Electronic Supplementary Information (ESI)

Alloyed triple half-Heusler: a route toward high performance thermoelectrics with intrinsically low lattice thermal conductivity

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Supplementary section 1

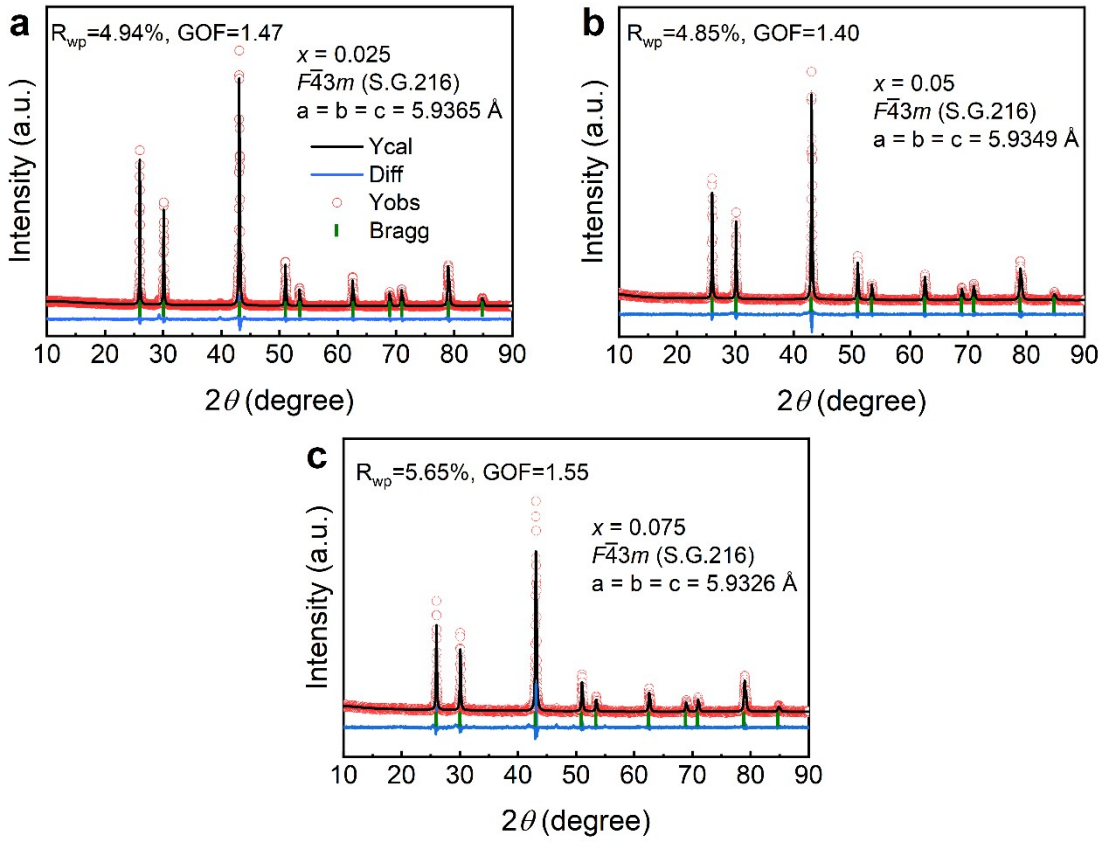

Fig. S1 (a-c) XRD patterns of the Ti($Fe_{0.5+x}Co_{0.25}Cu_{0.25-x}$)Sb ($x$ = 0.025, 0.05, and 0.075) samples together with their Rietveld refinement results.

Supplementary section 2

1.1 Single parabolic band model

Assuming the carrier conduction occurs within a single parabolic band (SPB),[1] we can obtain the following equations according to the Boltzmann transport theory:

The Seebeck coefficient,

$$S(\eta) = \pm \frac{k_B}{e}\left[\frac{(r+5/2)F_{(r+3/2)}(\eta)}{(r+3/2)F_{(r+1/2)}(\eta)} - \eta\right] \quad (1)$$

The Hall carrier concentration,

$$n_H = \frac{\left(2m^* k_B T\right)^2}{3\pi^2\hbar^3} \frac{(r+3/2)F_{(r+1/2)}^2(\eta)}{(2r+3/2)F_{(2r+1/2)}(\eta)} \quad (2)$$

