# Electronic Supplementary Information

Large mass field fluctuation and lattice anharmonicity effects promote thermoelectric and mechanical performances in NbFeSb half-heusler alloys via Ti/Zr/Hf stepwise doping

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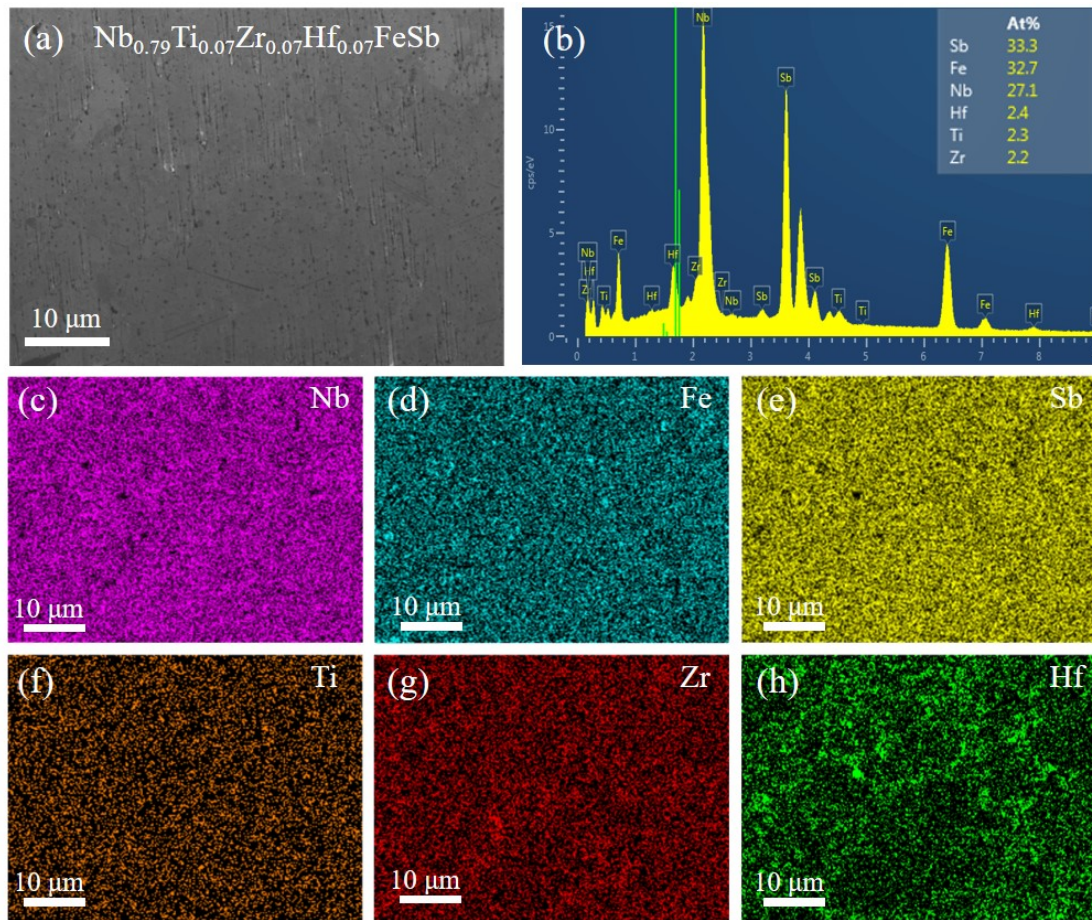
