

Supporting Information of

Computational prediction of high thermoelectric performance in p-type half-Heusler compounds with low band effective mass

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Deformation potential (DP) theory:

For an isotropic band system,^[1] the carrier mobility μ and scatter time τ can be expressed as:

$$\mu = \frac{2\sqrt{2\pi}e\hbar^4 c_{ii}}{3(k_B T)^{3/2} m_b^{*5/2} \Xi^2} \quad (\text{S1})$$

$$\tau = \frac{\mu m_b^*}{e} = \frac{2\sqrt{2\pi}\hbar^4 c_{ii}}{3(k_B T m_b^*)^{3/2} \Xi^2} \quad (\text{S2})$$

where c_{ii} is the lattice elastic constant ($i = 1, 2, 3$). The band effective mass tensor $m_{k,l}^* = \hbar^2 / [\partial^2 E / \partial k_k \partial k_l]$ of holes along the three directions are calculated near the valence band edge. The single band effective mass for the i th band is given by $m_{b,i}^* = \sqrt[3]{m_{11}^* \cdot m_{22}^* \cdot m_{33}^*}$, ($k = l = 1, 2, 3$). The deformation potential constants for holes are calculated as $\Xi = \frac{\partial E_{edge}}{\partial(\Delta a) / a_0}$, where E_{edge} is the energy of the VBM, a_0 is the lattice constant, $\Delta a = a - a_0$ is the corresponding lattice distortion. The deformation potential constant Ξ represent the shift of band edges per unit strain.

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Lorenz number calculation:

In the SPB model^[2] and assuming carriers are mostly scattered by acoustic phonons, the Lorenz number is

$$L = \left(\frac{k_B}{e}\right)^2 \frac{3F_0(\eta)F_2(\eta) - 4F_1^2(\eta)}{F_0^2(\eta)} \quad (\text{S3})$$

where $F_n(\eta) = \int_0^\infty \frac{x^n dx}{1 + \exp(x - \eta)}$ is the Fermi integrals and η is the reduced chemical potential. η is

derived from the measured Seebeck coefficient via

$$S = \frac{k_B}{e} \left(\frac{2F_1(\eta)}{F_0(\eta)} - \eta \right) \quad (\text{S4})$$

Slack's expression:

According to Slack's expression,^[3] the lattice thermal conductivity can be given as:

$$\kappa_L = A \frac{\overline{M} \Theta_D^3 V_{per}^{1/3}}{\gamma^2 n^{2/3} T} \quad (\text{S5})$$

where \overline{M} is the average atomic mass, Θ_D is the Debye temperature, V_{per} is the volume per atom, n is the number of atoms in the primitive cell, and A is a physical constant $\approx 3.1 \times 10^{-6}$ when the units of κ_L , \overline{M} , and $V_{per}^{1/3}$ are taken as $\text{Wm}^{-1}\text{K}^{-1}$, amu, and angstroms, respectively. γ is Grüneisen parameter calculated by the DFPT combined with the quasi-harmonic approximation (QHA):

$$\gamma = \frac{3\beta B V_m}{C_v} \quad (\text{S6})$$

where β is the linear thermal expansion coefficient, B is the bulk modulus, V_m is the the molar volume, and C_v is the isometric heat capacity, which can be calculated from the phonon dispersions:

$$C_v = \sum_{n,\mathbf{q}} k_B \left(\frac{\hbar \omega_n(\mathbf{q})}{k_B T} \right)^2 \frac{e^{\hbar \omega_n(\mathbf{q})/k_B T}}{\left(e^{\hbar \omega_n(\mathbf{q})/k_B T} - 1 \right)^2} \quad (\text{S7})$$

where $\omega_n(\mathbf{q})$ is the phonon frequency of the n -th branch with wave vector \mathbf{q} . It is noted that we specify the volume changes in 3%, 2%, 1%, 0%, -1%, -2%, -3% for the QHA. The Debye temperature Θ_D is evaluated from formula on sound velocity v_s :^[4]

