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Supplementary Material

18-electron Half-Heusler Compound $Ti_{0.75}NiSb$ with Intrinsic Ti Vacancies as Promising Thermoelectric Materials

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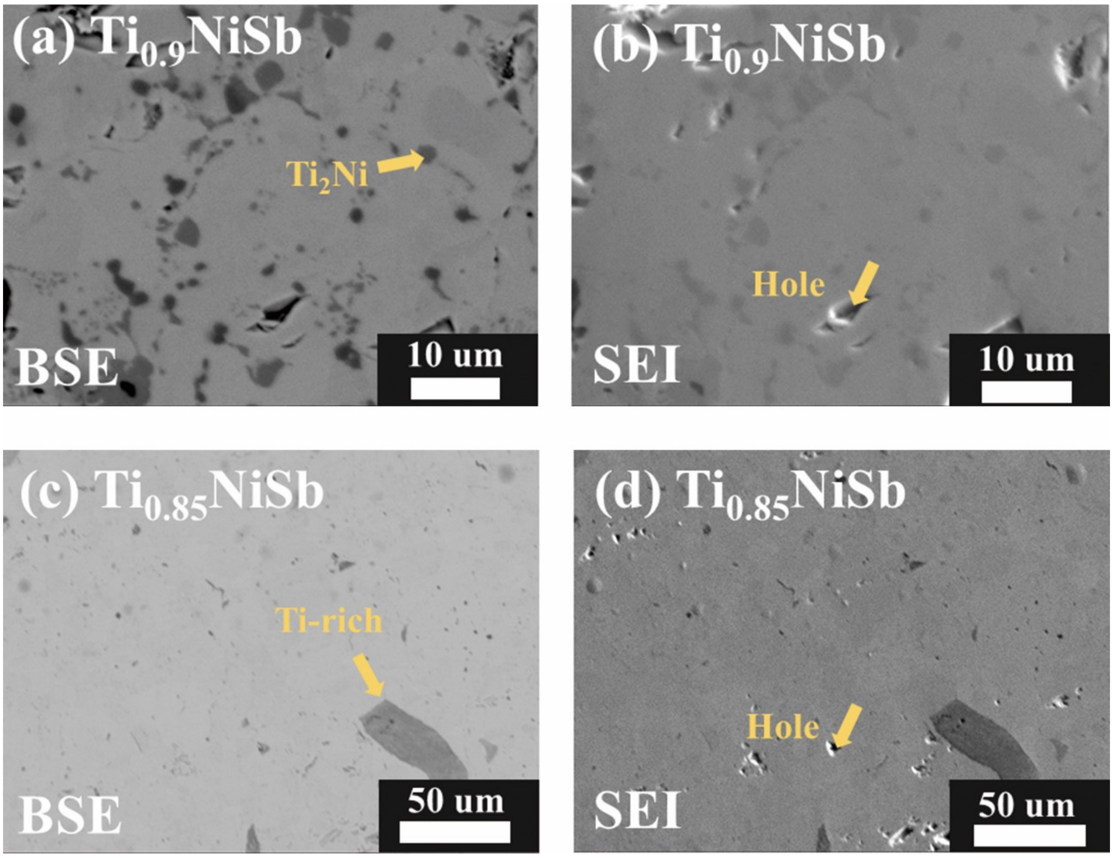
EPMA characterizations of $Ti_{1-x}NiSb$ (x=0.1, 0.15, 0.2, 0.225, 0.3) sample