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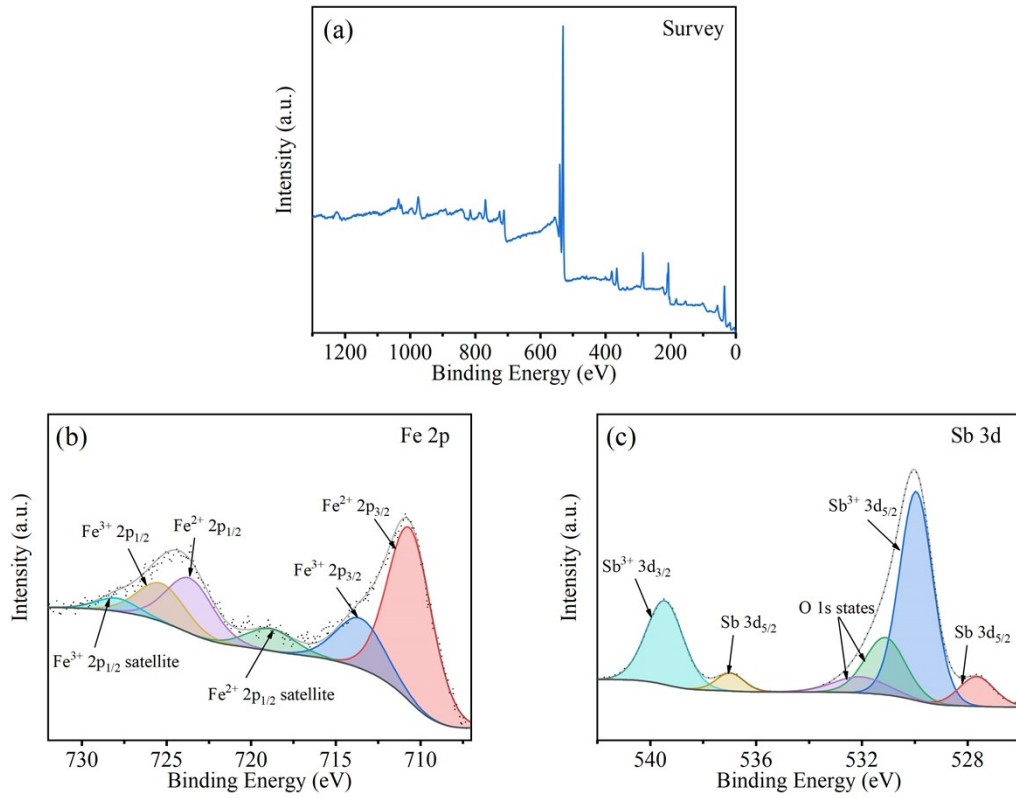
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Supplementary Figures
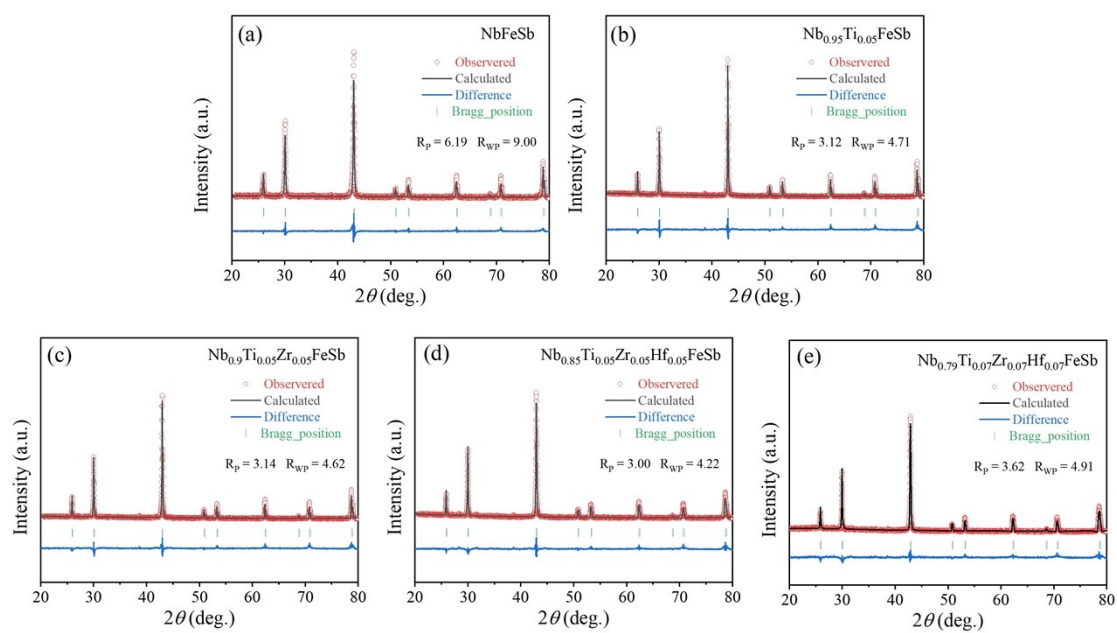
Fig. S1. Rietveld refinement result of the $Nb_{1-x-y-z}Ti_xZr_yHf_zFeSb$ (x, y, z = 0, 0.05, 0.07) sample.

