Boosting thermoelectric performance of Yb filled skutterudites through incorporation of YSb nanoprecipitates

Dandan Qin [1, *], Wenjing Shi [2], Xin Wang [1], Cunlei Zou [1], Chun Shang [1], Xiangcheng Cui [1], Huijun Kang [3], Yunzhuo Lu [1,*], Jiehe Sui [2,*]

[1] *School of Materials Science and Engineering, Dalian Jiaotong University, Dalian 116028, China*

[2] *State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Harbin 150001, China*

[3] *Key Laboratory of Solidification Control and Digital Preparation Technology (Liaoning Province), School of Materials Science and Engineering, Dalian University of Technology, Dalian 116024, China*

* *To whom correspondence should be addressed. E-mail: qindandan@djtu.edu.cn (Dandan Qin), luyz@djtu.edu.cn (Yunzhuo Lu), suijiehe@hit.edu.cn (Jiehe Sui)*

S-I: Materials and Methods

Sample synthesis: Starting materials including Y piece (99.9%, Alfa Aesar), Ce ingot (99.8%, Alfa Aesar), Co piece (99.95%, Alfa Aesar), Sb ball (99.999%, Alfa Aesar) were firstly weighted according to stoichiometric $Y_{0.05}Yb_xCo_4Sb_{12}$ (x = 0.15, 0.2, 0.25, 0.3) and $Yb_{0.2}Co_4Sb_{12}$, then sealed in the silica tubes under vacuum. All the procedure mentioned above were carried out in a glove box with Ar atmosphere. The sealed tubes were then transmitted to a box furnace and slowly heated to 1423 K in 20 h, soaked at the fixed temperature for 3 h, and then furnace cooled to the room temperature. The reacted ingots were put in the cleaned quartz tubes with a fine nozzle, which were induction-molten and then injected on the cool copper wheel with a rotating speed of 50 m s^{-1} under the high-purity Ar atmosphere. The obtained ribbons were ground into fine powders and then were densified by the hot-press method at 1023 K for 1 h with an axial pressure of 90 MPa under vacuum of 5×10^{-3} Pa.

Microstructure characterization: The phase structures are determined using a

PANalyticalX'Pert Pro X-ray diffractometer with Cu $K\alpha$ radiation (λ=1.5418 Å). The morphology and actual composition are analyzed by a HELIOS Nanolab 600i scanning electronic microscope (SEM) with the energy-dispersive X-ray spectroscopy (EDS).

Properties characterization: The sintered bulk pellet is cut into bar with dimension of $2 \times 2 \times 12$ mm^3 for the electrical resistivity and Seebeck coefficient measurement on a system (CTA) under low-pressure helium atmosphere from 300 K to 873 K. The thermal conductivity κ can be calculated according to the relationship $\kappa = D\rho C_p$, where D is thermal diffusivity coefficient, ρ is the density, and C_p is specific capacity. Disk with diameter of 12.7 mm and thickness of 1.5 mm is prepared to measure the thermal diffusivity coefficient D using laser flash analysis method (Netzsch LFA 427) under a continuous nitrogen flow from 300 K to 873 K. The density is determined by Archimedes method, and relative densities of all samples are higher than 96%. The C_p is calculated using Dulong-Petit relationship. The Hall coefficient (R_H) is obtained using the van der Pauw technique with a reversible magnetic field of 1.5 T. The carrier concentration (n_H) and the carrier mobility (μ_H) are calculated by $n_H = 1/eR_H$ and $\mu_H = \sigma R_H$, respectively.

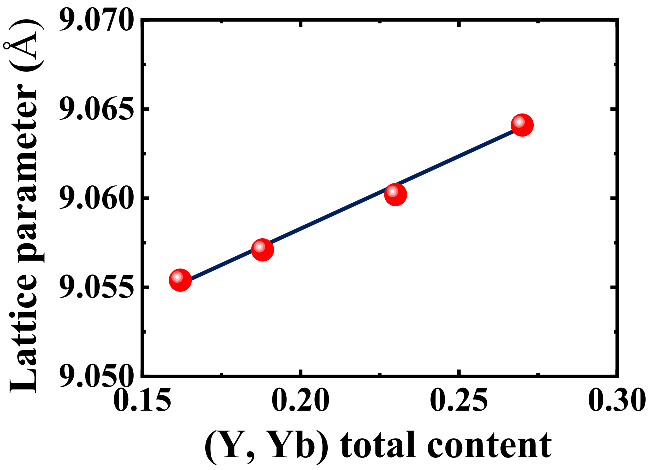

Figure S1. The (Y, Yb) total content dependent lattice parameter.

Table S1. The actual filling fraction for Y and Yb elements, and lattice parameter for $Y_{0.05}Yb_xCo_4Sb_{12}$ and $Yb_{0.2}Co_4Sb_{12}$ alloys.

