	76.0	30.1	5g. Ce+Fe in RF 1600C + add Sb 700C/60h+X-ray + HP 600C/950lbs/2h	very clean filled skutterudite X-ray
	1-OX501										3.40E+21	3.8	0.48			MPA shows about 98% $\text{Ce}_{5.6}\text{Fe}_{23.8}\text{Sb}_{70.6}$ (95.3% Ce filling)	better than M2358 and M2358-1
	2-OX501										3.39E+21	3.7	0.48			+ 2% FeSb_2 and Fe-richFeSb (notice: no CeSb_2 present!)	
	3-OX501													23		---> after Seebeck measurement up to 525C	note higher μ_H and S
$\text{Ce}_{2-x}\text{Ru}_x\text{Sb}_{12}$	M2379		9.2716	117.96			8.346	4.01E+22	0.211							X-ray + 1100C/24h + X-ray	filled skutterudite X-ray
																no improvement after anneal at 1100C (amount of RuSb_2 actually increased)	but strong presence of RuSb_2
$\text{CeRu}_x\text{Sb}_{12}$	DX500		9.2611	117.96			8.320	4.00E+22	0.211							Ce+Ru in RF 1630C + add Sb 700C/60h+X-ray	filled skutterudite X-ray
																need new preparation process to prevent/eliminate RuSb_2 formation	but strong presence of Sb, RuSb_2
$\text{CeFe}_{0.5}\text{Ru}_{0.5}\text{Sb}_{12}$	DX501		9.1700	106.65	7.853	98.8	7.945	4.15E+22	0.230				0.46	77.5	30.1	Ce+Fe+Ru 1540C/30s +add Sb 700C/72h +X-ray+HP 600C/950lbs/2h+MPA	clean filled skutterudite X-ray
	1-DX501										2.01E+21	6.4	0.49			MPA : 97% $\text{Ce}_{5.9}\text{Fe}_{19.3}\text{Ru}_{2.6}\text{Sb}_{72.2}$ (100% Ce filling)	
	3-DX501										2.62E+21	4.6	0.49			+ 3% $\text{Fe}_{26.2}\text{Ru}_{2.4}\text{Sb}_{70.3}$ arsenopyrite-type + Ce_2Sb phases	
$\text{Ce}_{0.92}\text{Fe}_{1.08}\text{Ru}_{1.0}\text{Sb}_{12}$	DX502		9.1793	109.99	7.831	97.7	8.018	4.14E+22	0.227				0.48	72.9	29.4	Ce+Fe+Ru 1540C/30s+add Sb 700C/72h+X-ray+HP 625C/2h/950lbs+MPA	filled skutterudite X-ray
	1-DX502										2.54E+21	4.9	0.51			MPA : 95% $\text{Ce}_{5.7}\text{Fe}_{18.0}\text{Ru}_{5.1}\text{Sb}_{71.2}$ (96.9% Ce filling)	but some free Sb, Ce..
	3-DX502										4.37E+00	30.2	0.48			+ 5% $\text{Ce}_{0.1}\text{Fe}_{24.2}\text{Ru}_{8.1}\text{Sb}_{87.6}$ arsenopyrite-type phases	
$\text{Ce}_{0.92}\text{Fe}_{2.08}\text{Ru}_{1.46}\text{Sb}_{12}$	DX503		9.1793	111.16			8.105	4.14E+22	0.224							Ce+Fe+Ru 1540C/30s + add Sb 700C/72h + X-ray	two filled skutterudite X-ray
			9.2533													note that only traces of RuSb_2 can be detected in X-ray pattern: anneal longer?	plus some traces of Sb, Ce..

- T: transition metal
- Pn: pnictogen
- Filling element: rare earth

FIGURE 1

Figure 2

ID: Ru/Ir/Te/Sb lbd OX5 + Si

rot. cell, 380, 40, 20

File: OX5-S.MDI Scan: 10-70/.05/3/#1201, Anode: CU

Zero=.05

1> 27-1402: Silicon, syn [NR]

2> IrSb3 isostructure d/d (0) = 1.0012

FIGURE 3

ID: Ru/Ir/Sb/Te labeled OX5 #2 + Si rot, cell, 380, 40, 20
 File: OX5-2S.MDI Scan: 10-70/.05/3/#1201, Anode: CU Zero=-.15

1> 27-1402: Silicon, syn [NR] 2> IrO3 isostructure d/d (h) = 1.0008

FIGURE 4

ID: Ru/Ir/Sb/Te labeled OX5-3 + Si rot. cell. 380, 40, 20
 File: OX5-3S.MDI Scan: 10-70/.05/3/#1201, Anode: CU Zero=-.05