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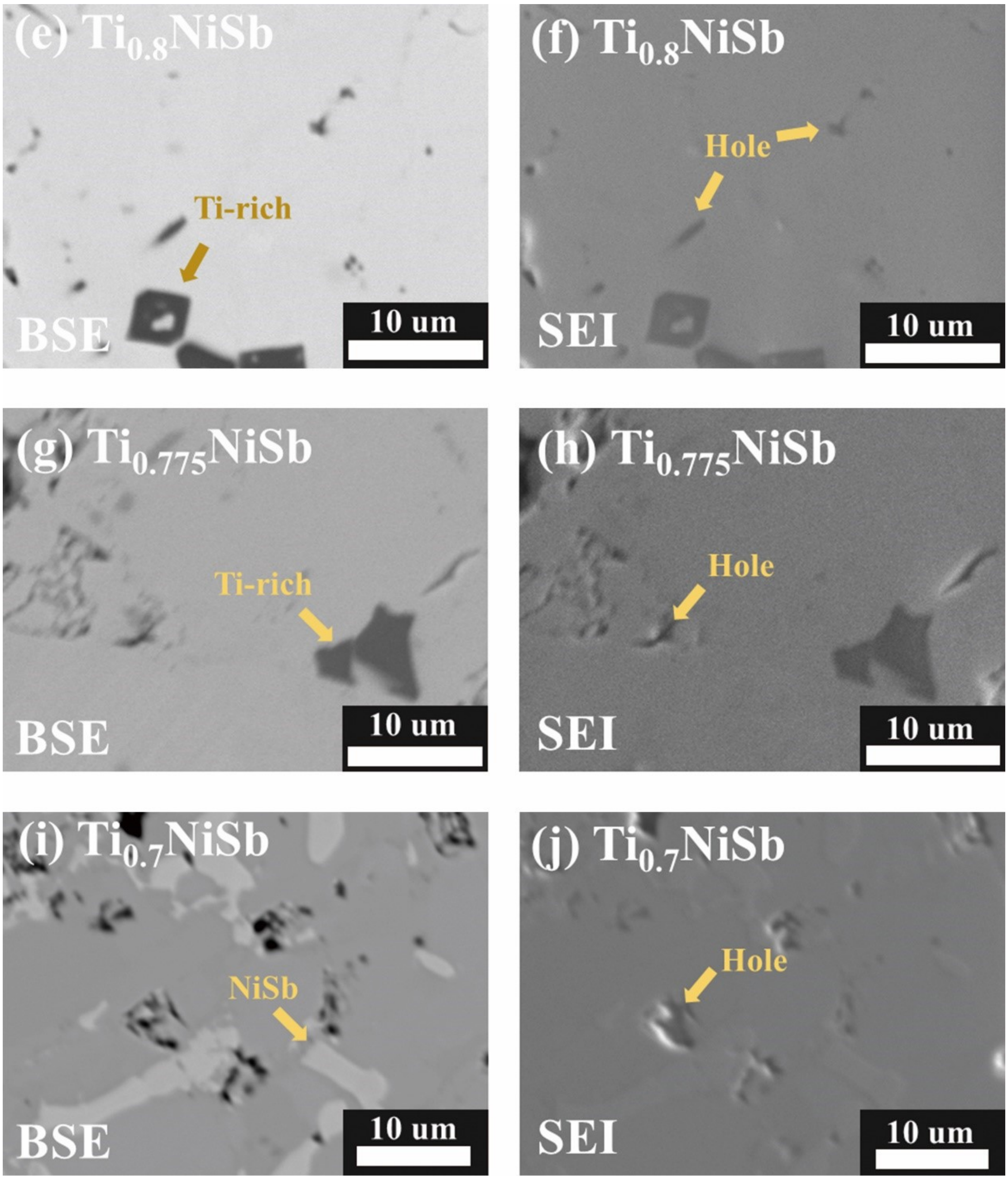

Figure S1. (a-j) BSE and SEI images of the polished surfaces of $Ti_{1-x}NiSb$ (x=0.1, 0.15, 0.2, 0.225, 0.3) samples, respectively.

As shown in Figure S1, in $Ti_{0.9}NiSb$, the second phase is Ti_2Ni. In $Ti_{0.85}NiSb$, $Ti_{0.8}NiSb$, $Ti_{0.775}NiSb$, the second phases are the Ti-rich one. In $Ti_{0.7}NiSb$, the second phase is NiSb.

