Prediction of Room Temperature High Thermoelectric Performance in n-type La(Ru$_{1-x}$Rh$_x$)$_4$Sb$_{12}$

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First principles calculations are used to investigate the band structure and the transport related properties of unfilled and filled 4$d$ skutterudite antimonides. The calculations show that, while RhSb$_3$ and p-type La(Rh,Ru)$_4$Sb$_{12}$ are unfavorable for thermoelectric application, n-type La(Rh,Ru)$_4$Sb$_{12}$ is very likely a high figure of merit thermoelectric material in the important temperature range 150-300 K.

The widespread application of thermoelectric (TE) coolers has been hindered by the fact that these devices have limited efficiencies related to the lack of sufficiently high performance materials to use in the active elements. The TE performance of a material is characterized by a dimensionless figure of merit $ZT = \sigma S^2 T/(k_L + k_e)$ where $\sigma$ and $k_e$ are the electrical and thermal conductivity, $S$ is the Seebeck coefficient and $k_L$ is the lattice thermal conductivity. Almost all TE coolers are based on alloys of Bi$_2$Te$_3$, which has maximum $ZT$ values slightly exceeding 1.0 around room temperature, but substantially decreasing performance as temperature is reduced.

Recently, there has been a renewed effort to find better materials in the temperature range 100-300 K with a primary focus on novel systems. This effort has been partially successful in that three new high $ZT$ compounds have been discovered: $\beta$-Zn$_4$Sb$_3$ and two filled skutterudites CeFe$_4$Sb$_{12}$ and La(Fe,Co)$_4$Sb$_{12}$. While these materials all have their maximum $ZT$ values substantially above room temperature and are not applicable to cooling applications, considerable understanding, particularly of skutterudites, has emerged leading to the hope that even higher performance compositions may be found and perhaps that lower temperature operation may be possible. Here we report first principles results that when combined with existing knowledge of skutterudites materials, point to a specific composition with a strong potential for high values of $ZT$ (in excess of 1.0) over a wide technologically important temperature range from 150-300 K.

The conventional cubic cell of a binary skutterudite, for instance CoSb$_3$, contains eight molecular units (space group Im$ar{3}$m). The metal can be also Rh or Ir, and Sb an other pnictogen element (P, As). The metal atoms form a cubic sub-lattice partially filled by six almost square pnictogen rings oriented according to the cubic directions. This results in six bonds connecting one Co with the six surrounding Sb whereas every pnictogen forms two strong covalent bond with other Sb and two partially ionic bonds with Co. The high values of $ZT$, with a rare earth filling the empty octans of the cubic cell, rests on two important effects: a low glass-like $k_L$ due to the effect of the filling atom vibrations and on high power factors $\sigma S^2$ related to the electronic features. In La(Fe,Co)$_4$Sb$_{12}$, in particular, La-filling has the important effect to decrease $k_L$ about one order of magnitude with respect binary CoSb$_3$ and to lower the top of the valence band to near a low-energy high effective mass band. This is responsible for the high thermopower in p-type materials.

In this letter, we investigate by means of first principles calculations the electronic properties of skutterudites based on RhSb$_3$ and find that La(Ru,Rh)$_4$Sb$_{12}$ is promising for n-type TE application. Although the thermal conductivity of RhSb$_3$ is not glass-like, we can expect that filling with La will yield a low $k_L$ material because the volume available to La’s vibration allows considerable amplitudes and a clear relation between filling and $k_L$ in skutterudites is known experimentally. This conjecture is supported by the experimental finding that $k_L$ in LaFe$_4$Sb$_{12}$ is lower than 20 mWcm$^{-1}$K$^{-1}$. Based on experimental trends of $k_L$ vs. void size in skutterudites we expect $k_L$ for La(Ru,Rh)$_4$Sb$_{12}$ to be in the range 10-15 mWcm$^{-1}$K$^{-1}$.