1> 27-1402: Silicon, syn [NR] 2> IrSb3 isostructure d/d (0) =1.0015

FIGURE 5

$Ru_4Ir_4Sb_{20}Te_4$

ID: Ru/Ir/Te/Sb 1bld OX6 + Si

rot, cell, 380, 40, 20

File: OX6-S.MDI

Scan: 10-70/.05/3/#1201, Anode: CU

Zero=.15

1> 27-1402: Silicon, syn [NR]

2> IrSb3 isostructure d/d(0)=1.0014

3> 23-1000: Tellurium

FIGURE 6

ID: Ru/Ir/Sb/Te labeled OX6 #2 + Si

rot, cell, 380, 40, 20

File: OX6-2S.MDI

Scan: 10-70/.05/3/#1201, Anode: CU

Zero=-.05

1> 27-1402: Silicon, syn [NR]

2> IrSb3 isostructure d/d(0)=1.0015

FIGURE 7

ID: Ru/Ir/Sb/Te labeled OX6-3 + Si rot. cell, 380. 40. 20
 File: OX6-3S.MDI Scan: 10-70/.05/3/#1201, Anode: CU Zero=-.2

FIGURE 8

ID: Ru/Ir/Sb/Te labeled OX13 + Si

rot, cell, 380, 40, 20

File: OX-13S.MDI

Scan: 10-70/.05/3/#1201, Anode: CU

Zero=-.1

1> 27-1402: Silicon, syn [NR]

2> IrSb3 isostructure d/d(0)=1.0016

FIGURE 3

ID: Ru/Ir/Sb/Te labeled OX16 + Si rot. cell, 380, 40, 20
 File: OX16-S.MDI Scan: 10-70/.05/3/#1201, Anode: CU Zero=-.05

1> 27-1402: Silicon, syn [NR] 2> IrSb3 isostructure d/d (0) = 1.0014

FIGURE 10

ID: Ru/Ir/Sb/Te labeled ~~OX17~~ + Si
 File: OX17-S.MDI Scan: 10-70/.05/3/#1201. Anode: CU
 Zero=-.15

FIGURE II

ID: Ru/Ir/Sb/Te labeled OX23 + Si rot. cell, 380, 40, 20
 File: OX23-S.MDI Scan: 10-70/.05/3/#1201, Anode: CU Zero=-.05

1> 27-1402: Silicon, syn [NR] 2> IrSb3 isostructure d/d(0)=1.0010

FIGURE 12

ID: Ru/Ir/Sb/Te labeled OX24 + Si rot, cell, 380, 40, 20
File: OX24-S.MDI Scan: 10-70/.05/3/#1201, Anode: CU

Zero=-.05

1> 27-1402: Silicon, syn [NR]

2> IrSb3 isostructure d/d (0) =1.0026

FIGURE 13

ID: Ru/Ir/Sb/Te labeled OX41 + Si rot. cell. 380. 40. 20
 File: OX41-S.MDI Scan: 10-70/.05/3/#1201, Anode: CU

Zero--05

1> 27-1402: Silicon, syn [NR]

2> IrSb3 isostructure d/d (0) = 1.0015

FIGURE 14

ID: Ru/In/Pt/Sb/Te 1bld DX1 + Si rot. cell. 380, 40, 20

File: DX1-S.MDI Scan: 10-70/.05/ 3/#1201, Anode: CU

2T(0)=-.06

1> 27-1402: Silicon, syn - Si

2> P17-0888 Ir Sb3, d/d(0)=-1.0007

FIGURE 15

ID: Ru/Ir/Pt/Sb/Te 1bld DX2 + Si rot. cell. 380. 40. 20
 File: DX2-S.MDI Scan: 10-70/.05/ 3/#1201. Anode: CU 2T(0)=-.02

1> 27-1402: Silicon, syn - Si

2> P17-0888 Ir Sb3, d/d(0)=-1.0018

FIGURE 16

20-000000
 22-000000
 24-000000
 26-000000
 28-000000
 30-000000
 32-000000
 34-000000
 36-000000
 38-000000
 40-000000
 42-000000
 44-000000
 46-000000
 48-000000
 50-000000
 52-000000
 54-000000
 56-000000
 58-000000
 60-000000
 62-000000
 64-000000
 66-000000
 68-000000
 70-000000

ID: Ir/Ru/Sb/Te/Pt dpd 1bld DX4+Si rot, cell, 380, 40, 20
 File: DX4-S.MDI Scan: 10-70/.05/ 3/#1201, Anode: CU 2T (0) = -.1

1> 27-1402: Silicon, syn - Si
 2> P17-0888 Ir Sb3, d/d (0) = 1.0007

FIGURE 17

HR: @ 600°C for 4 hrs. (better 550)

2.41g.