The Lorentz number,

$$L = \left(\frac{k_B}{e}\right)^2\left\{\frac{(r+7/2)F_{(r+5/2)}(\eta)}{(r+3/2)F_{(r+3/2)}(\eta)} - \left[\frac{(r+5/2)F_{(r+3/2)}(\eta)}{(r+3/2)F_{(r+1/2)}(\eta)}\right]^2\right\} \quad (3)$$

The Fermi integral,

$$F_j(\eta) = \int_0^\infty \frac{\xi^j d\xi}{1 + exp(\xi - \eta)} \quad (4)$$

Where $\eta = E_F/k_BT$ is the reduced Fermi level, ξ the reduced carrier energy, m^* the density of states (DOS) effective mass, $\hbar$ the reduced Planck constant, and the scattering factor r relates to the energy dependence of the carrier relaxation time τ via $\tau = \tau_0\varepsilon^r$. When the charge carriers are scattered by acoustic phonon, the parameter r is equal to - 1/2.

The drift mobility for acoustic phonon scattering can be expressed as[2]:

$$\mu_{ph} = \frac{\sqrt{2}e\pi\hbar^4 \quad v_L^2\rho \quad F_0(\eta)}{3(k_BT)^{3/2}\Xi^2(m_b^*)^{5/2}F_{1/2}(\eta)} \quad (5)$$

where v_L is the velocity of longitudinal waves, ρ the sample density, Ξ the deformation potential, and m_b^* the band effective mass.

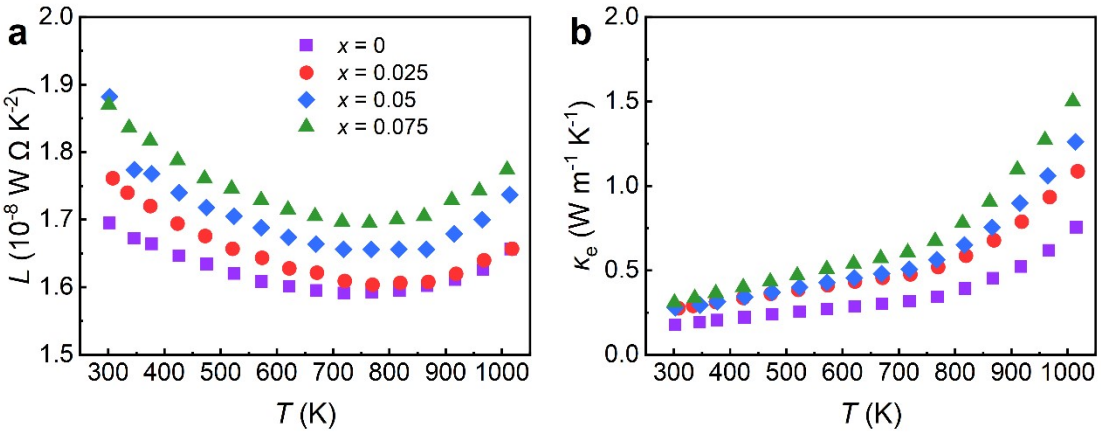

Fig. S2 Temperature dependence of (a) calculated Lorentz number (L) and (b) electronic thermal conductivity (κ_e) for $Ti(Fe_{0.5+x}Co_{0.25}Cu_{0.25-x})Sb$ (x = 0, 0.025, 0.05, and 0.075) samples.