Our electronic structure calculations were performed using a well converged ($R_{KM} = 7.0$, $R_{MT} = 2.50$, 2.25, 2.25, 2.20 for La, Ru, Rh, Sb respectively) linearized augmented plane wave (LAPW) method including $s$, $p$, and $d$ local orbital extensions in the framework of local density functional theory (Hedlin-Lundqvist parameterization). A fully relativistic calculation was used for core states whereas the valence states were done in a scalar relativistic scheme. The Brillouin zone (BZ) sampling in the self consistent calculation is done by means of a $(4,4,4)$ special point grid whereas the density of states, $N(e)$, and related quantities are integrated on 295 k points tetrahedral mesh.

We used the experimental lattice constant for LaRu$_4$ Sb$_{12}$ ($a_{L} = 9.26$ Å); the two symmetry unconstrained structural parameters related to the Sb position were determined by means of a best fit to a quadratic curve of total energy calculations exploring 2-parameter surface.
We obtain $x = 0.1583$ and $y = 0.3412$ in the notation of Ref. [4]. These structural parameters were used also for the calculation on La(Ru,Rh)$_4$Sb$_{12}$ performed in virtual crystal approximation (VCA), realized in LAPW adding one electron in valence and increasing the atomic number of the transition metal of one fourth. As discussed below, excellent rigid band behavior was found between LaRu$_4$Sb$_{12}$ and VCA La(Ru,Rh)$_4$Sb$_{12}$ supporting the validity of VCA, a posteriori, and implying only weak scattering by alloy disorder.

RhSb$_3$, whose experimental structural parameters are $\alpha_L = 9.23$ Å and $(x, y) = (1.517, .3420)$, is a zero-gap semiconductor because the top of the valence band at BZ center belongs to a 3-fold degenerate representation (see Fig. 1). Anyway the highest occupied band shows strong Sb-$p$ component that might interact, after filling, with La-$f$ resonance as happens both in cobalt phosphide and antimonide.

The band structure (BS) of the corresponding filled material, LaRu$_4$Sb$_{12}$, is drastically different from binary RhSb$_3$ because the effect of La is to introduce $f$-resonance in conduction band (CB) and to make available extra-electrons that modify the electronic structure. This has been proved studying the BS of hypothetical YRu$_4$Sb$_{12}$. The different arrangement of the bands near $\varepsilon_F$ in RuSb$_3$ with respect of CoSb$_3$, as in Ref. [5], could be strongly related to the different electro-negativity of Rh (Pauling electro-negativity: $\varepsilon_R = 2.28$) and Co ($\varepsilon_C = 1.88$) with respect of Sb ($\varepsilon_S = 2.05$) inverting the ionicity of bonds.

Undoped LaRu$_4$Sb$_{12}$ is a metal but its BS is very promising for n-type TE application if alloying can be done that brings $\varepsilon_F$ to the gap without changing the main features of the heavy multi-valley structure above the indirect gap in the CB; p-type TE is not favorable at reasonable doping because of the lack of heavy hole bands near the Fermi level.

![Fig. 1. Scalar relativistic band structure for RhSb$_3$ in an energy window centered at the valence band top. Notice the zero-gap character due to 3-fold degenerate band at BZ center.](image)

![Fig. 2. Comparison between the scalar relativistic bands for LaRu$_4$Sb$_{12}$ (gray line) and VCA La(Ru$_{75}$Rh$_{25}$)$_4$Sb$_{12}$ (black). The energy zero is fixed at the respective tops of the valence band. Due to the rigid behavior of the BS, the scattering effect related to the alloying must be quite small.](image)

In Fig. 2 we compare the BS of pure LaRu$_4$Sb$_{12}$ and La(Ru$_{75}$Rh$_{25}$)$_4$Sb$_{12}$ showing that, after alloying, an indirect gap semiconductor ($E_g^\text{ind} = 0.16$ eV) is recovered without great qualitative changes. The rigid behavior of the BS indicates only weak electron scattering due to alloying and the potential for high mobility. The high effective mass multi-degenerate minima in conduction band (Tab. 3) underline the high Seebeck coefficient that we have calculated from the BS.