ID: Ru/Ir/Pt/Sb/Te 1b1d DX6 + Si statcell. 380, 40.20
File: DX6-S.MDI Scan: 10-70/.05/ 3/#1201, Anode: CU

1> 27-1402: Silicon, syn - Si
3> P19-1108 Ru Te₂, d/d(0) = 1.0067

2> P17-0888 Ir Sb₃, d/d(0) = 1.0009

FIGURE 18

6/1/95
 1.4441g
 for 2nd run
 6/1/95
 1.4441g

ID: Au/Co/Sb/Te 1b1d OX25 + Si rot, cell, 380, 40, 20

File: OX25-S.MDI

Scan: 10-70/.05/ 3/#1201, Anode: CU

2 θ (°) = - .14

2> P17-0888 Ir Sb3, d/d (0) = 0.9782

1> 27-1402: Silicon, syn - Si

3> P17-0888 Ir Sb3, d/d (0) = 1.0019

FIGURE 19

6/1/95
 4P @ 4hr
 for 2nd analysis
 of 500

ID: Ru/Co/Sb/Te labeled OX26 + Si rot. cell. 380.40.20
 File: OX26-S.MDI Scan: 10-70/.05/ 3/#1201, Anode: CU 2T(0) = -.12

1> 27-1402: Silicon, syn - Si
 3> P17-0888 Ir Sb3, d/d(0) = 0.9774

FIGURE 20

ID: Co/Ru/Sb/Te labeled OX46 + Si rot. cell, 380, 40, 20

File: OX46-S.MP

Scan: 10-70/.05/ 3/#1201, Anode: CU

2 θ (0) = -.12

1> 27-1402: Silicon, syn - Si

3> 05-0727: Co - Cobalt

2> P17-0888, Ir Sb₃, d/d (0) = .9775

FIGURE 21

ID: Ru/Co/Sb/Te 1bld DX-3 + Si rot, cell, 380, 40, 20

File: DX3-S.MDI

Scan: 10-70/.05/ 3/#1201, Anode: CU

2T (0) = -.06

1> 27-1402: Silicon, syn - Si
3> 35-0732: Antimony, syn - Sb

2> P17-0888 Ir Sb₃, d/d (0) = 0.9778 9.0473
4> 17-0888: Ir Sb₃ - Antimony Iridium

FIGURE 22

500/44, 25/95
hot-pressed

ID: Ru/Co/Sb/Te/Pd-dopd 1b1d DX5+Si rot, cell, 380, 4020

File: DX5-S.MDI

Scan: 10-70/.05/ 3/#1201, Anode: CU

2T (0) = -.08

1> 27-1402: Silicon, syn - Si
3> 35-0732: Antimony, syn - Sb

2> P17-0888 Ir Sb₃, d/d (0) = 0.9776 g.0460
4> P17-0888 Ir Sb₃, d/d (0) = 1.0014

FIGURE 23

Figure : 24

Figure : 25

Figure : 26

Figure : 27

Figure : 28

Figure : 29

Figure : 30

Ce/Ru/Sb labeled DX500 + Si rotcell, 380, 40, 20

[2] <P17-0888.DSP> [rSb3 isostructure d/d(0)=1.003
[1] <27-1402> Silica, sym - Si

FIGURE 31

Ce/Fe/Ru/Sb lld DX501 + Si rotcell,380,40,20

[2] <P17-0888.DSP> kSb3 isostructure=0.9915
[1] <27-1402> Silicon, syn - Si

FIGURE 32

[4] <08-0056> Ce - C. A
 [3] <35-0732> Antimony, syn - Sb
 [2] <P17-0888.DSP> IrSb3 isostructure=0.9920
 [1] <27-1402> Silicon, syn - Si

Ce/Fe/Ru/Sb lld DX502 + Si rotcell,380,40,20

FIGURE 33

[5] <06-0690> Iron, sy
 [4] <35-0732> Antimony, sy
 [3] <17-0888> IrSb3 - Antimony Iridium
 [2] <P17-0888.DSP> IrSb3 isostructure=0.9920
 [1] <27-1402> Silicon, syn - Si

Ce/Fe/Ru/Sb Ild dx503 + Si,w rotcell,380,40,20

FIGURE 34

Figure 35

Figure 36

Figure 37

Figure 38

Figure 39

Figure 40

Figure 41

Figure 42