Fig. S2. (a) Scanning electron microscopy (SEM) image of a polished surface of the Nb$_{0.79}$Ti$_{0.07}$Zr$_{0.07}$Hf$_{0.07}$FeSb sample. (b) Corresponding energy dispersive spectrometry (EDS) and mappings of (c) Nb, (d) Fe, (e) Sb, (f) Ti, (g) Zr, (h) Hf.

Fig. S3. X-ray photoelectron spectra (XPS) of the $Nb_{0.82}Ti_{0.06}Zr_{0.06}Hf_{0.06}FeSb$ sample for (a) full spectrum, (b) Fe 2p, (c) Sb 3d.
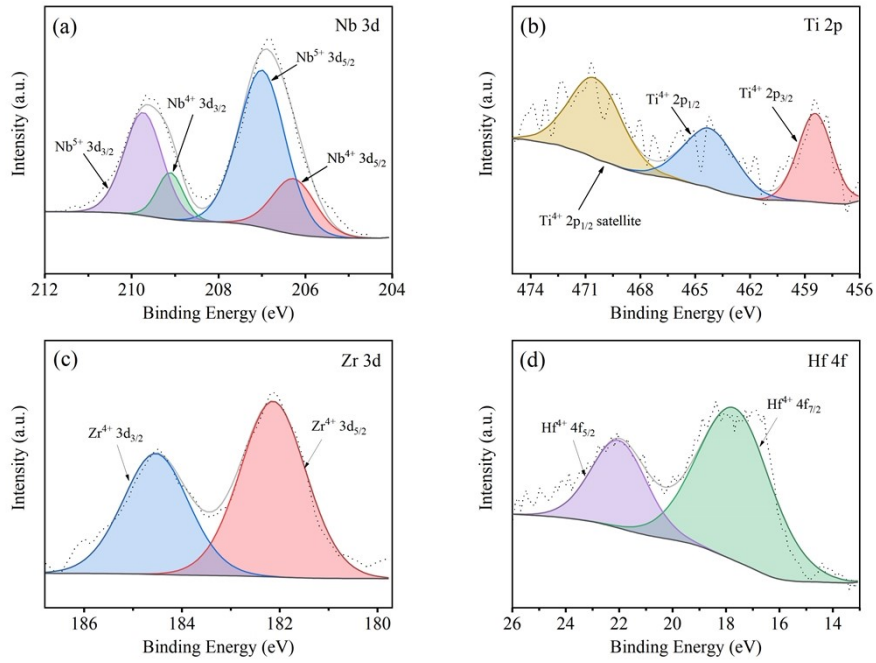
Fig S4. X-ray photoelectron spectra (XPS) of the $Nb_{0.82}Ti_{0.06}Zr_{0.06}Hf_{0.06}FeSb$ sample for (a) Nb 3d, (b) Ti 2p, (c) Zr 3d, (d) Hf 4f.
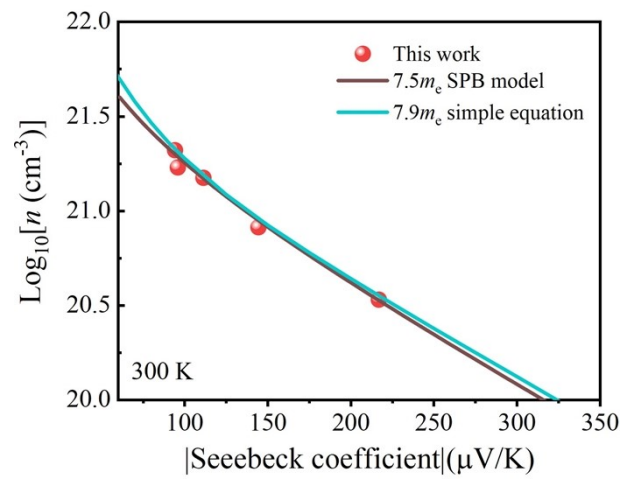