Electric transport model

Based on the SPB model, the Seebeck coefficient (α), hall concentration (n_H), Lorenz number (L) can be expressed as follow:

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

$$n_H = \frac{(2m_d^* k_B T)^{3/2}}{3\pi^2 h^3} \frac{(r+3/2)^2 F_{r+1/2}^2(\eta)}{(2r+3/2)F_{2r+1/2}(\eta)} \tag{2}$$

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

where k_B is Boltzmann constant, e is carrier charge, r is scattering parameter, $F_i(\eta)$ is Fermi-Dirac integral, η is reduced Fermi level $E_f/(k_B T)$, m_d^* is the effective mass, h is Planck constant.

Prediction of the thermoelectric properties of $Ti_{0.75}NiSb$

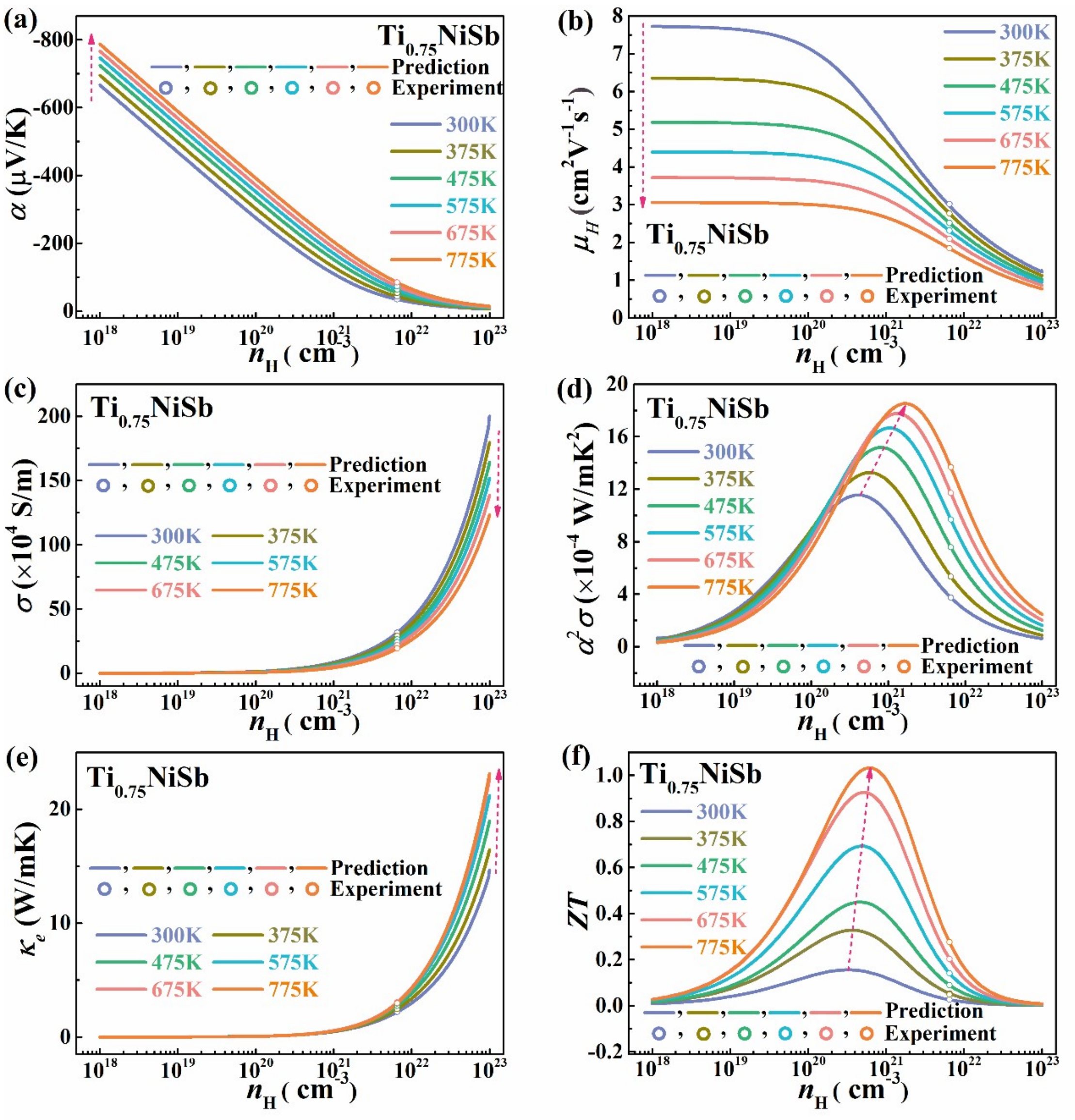

Figure S2. Experimental and calculated Seebeck coefficient(a), hall mobility(b), electrical conductivity(c), power factors(d), electronic thermal conductivity(e), *ZT*(f) as a function of Hall carrier concentration for $Ti_{0.75}NiSb$.

Thermal Stability Test of $Ti_{0.75}NiSb$

TE performance cycle test on $Ti_{0.75}NiSb$. And the results are shown below.