$$\Theta_D = v_s \frac{h}{k_B} (6\pi^2 n_a)^{1/3} \quad (\text{S8})$$

where n_a is the number density of atoms. The sound velocity v_s can be calculated by the following formula:^[5]

$$v_s = \left[\frac{1}{3} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right]^{-1/3} \quad (\text{S9})$$

where transversal velocity v_t and longitudinal velocities v_l are obtained from equations as follows:

$$v_t = \sqrt{\frac{G}{\rho}} \quad (\text{S10})$$

$$v_l = \sqrt{\frac{\left(B + \frac{4}{3} G \right)}{\rho}} \quad (\text{S11})$$

where B , G , and ρ are the bulk modulus, the shear modulus, and the density, respectively.

According to the Voigt-Reuss-Hill approximation,^[6] B and G can be expressed as:

$$B = \frac{c_{11} + 2c_{12}}{3} \quad (\text{S12})$$

$$G = \frac{G_V + G_R}{2} \quad (\text{S13})$$

$$G_V = \frac{c_{11} - c_{12} + 3c_{44}}{5} \quad (\text{S14})$$

$$G_R = \frac{5(c_{11} - c_{12})c_{44}}{4c_{44} + 3(c_{11} - c_{12})} \quad (\text{S15})$$

where c_{11} , c_{12} , and c_{44} are three independent elastic constants for cubic lattice.

Klemens's Model

At temperatures above the Debye temperature, the ratio of the lattice thermal conductivity of a material containing point defects with that of the parent material can be written in the following manner:^[7]

$$\frac{\kappa_L}{\kappa_{L0}} = \frac{\tan^{-1}(u)}{u} \quad (\text{S16})$$

Here κ_L and κ_{L0} are the lattice thermal conductivity of the defected and parent materials, respectively, and the parameter u is defined by:

$$u = \left(\frac{\pi^2 \Theta_D V_{per}}{h v_a^2} \kappa_{L0} \Gamma \right)^{1/2} \quad (S17)$$

where h is the Planck constant. We calculated the disorder scattering parameter, Γ , according to the assumption $\Gamma = \Gamma_m + \Gamma_s$, where the scattering parameters Γ_m and Γ_s are due to mass and strain field fluctuations, respectively. For the ternary half-Heusler compounds, Γ_m and Γ_s are given by:

$$\Gamma_m = \frac{1}{3} \left(\frac{\overline{M}}{\overline{M}} \right)^2 x(1-x) \left(\frac{M_1 - M_2}{\overline{M}} \right)^2 \quad (S18)$$

$$\Gamma_s = \frac{1}{3} \left(\frac{\overline{M}}{\overline{M}} \right)^2 x(1-x) \varepsilon \left(\frac{r_1 - r_2}{\overline{r}} \right)^2 \quad (S19)$$

$$\overline{M} = M_1(1-x) + M_2x \quad (S20)$$

$$\overline{\overline{M}} = \frac{1}{3} (\overline{M} + M_3 + M_4) \quad (S21)$$

$$\overline{r} = r_1(1-x) + r_2x \quad (S22)$$

where, M_1 and M_2 are the atomic weight of the master atom and substituting atom, respectively; M_3 and M_4 are the atomic weight of undoped atoms; r_1 and r_2 are the atomic radius of the master atom and substituting atom, respectively. For example, in FeNb_{1-x}Ti_xSb system, M_1 , M_2 , M_3 and M_4 are the atomic weight of Nb, Ti, Fe and Sb, respectively; r_1 and r_2 are the atomic radius of Nb and Ti, respectively. x is the content of substituting atom, and ε is regarded as a phenomenological adjustable parameter and is directly estimated by following relationship:^[8]

$$\varepsilon = \frac{2}{9} \left(\frac{6.4 \times \gamma(1 + \nu_p)}{(1 - \nu_p)} \right)^2 \quad (S23)$$

where ν_p the Poisson ratio, which can be derived from the longitudinal (ν_l) and transverse (ν_t) sound velocities by the relationship as:

$$\nu_p = \frac{1 - 2(\nu_t/\nu_l)^2}{2 - 2(\nu_t/\nu_l)^2} \quad (S24)$$

Table S1. The calculated lattice constant (a), zero-pressure bulk modulus (B_0) of Ru M Sb ($M=V$, Nb, Ta) HH compounds in the conventional cell. The lattice constant (a) and zero-pressure bulk modulus (B_0) were obtained by fitting the calculated total energy-atomic volume ($E-V$) results to the Murnaghan equation of state (EOS). Experimental^[9] and calculated^[10] data for comparison are also given.