Fig. S5. The |S|-dependent $\text{Log}_{10}(n)$ calculated by the simple Equation, the SPB model.
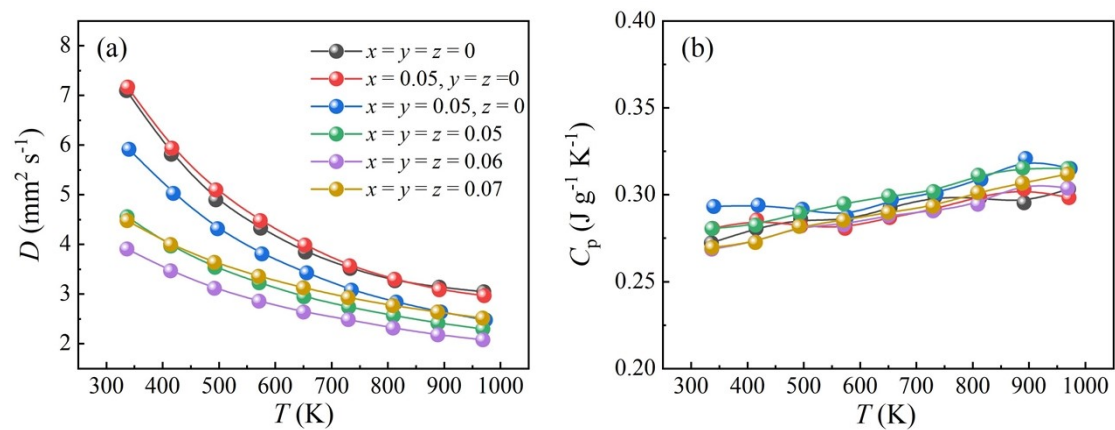
Fig. S6. Temperature-dependent (a) thermal diffusivity D and (b) heat capacity C_p
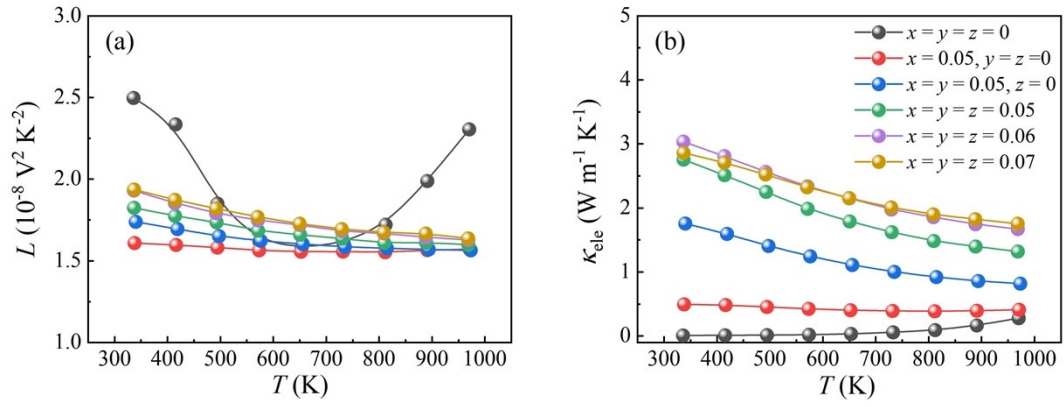
Fig. S7. (a) Calculated Lorentz number using the SPB model and (b) Electronic thermal conductivity for the $Nb_{1-x-y-z}Ti_xZr_yHf_zFeSb$ ($x, y, z = 0, 0.05, 0.06, 0.07$) samples.
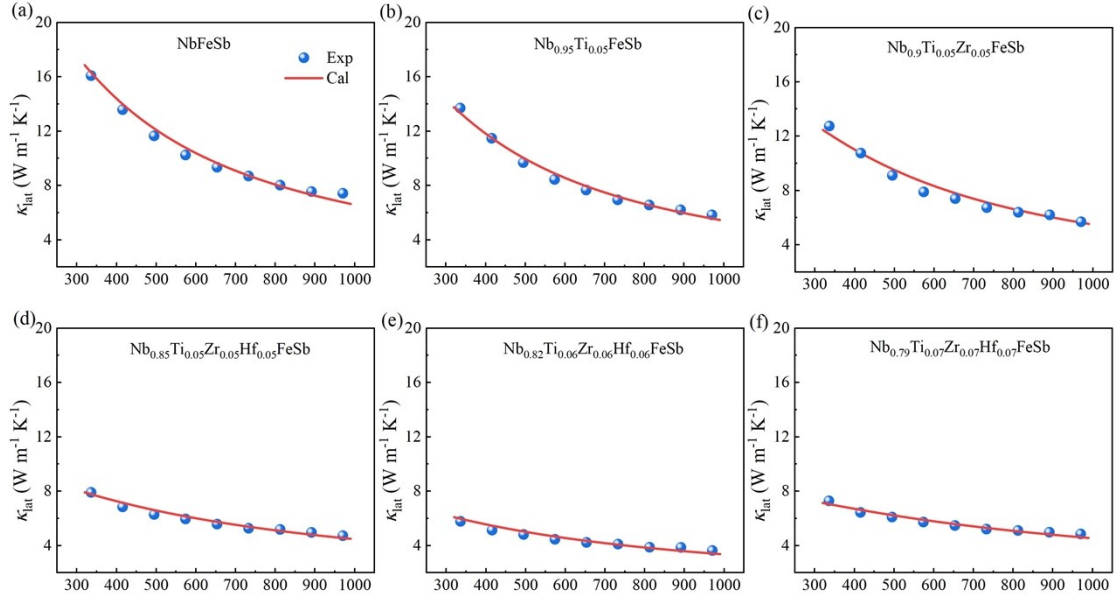
Fig. S8. The temperature dependence of lattice thermal conductivity of $Nb_{1-x-y-z}Ti_xZr_yHf_zFeSb$ (x, y,