Nominal composition	Actual Y content	Actual Yb content	Lattice parameter (Å)	Density (g cm^{-3})
$Y_{0.05}Yb_{0.15}Co_4Sb_{12}$	0.032	0.13	9.0554	7.56

$Y_{0.05}Yb_{0.2}Co_4Sb_{12}$	0.003	0.18	9.0571	7.57
$Y_{0.05}Yb_{0.25}Co_4Sb_{12}$	0.000	0.23	9.0602	7.54
$Y_{0.05}Yb_{0.3}Co_4Sb_{12}$	0.000	0.27	9.0641	7.56
$Yb_{0.2}Co_4Sb_{12}$	—	0.175	9.0697	7.55

The calculation of κ_l with Callaway mode

Based on the Callaway mode, the κ_l can be expressed as [1-3]:

$$\kappa_l = \frac{k_B}{2\pi^2 \upsilon}\left(\frac{k_B T}{\hbar}\right)^3 \int_0^{\theta_D/T} \tau_c \frac{x^4 e^x}{\left(e^x - 1\right)^2} dx \tag{1}$$

where k_B is the Boltzmann constant, $\hbar$ is the Plank's reduced constant, υ is the average sound (phonon-group) velocity, x is the usual dimensionless variable $\hbar\omega/k_BT$ and τ_c is the combined relaxation time, and θ_D is the Debye temperature. For skutterudites

$$\theta_D = \beta(M\delta^3)^{-1/2} \tag{2}$$

where β is a function of elastic constants, M the average atom weight, and δ^3 the volume.

For the present case, three phonon scattering mechanisms including boundary scattering, point-defect scattering, and phonon-phonon scattering are considered to calculate the frequency-dependent relaxation time,

$$\tau_c^{-1} = \frac{\upsilon}{l} + A\omega^4 + B\omega^2 T e^{\left(-\frac{\theta_D}{3T}\right)} \tag{3}$$

where l is the average grain size, the coefficients A and B are fitting parameters. The values of relevant parameters are shown in **Table S2** and **S3**. Compared with the pristine sample, the samples with YSb nanoparticles exhibit lower κ_l. Therefore, it is plausible to infer that this reduction in κ_l can be ascribed to the phonon scattering caused by the nanoparticles. The nanoparticles' contribution to the relaxation time τ_{NP}^{-1} is estimated using a Matthiessen-type interpolation between the scattering regimes of the long and short wavelengths [4-6]

$$\tau_{NP}^{-1} = \upsilon\,(\sigma_s^{-1} + \sigma_l^{-1})\,V_P \tag{4}$$

$$\sigma_s = 2\pi R^2 \tag{5}$$

$$\sigma_l = \frac{4}{9}\pi R^2 \left(\frac{\Delta D}{D}\right)\left(\frac{\omega R}{\upsilon}\right)^4 \tag{6}$$

where V_P is the density of nanoparticles, σ_s and σ_l are the cross-section limits, R is the average size of the particles, D is the corresponding mass density, ΔD is the mass density difference between the nanoscale particle and the matrix, ω is the phonon frequency, respectively. Therefore, the combined phonon relaxation field should be written as

$$\tau_c^{-1} = \frac{\upsilon}{l} + A\omega^4 + B\omega^2 T e^{\left(-\frac{\theta_D}{3T}\right)} + \upsilon\left(\sigma_s^{-1} + \sigma_l^{-1}\right)V_P \tag{7}$$

Table S2. Input parameters for calculation of relaxation time of phonon scattering for $Y_{0.05}Yb_{0.2}Co_4Sb_{12}$ composites.

L (μm)	θ_D (K)	υ (m/s)	R (nm)	D_n (gcm^{-3})	D_m (gcm^{-3})	ΔD (gcm^{-3})
0.5	287	3000	25	5.97	7.6	1.77

Table S3. Values of lattice thermal conductivity fit parameters for $Y_{0.05}Yb_{0.2}Co_4Sb_{12}$ and $Yb_{0.2}Co_4Sb_{12}$ alloys.

Composition	A (10^{-43} s^3)	B (10^{-17} s/K)	V_p (10^{21}m^{-3})
$Yb_{0.2}Co_4Sb_{12}$	26.67	0.98	0
$Y_{0.05}Yb_{0.2}Co_4Sb_{12}$	26.15	1.08	6.12

Reference:

[1] G. S. Yang, R. M. Niu, L. N. Sang, X. Z. Liao, D. R. G. Mitchell, N. Ye, J. Pei, J. F. Li, X. L. Wang. *Advanced Energy Materials* 2020, 10.

[2] H. L. Zhuang, H. H. Hu, J. Pei, B. Su, J. W. Li, Y. L. Jiang, Z. R. Han, J. F. Li. *Energy & Environmental Science* 2022, 15, 2039-2048.

[3] J. Callaway, H. C. Von Baeyer. *Physical Review* 1960, 120, 1149-1154.

[4] H. Jiaqing, S. N. Girard, Z. Jin-Cheng, Z. Lidong, M. G. Kanatzidis, V. P. Dravid. *Advanced materials* 2012, 24, 4440-4444.

[5] H. Jiaqing, A. John, M. G. Kanatzidis, V. P. Dravid. *Nano Lett* 2012, 12, 343.

[6] C. B. Vining. *Journal of Applied Physics* 1991, 69, 331-330.