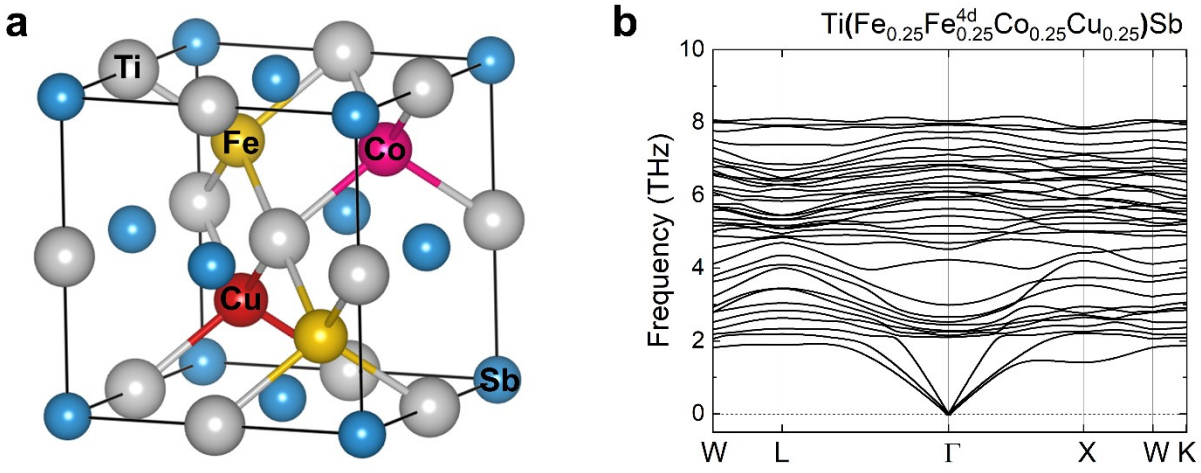

Fig. S3 (a) The crystal structure of $Ti(Fe_{0.25}Fe_{0.25}{}^{4d}Co_{0.25}Cu_{0.25})Sb$. (b) The phonon dispersion of $Ti(Fe_{0.25}Fe_{0.25}{}^{4d}Co_{0.25}Cu_{0.25})Sb$.

1.2 Minimum lattice conductivity of Ti($Fe_{0.5+x}Co_{0.25}Ni_{0.25-x}$)Sb samples

According to the Cahill model,[3] the minimum lattice thermal conductivity can be written as the following formula:

$$\kappa_{min} = \left(\frac{\pi}{6}\right)^{1/3} k_B n^{2/3} \sum_i v_i \left(\frac{T}{\theta_i}\right)^2 \int_0^{\theta_i/T} \frac{x^3 e^x}{(e^x - 1)^2} dx \tag{6}$$

Here, n, v_i and θ_i are the number density of atoms, the acoustic phonon velocity and the Debye temperature for each acoustic mode, respectively. Parameter θ_i can be obtained by the relationship $\theta_i = v_i\,(\hbar/k_B)(6\pi^2 n)^{1/3}$.

1.3 Elastic properties of Ti($Fe_{0.5+x}Co_{0.25}Ni_{0.25-x}$)Sb samples

Average sound velocity v_s can be extracted from:

$$v_s = \left[\frac{1}{3}\left(\frac{1}{v_l^3} + \frac{2}{v_t^3}\right)\right]^{-\frac{1}{3}} \tag{7}$$

where v_l and v_t are the longitudinal and transverse sound velocity respectively, which have been obtained as described in the experimental details section.

Debye temperature θ_D is calculated by:

$$\theta_D = \frac{h}{k_B}\left[\frac{3N N_A \rho}{4\pi M}\right]^{\frac{1}{3}} v_s \tag{8}$$

where h is the Planck constant, k_B is the Boltzmann constant, N represents the number of atoms in the molecule, N_A is the Avogadro constant, ρ is the mass density, M represents the molecular weight of the sample, respectively.

The Poisson ratio (v_p), shear modulus (G), bulk modulus (B) and Young's modulus (E) can be derived by the relationship as:

$$v_p = \frac{v_l^2 - 2v_t^2}{2\left(v_l^2 - v_t^2\right)} \tag{9}$$

$$\nu_p = \frac{\nu_l^2 - 2\nu_t^2}{2\left(\nu_l^2 - \nu_t^2\right)} \tag{10}$$

$$B = \frac{\rho\left(3\nu_l^2 - 4\nu_t^2\right)}{3} \tag{11}$$

$$\mathrm{E} = \frac{\rho\nu_{\mathrm{t}}^2\left(3\nu_{\mathrm{l}}^2 - 4\nu_{\mathrm{t}}^2\right)}{\left(\nu_{\mathrm{l}}^2 - \nu_{\mathrm{t}}^2\right)} \tag{12}$$

Table S1. Room-temperature transverse sound velocities (v_t), longitudinal sound velocities (v_l), average sound velocities (v_s), Poisson ratio (υ_p), shear modulus (G), bulk modulus (B), Young's moduli (E), and mass densities (ρ) for $Ti(Fe_{0.5+x}Co_{0.25}Ni_{0.25-x})Sb$ (x= 0, 0.025, 0.05, 0.075) samples.