z = 0, 0.05, 0.06, 0.07) sample and fitting by Debye-Callaway model.
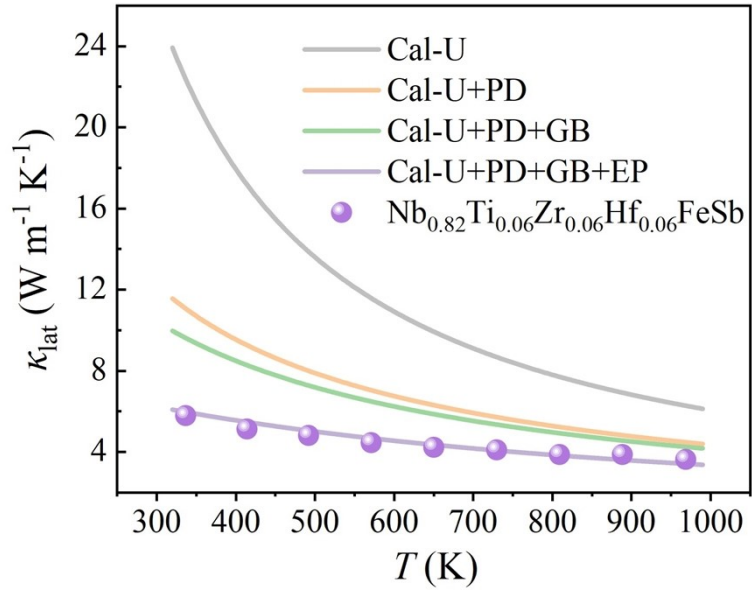
Fig. S9. Experimental and theoretical curves for κ_{lat} of the samples of $x = y = z = 0.06$.