Materials	Reference	a (Å)	B_0 (GPa)	E_g (eV)
RuVSb	this work	6.046	162	0.199
	literatures	6.065 ^[9]	/	0.223 ^[10]
RuNbSb	this work	6.200	169	0.358
	literatures	6.137 ^[9]	/	0.362 ^[10]
RuTaSb	this work	6.192	177	0.651
	literatures	6.135 ^[9]	/	0.655 ^[10]

Table S2. The energy difference Δ between these two maxima in valence bands and the corresponding carrier concentration n when the energy gap is crossed by the Fermi level.

Materials	RuVSb	RuNbSb	RuTaS	FeNbSb
	b			
Δ (eV)	0.21	0.32	0.34	0.36
n (10^{21} cm ⁻³)	4.3	5.0	5.9	11.7

Table S3. The calculated effective masses using the curvature of the valence bands. The values related to the transport properties are given with the unit of m^*/m_e . Three values are calculated along different directions. Table S3 shows the calculated effective masses of RuMSb ($M=V, Nb, Ta$) along different directions are all lower than that of FeNbSb. The calculated results of FeNbSb here are in good agreement with the calculated ones in Ref. [11].

Compound	band	m^*/m_e	m^*/m_e	m^*/m_e	m_b^*/m_e
		LW	LK	$L\Gamma$	
RuVSb	VBM-light	0.4	0.4	1.5	0.6
	VBM-heavy	0.6	0.6	1.6	0.8
RuNbSb	VBM-light	0.3	0.3	1.2	0.5
	VBM-heavy	0.4	0.4	1.3	0.6
RuTaSb	VBM-light	0.3	0.3	1.4	0.5
	VBM-heavy	0.4	0.4	1.4	0.6
FeNbSb	VBM-light	0.5	0.5	2.1	0.8
	VBM-heavy	0.7	0.7	2.1	1.0

Table S4. The optimized power factor values (PF_{opt}) and the corresponding optimal carrier concentration (n_{opt}) for RuMSb ($M = V, Nb, Ta$) compounds at high temperature of $T = 800K$. The values for FeNbSb are also shown for comparison.

Compound	PF_{opt} ($10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$)	n_{opt} (10^{21} cm^{-3})
RuVSb	6.1	5.0
RuNbSb	11.6	2.5
RuTaSb	11.3	4.4
FeNbSb	5.5	2.8