Starting from LAPW BS we derived, using standard kinetic theory, [3, 4] the temperature dependence of the thermopower at different doping levels giving a direct way to compare with experimental measures. The transport coefficients are calculated using (atomic units):

$$\frac{\sigma}{\tau} = \frac{e^2}{3} \int d\varepsilon (-\frac{\partial f_0}{\partial \varepsilon})N(\varepsilon)\varepsilon^2(\varepsilon),$$

$$S = \frac{e\tau}{3\sigma T} \int d\varepsilon (-\frac{\partial f_0}{\partial \varepsilon})N(\varepsilon)\varepsilon^2(\varepsilon - \varepsilon_F),$$

where $\varepsilon_F$ is the chemical potential, $e$ the electron charge, $f_0$ the Fermi distribution function and $v(\varepsilon)$ the average velocity of electron with energy $\varepsilon$; the constant scattering time ($\tau$) approximation is assumed.

The measured values of Seebeck coefficient for LaFe$_2$CoSb$_{12}$ and CeFe$_2$Sb$_{12}$ are about $100 \ \mu V K^{-1}$ at room temperature [6, 7] in the compound we present, La(Ru$_{75}$Rh$_{25}$)$_4$Sb$_{12}$, $S$ ranges from $-150$ to $-200 \ \mu V K^{-1}$ for different doping from $4.5 \ 10^{18}$ to $3.7 \ 10^{20}$ electron cm$^{-3}$. As shown in Fig. 3 the temperature dependence is very favorable having a maximum below 200 K and remaining quite stable at higher temperature.
FIG. 3. Temperature dependence of Seebeck coefficient for La(Ru,75Rh,25)₄Sb₁₂ at different doping concentrations in electron per cm⁻³.

In summary, we have presented band structure calculations for RhSb₃, LaRu₄Sb₁₂ and La(Ru,75Rh,25)₄Sb₁₂. Our results and the experimental trends suggest La(Ru₁₋ₓRhₓ)₄Sb₁₂ as a very promising material for n-type TE application because of (1) expected low thermal conductivity, (2) multi-valley high effective mass character of the CB, (3) rigid behavior of the band structure after alloying, (4) high Seebeck coefficients in the temperature range useful to cooler device applications. It should be emphasized that although the results indicate weak n-type carrier scattering due to Ru-Rh disorder, the sensitivity of the band structure to La filling indicates strong scattering by La defects, so preparing samples with maximum filling is key to assessing the TE potential of La(Ru₁₋ₓRhₓ)₄Sb₁₂. We underline that the difficulty to prepare n-type highly filled skutterudites has been overcome using high pressure synthesis for CoSb₃ and this should work also here.

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TABLE I. Effective masses for VCA La(Ru,75Rh,25)₄Sb₁₂ along the high symmetry directions in BZ at Γ, N and at the minimum near ∆ direction, Kᵥm=(0.170, 0.486, 0.001) in unit of 2π/a. ε denotes the band energy with respect to the top of the valence band (see Fig. 3); η is the number of equivalent valleys. The effective masses are along ∆, Λ, Σ for Γ⁺; along Σ, G and D for N⁺. For Kᵥm the effective masses are along the cubic directions. Both the six N⁺ and 24 Kᵥm pockets are active in transport above 150 K for any n-type doping.

| ε (eV) | η  | m₁ | m₂ | m₃ |
|-------|----|----|----|----|
| Γ⁺    | 0.000 | 1  | -0.13 | -0.13 | -0.12 |
| N⁺    | 0.162 | 6  | 1.16 | 0.36 | 2.00 |
| Kᵥm   | 0.172 | 24 | 12.12 | 0.24 | 3.90 |

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