(a)

$Nb_{0.79}Ti_{0.07}Zr_{0.07}Hf_{0.07}FeSb$

♦ Hf_2Fe

Intensity (a.u.)

Sample 2

Sample 1

PDF#51-1242 NbFeSb

20   30   40   50   60   70   80

2θ (deg.)
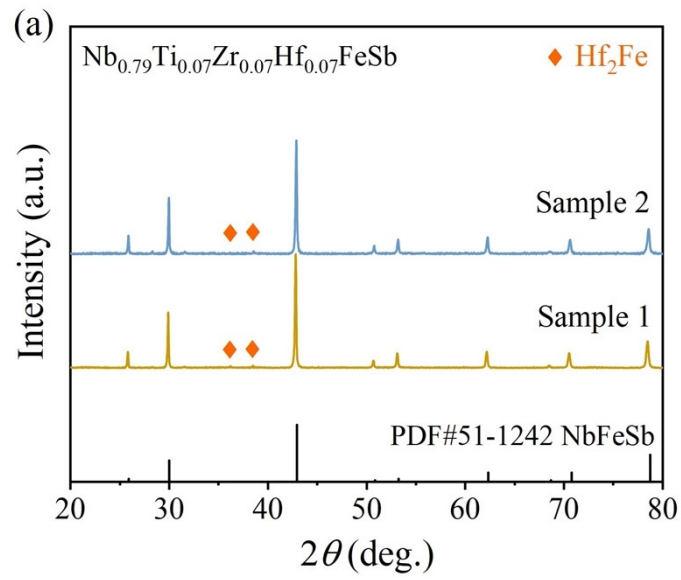
Fig. S10. Powder XRD patterns of $Nb_{0.79}Ti_{0.07}Zr_{0.07}Hf_{0.07}FeSb$ sample 1 and 2.

Supplementary Tables

Table S1. The mixing entropy, mixing enthalpy and mixing Gibbs free energy at 1123 K for the $Nb_{1-x-y-z}Ti_xZr_yHf_zFeSb$ (x, y, z = 0, 0.05, 0.06, 0.07) samples.

x, y, z	ΔS (J mol^{-1} K^{-1})	ΔH (KJ mol^{-1})	ΔG (KJ mol^{-1})
$x = y = z = 0$	0	0	0
$x = 0.05, y = z = 0$	1.65	0.38	-1.47
$x = y = 0.05, z = 0$	3.28	1.08	-2.60
$x = y = z = 0.05$	4.88	1.74	-3.74
$x = y = z = 0.06$	5.56	1.85	-4.40
$x = y = z = 0.07$	6.19	1.94	-5.01

Table S2. The Rietveld refinement details of $Nb_{1-x-y-z}Ti_xZr_yHf_zFeSb$ (x, y, z = 0, 0.05, 0.06, 0.07) samples.

x, y, z	R_p	R_{wp}	χ^2	a (Å)
$x = y = z = 0$	6.19	9.00	4.06	5.9534
$x = 0.05, y = z = 0$	3.12	4.71	4.72	5.9462
$x = y = 0.05, z = 0$	3.14	4.62	4.44	5.9522
$x = y = z = 0.05$	3.00	4.22	4.06	5.9578
$x = y = z = 0.06$	2.80	3.81	2.83	5.9656
$x = y = z = 0.07$	2.92	3.98	2.93	5.9677

Table S3. Actual and nominal composition of the $Nb_{1-x-y-z}Ti_xZr_yHf_zFeSb$ (x, y, z = 0, 0.05, 0.06, 0.07) samples.