Samples	v_t (m·s^{-1})	v_l (m·s^{-1})	v_s (m·s^{-1})	Poisson ratio	Shear modulus (GPa)	Bulk modulus (GPa)	Young's modulus (GPa)	ρ (g·cm^{-3})
x=0.000	3087	5712	3445	0.294	69	144	178	7.21
x=0.025	3059	5367	3400	0.259	67	178	170	7.21
x=0.050	3004	5328	3342	0.267	66	120	167	7.32
x=0.075	2974	5322	3310	0.273	64	119	162	7.21

1.4 Low-temperature heat capacity fitting

Table S2. Parameters used to fit the low temperature heat capacity (C_p) of $Ti(Fe_{0.5}Co_{0.25}Cu_{0.25})Sb$ by using one Debye and one Einstein mode.

Fitting parameters	Values
δ (10^{-3} J mol^{-1} K^{-2})	1.4
β (10^{-5} J mol^{-1} K^{-4})	6.26
A (J mol^{-1} K^{-1})	10.17
Θ_E (K)	146
ω/ν (THz)	19.2/3.06

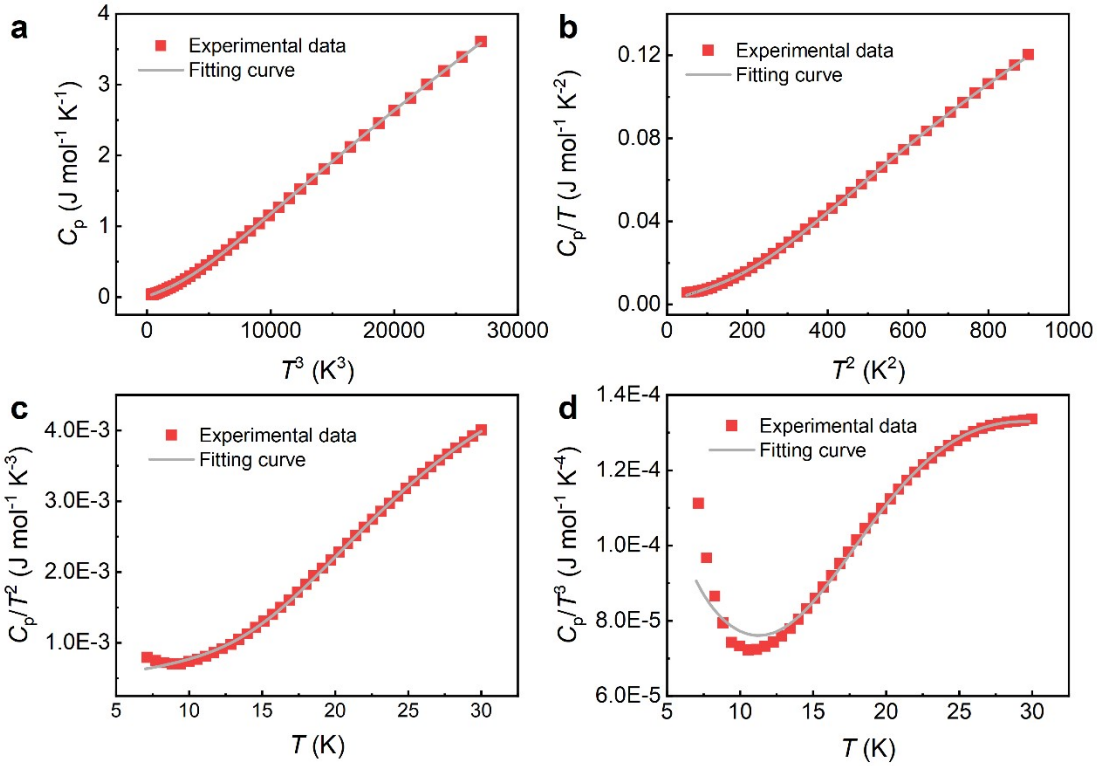

Fig. S4 Heat capacity fitting for the $Ti(Fe_{0.5}Co_{0.25}Cu_{0.25})Sb$ sample from 7 K to 30 K. (a)-(d) C_p versus T^3, C_p/T versus T^2, C_p/T^2 versus T, and C_p/T^2 versus T for $Ti(Fe_{0.5}Co_{0.25}Cu_{0.25})Sb$ by using one Debye mode plus one Einstein mode from 7 K to 30 K.