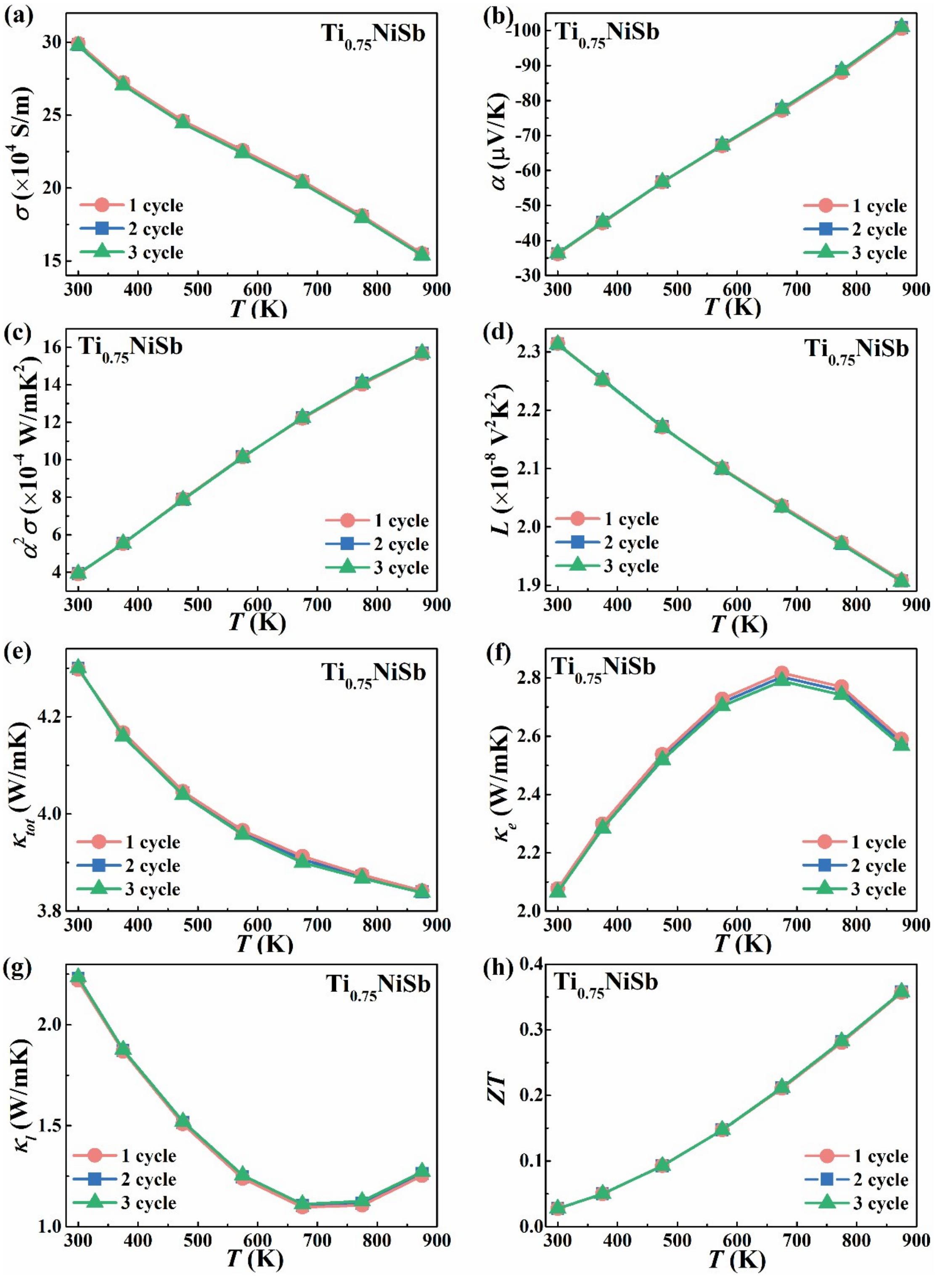

Figure S3. Temperature dependent (a) electrical conductivity, (b) Seebeck coefficient, (c) power factor, (d) Lorenz number, (e) thermal conductivity, (f) electronic thermal conductivity, (g) lattice thermal conductivity lattice thermal conductivity and (h) *ZT* for $Ti_{0.75}NiSb$ samples.

Multiple cycle tests did not significantly affect the TE performance of $Ti_{0.75}NiSb$ which indicates that $Ti_{0.75}NiSb$ has certain thermal stability.

Calculated elastic properties of $Ti_{0.75}NiSb$ compound

The average sound velocity (v_s), bulk modulus (B), shear modulus (G) and Young's modulus (E), Poisson ratio (r), Grüneisen parameter (γ) are given respectively by[1]:

$$v_s = \left[\frac{1}{3}\left(\frac{2}{{v_t}^2} + \frac{1}{{v_l}^2}\right)^{1/3}\right] \quad (4)$$

$$B = \left({v_l}^2 - \frac{4}{3}{v_s}^2\right)\rho \quad (5)$$

$$\theta_D = \left(\frac{h}{k_B}\right)\left(\frac{3N}{4\pi V}\right)^{1/3} v_s \quad (6)$$

$$G = \rho {v_t}^2 \quad (7)$$

$$E = \frac{9BG}{3B+G} = \frac{\rho {v_t}^2(3{v_l}^2 - 4{v_t}^2)}{{v_l}^2 - {v_t}^2} \quad (8)$$

$$v = \frac{1 - 2(v_t/v_l)^2}{2 - 2(v_t/v_l)^2} \quad (9)$$