Nominal composition	Actual composition	SEM/EDS composition (at %)					
		Nb	Ti	Zr	Hf	Fe	Sb
$x = y = z = 0$	$Nb_{1.02}Fe_{0.98}Sb$	34.3				32.8	33.0
$x = 0.05, y = z = 0$	$Nb_{0.97}Ti_{0.05}Fe_{0.98}Sb_{0.99}$	32.4	1.7			32.8	33.0
$x = y = 0.05, z = 0$	$Nb_{0.92}Ti_{0.05}Zr_{0.05}Fe_{0.99}Sb_{0.99}$	30.7	1.6	1.8		33.1	32.9
$x = y = z = 0.05$	$Nb_{0.88}Ti_{0.05}Zr_{0.05}Hf_{0.05}Fe_{0.96}Sb$	29.6	1.8	1.6	1.7	32.1	33.3
$x = y = z = 0.06$	$Nb_{0.86}Ti_{0.06}Zr_{0.05}Hf_{0.06}Fe_{0.98}Sb$	28.5	1.9	1.8	2.1	32.6	33.1
$x = y = z = 0.07$	$Nb_{0.81}Ti_{0.07}Zr_{0.07}Hf_{0.07}Fe_{0.98}Sb$	27.1	2.3	2.2	2.4	32.7	33.3

Table S4. The fitting parameters for the $Nb_{1-x-y-z}Ti_xZr_yHf_zFeSb$ (x, y, z = 0, 0.05, 0.06, 0.07) samples.

Nominal composition	ε ($G=0$)	A (10^{-43} s^3)	B (10^{-18} s/K)	C (10^{-16} s)
$x = y = z = 0$	1.45	0	1.45	2.50
$x = 0.05, y = z = 0$	30.7	1.01	1.80	2.70
$x = y = 0.05, z = 0$	33.9	2.36	1.65	3.00
$x = y = z = 0.05$	36.3	7.62	1.40	3.20
$x = y = z = 0.06$	28.5	8.37	1.95	3.60
$x = y = z = 0.07$	33.3	11.9	1.10	4.00

Table S5. The atom radius and mass of Nb, Ti, Zr, Hf element.

	Nb	Ti	Zr	Hf
Radius (pm)	146	147	160	159
Mass (g cm^{-1})	92.91	47.87	91.22	178.49

Table S6. The Young's modulus (E) bulk modulus (K), and compression modulus (E_s) of the Nb$_{1-x-y-}$

$_z$Ti$_x$Zr$_y$Hf$_z$FeSb (x, y, z = 0, 0.05, 0.06, 0.07) samples.

x, y, z	E (GPa)	K (GPa)	E_s (GPa)
$x = y = z = 0$	261.0	133.7	25.5
$x = 0.05, y = z = 0$	293.0	157.7	38.4
$x = y = 0.05, z = 0$	295.4	164.2	39.2
$x = y = z = 0.05$	267.3	151.9	35.9
$x = y = z = 0.06$	283.1	148.7	31.8
$x = y = z = 0.07$	258.6	142.9	37.5

Modeling of lattice thermal conductivity

Based on the Debye-Callaway theory, the κ_{lat} can be expressed as:

$$\kappa_L = \int_0^{\frac{\theta_D}{T}} \kappa_S(x)dx = \frac{k_B}{2\pi^2 v_a}\left(\frac{k_B}{\hbar}\right)^3 T^3 \int_0^{\theta_D/T} \tau(x)\frac{x^4 e^x}{(e^x - 1)^2}dx$$

(1)

where $x = \hbar w/(k_B T)$ is the reduced phonon frequency, k_B, $\hbar$, θ_D are the Boltzmann

constant, the reduced Planck constant, the Debye temperature, respectively. τ is the sum of the relaxation times from different scattering mechanisms. Here, we mainly focus on the phonon-phonon Umklapp process (U), the point defect scattering (PD), the grain boundary scattering (GB) and the electro-acoustic coupling (EP).