1.5 Lattice thermal conductivity modeling

We modeled the lattice thermal conductivity based on the Debye-Callaway approximation.[4, 5] In this model, the lattice thermal conductivity can be written as

$$\kappa_L = \frac{k_B}{2\pi^2 v_s}\left(\frac{k_B}{\hbar}\right)^3 T^3 \int_0^{\theta_D/T} \tau_C \frac{x^4 e^x}{\left(e^x - 1\right)^2} dx \tag{13}$$

The phonon relaxation rate τ_C^{-1} can be determined by combining various scattering processes:

$$\tau_C^{-1} = \tau_B^{-1} + \tau_{PD}^{-1} + \tau_U^{-1} + \tau_{EP}^{-1} \tag{14}$$

where τ_B, τ_{PD}, τ_U, and τ_{EP} are relaxation times for boundary scattering, point defect scattering, Umklapp process, and electron-phonon (*EP*) scattering, respectively. The boundary scattering rate is temperature and frequency independent and can be represented by

$$\tau_B^{-1} = \frac{v_s}{L} \tag{15}$$

where L is the average grain size. The point defect scattering rate is frequency dependent, having a strong frequency dependence

$$\tau_{PD}^{-1} = A\omega^4 \tag{16}$$

where A is a material dependent point defect prefector. Umklapp processes are characterized by a relaxation rate proposed by Glassbrenner and Slack (GS)[6] with

$$\tau_U^{-1} = B\omega^2 T e^{-\theta_D/3T} \tag{17}$$

where B is the Umklapp prefactor. The electron-phonon scattering rate is frequency dependent, having a frequency dependence

$$\tau_{EP}^{-1} = C\omega^2 \tag{18}$$

where C is the electron-phonon scattering prefactor.

Table S3. Fitting parameters for the lattice thermal conductivity of $Ti(Fe_{0.5}Co_{0.25}Cu_{0.25})Sb$.

Fitting parameters	Values
L (μm)	0.66
A (10^{-42} s^{-3})	8.45
B (10^{-18} s K^{-1})	1.21
C (10^{-18} s)	1.15
v_s (m s^{-1})	3445
Θ_D (K)	395

Supplementary section 3

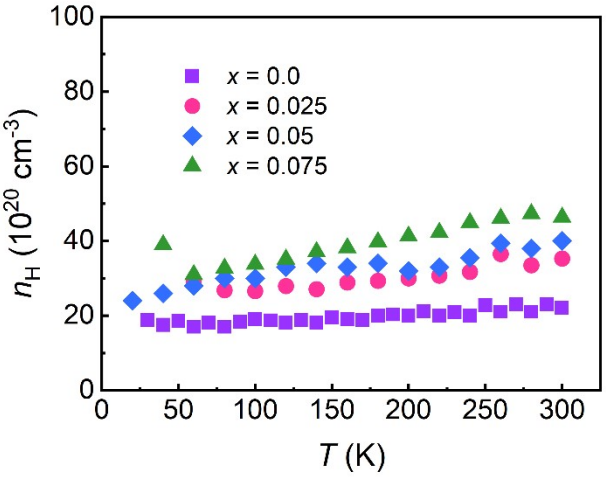

Fig. S5 Hall carrier concentrations of Ti($Fe_{0.5+x}Co_{0.25}Cu_{0.25-x}$)Sb ($x$ = 0, 0.025, 0.05, and 0.075) samples as a function of temperature. The almost temperature independent carrier concentration indicates a heavily doped semiconductor character of these samples.

References

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3 D. G. Cahill, S. K. Watson and R. O. Pohl, *Phys. Rev. B*, 1992, **46**, 6131-6140.

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