$$\gamma = \frac{3}{2}\left(\frac{1+r}{2-3r}\right) \quad (10)$$

here, v_l and v_t are longitudinal and transverse sound velocities obtained from ultrasonic measurements, respectively, and ρ represents the density of $Ti_{0.75}NiSb$, h is Planck's constant, k_B is the Boltzmann constant, N is the number of atoms in a unit cell, V is the unit-cell volume.

Table S1. Elastic properties for $Ti_{0.75}NiSb$ at room temperature, including longitudinal (v_l), shear (v_t), average (v_s) sound velocity, shear (G), bulk (B) and Young's (E) modulus, Debye temperature (Θ_D), and Poisson ratio (r), Grüneisen parameter (γ).

	$Ti_{0.75}NiSb$
Longitudinal sound velocity, v_l (ms^{-1})	5301
Shear sound velocity, v_t (ms^{-1})	2873
Average sound velocity, v_s (ms^{-1})	3206
Shear modulus, G (GPa)	59
Bulk modulus, B (GPa)	123
Young's modulus, E (GPa)	153
Debye temperature, θ_D (K)	360
Poisson ratio, v	0.29
Grüneisen parameter, γ	1.72

Supplementary references

1. An, D.; Wang, J.; Zhang, J.*, et al.*, Retarding Ostwald ripening through Gibbs adsorption and interfacial complexions leads to high-performance SnTe thermoelectrics. *Energy & Environmental Science* **2021,** *14* (10), 5469-5479.