In this work, τ is expressed as:

$$\tau^{-1} = \tau_{PD}^{-1} + \tau_{U}^{-1} + \tau_{GB}^{-1} + \tau_{EP}^{-1} = A\omega^4 + B\omega^2 T \exp\left(-\frac{\theta_D}{3T}\right) + \frac{v}{d} + C\omega^2 \tag{2}$$

Where d is the grain size and v/d represents boundary scattering. A is the pre-factor of point defect (PD) scattering relaxation time due to Ti doping. B is the prefactor of phonon-phonon Umklapp (U) scattering relaxation time, and C is the prefactor of electron phonon (EP) scattering relaxation time. For the polycrystalline pure FeNbSb, the dominated phonon scattering mechanism should be the phonon-phonon U scattering and boundary scattering. Therefore, through fitting the κ_l of polycrystalline FeNbSb, we can obtain the prefactor B of U scattering relaxation time. Scattering by point defects arises from both mass and strain differences within the lattice.

In the simple case of alloying:

$$\tau_{PD}^{-1} = \frac{V\omega^4}{4\pi v_a^3}(\Gamma_m + \Gamma_s) \tag{3}$$

Where V is the volume per atom, v_a is the average velocity. Γ_m and Γ_s are the disorder scattering parameters of mass and strain field fluctuation, respectively. We can obtain the prefactor A of point defect (PD) scattering relaxation time, the mass fluctuation (Γ_m) and strain field term (Γ_s) parameter are then given by

$$\Gamma_m = \frac{\sum_{i=1}^{n} c_i \left(\frac{\overline{M}_i}{\overline{\overline{M}}}\right)^2 f_i^1 f_i^2 \left(\frac{M_i^1 - M_i^2}{\overline{r}_i}\right)}{\left(\sum_{i=1}^{n} c_i\right)} \quad (4) \qquad \Gamma_s = \frac{\sum_{i=1}^{n} c_i \left(\frac{\overline{M}_i}{\overline{\overline{M}}}\right)^2 f_i^1 f_i^2 \varepsilon \left(\frac{r_i^1 - r_i^2}{\overline{r}_i}\right)}{\left(\sum_{i=1}^{n} c_i\right)} \quad (5)$$

where $\overline{M}_i$ is the average atomic mass of the i of sublattice, the $\overline{\overline{M}}$ is the average atomic mass of the compound, f_i is the fractional occupant, r_i is the radius of atom, ε is the phenomenological parameter which is a function of the Grüneisen parameter. The mass fluctuation term and the strain field term would be jointly determined by four or five parameters of $\overline{M}_i$, $\overline{\overline{M}}$, f_i, r_i, ε, respectively.

For $Nb_{1-x-y-z}Ti_xZr_yHf_zFeSb$ (x, y, z = 0, 0.05, 0.06, 0.07) samples, the existing phonon scattering sources should be the U process, boundary, point defects and electron-phonon interaction. The boundary scattering and point defects scattering relaxation times can be calculated independently. Therefore, through fitting the κ_l of corresponding sample, the prefactor C of the EP scattering relaxation time can be obtained.

Calculation of bulk modulus

The bulk modulus (K) has been calculated using the following equations:

$$K = \frac{E}{3(1 - 2v_p)} \quad (6)$$

$$E = \frac{\rho v_a^2 (3v_l^2 - 4v_t^2)}{(v_l^2 - v_t^2)} \quad (7)$$

$$v_p = \frac{1 - 2(v_t/v_l)^2}{2 - 2(v_t/v_l)^2} \quad (8)$$

Where E, v_p, v_a, v_l and v_t are the Young's modulus, Poisson's ratio, average sound

velocity, longitudinal sound velocity and transverse sound velocity, respectively.