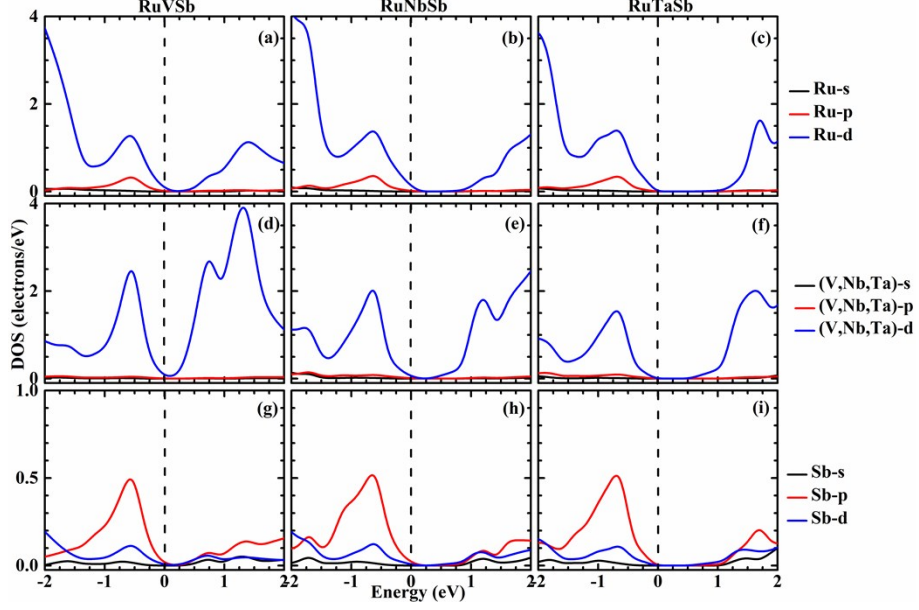


Figure S1. The projected DOS for (a,b,c) Ru atoms, (d,e,f) M atoms, and (g,h,i) Sb atoms in RuMSb ($M = \text{V, Nb, Ta}$) compounds.

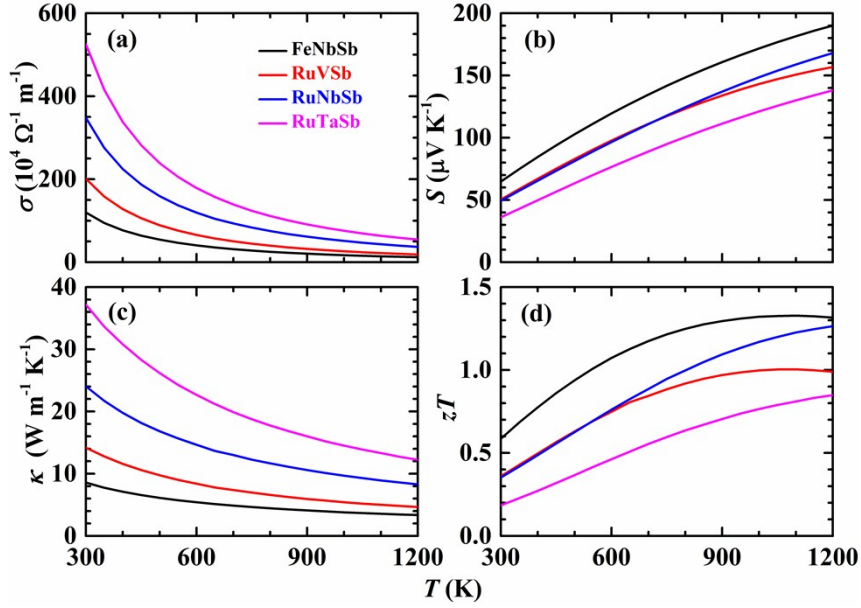


Figure S2. The temperature dependence of (a) electrical conductivity σ , (b) Seebeck coefficient S , (c) thermal conductivity κ and (d) zT value of RuMSb ($M = \text{V, Nb, Ta}$) at optimal carrier concentration. The values of FeNbSb are also shown for comparison. The total thermal conductivity κ consists of those from electrons (κ_e) and lattice (κ_L). In order to attain the maximum zT value, we used the minimum lattice thermal conductivity κ_{min} , which can be calculated^[12] via

$$\kappa_{min} = \frac{1}{2} \left[\left(\frac{\pi}{6} \right)^{1/3} \right] k_B (V)^{-2/3} (2v_t + v_l),$$

where V is the average volume per atom, k_B is the Boltzmann constant, v_t and v_l are the transversal and longitudinal velocities, respectively. The κ_{min} of RuVSb ,

RuNbSb, RuTaSb and FeNbSb are 0.82, 0.81, 0.75 and 0.96 $\text{W m}^{-1} \text{K}^{-1}$, respectively.

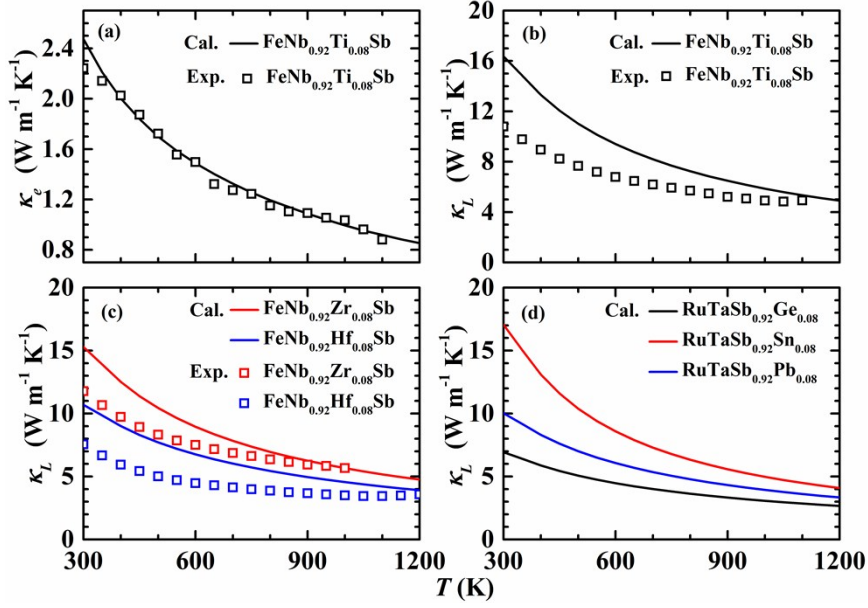


Figure S3. The calculated (a) electrical thermal conductivity κ_e and (b) lattice thermal conductivity κ_L versus temperature for $\text{FeNb}_{0.92}\text{Ti}_{0.08}\text{Sb}$ ($n = 1 \times 10^{21} \text{ cm}^{-3}$) and comparison with the experimental values.^[11] (c) The calculated and experimental κ_L versus temperature for $\text{FeNb}_{0.92}\text{Zr}_{0.08}\text{Sb}$ ($n = 1.2 \times 10^{21} \text{ cm}^{-3}$) and $\text{FeNb}_{0.92}\text{Hf}_{0.08}\text{Sb}$ ($n = 1.3 \times 10^{21} \text{ cm}^{-3}$). (d) The calculated κ_L versus temperature for $\text{RuTaSb}_{0.92}(\text{Ge}, \text{Sn}, \text{Pb})_{0.08}$. In order to calculate the κ_L of RuTaSb containing point defects, we assume that the doping efficacy of Ge/Sn/Pb dopants is equal to that of Ti doping at FeNbSb, i. e. the carrier concentration of $\text{RuTaSb}_{0.92}(\text{Ge}, \text{Sn}, \text{Pb})_{0.08}$ is $1 \times 10^{21} \text{ cm}^{-3}$.

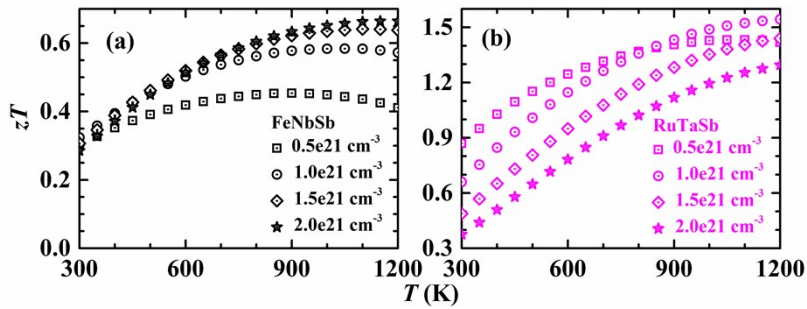


Figure S4. The calculated zT versus temperature for (a) FeNbSb and (b) RuTaSb at different carrier concentration n from 0.5 to $2.0 \times 10^{21} \text{ cm}^{-3}$. Clearly, the calculated zT of FeNbSb at 1200K increase with the increasing carrier concentration, while the maximum zT (zT_{max}) of RuTaSb at 1200K is obtained at $n = 1.0 \times 10^{21} \text{ cm}^{-3}$.

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