Supporting Information

High thermoelectric performance in *p*-type ZnSb upon Zn vacancies: An experimental and theoretical study

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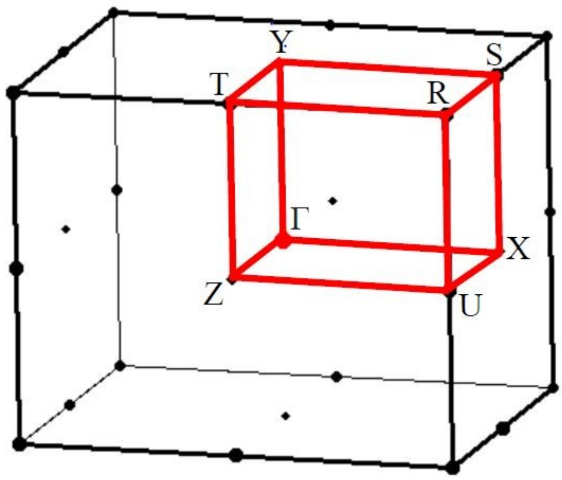


Figure S1. The Brillouin zone of pure ZnSb

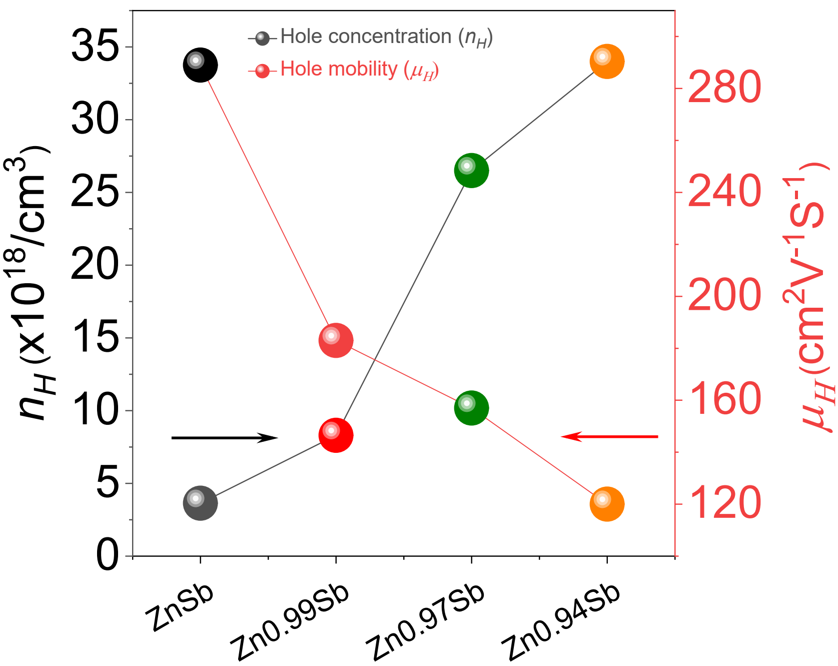


Figure S2. Hall plot of $Zn_{1-x}Sb$ (x = 0, 0.01, 0.03, 0.06) *vs.* n_H and μ_H.

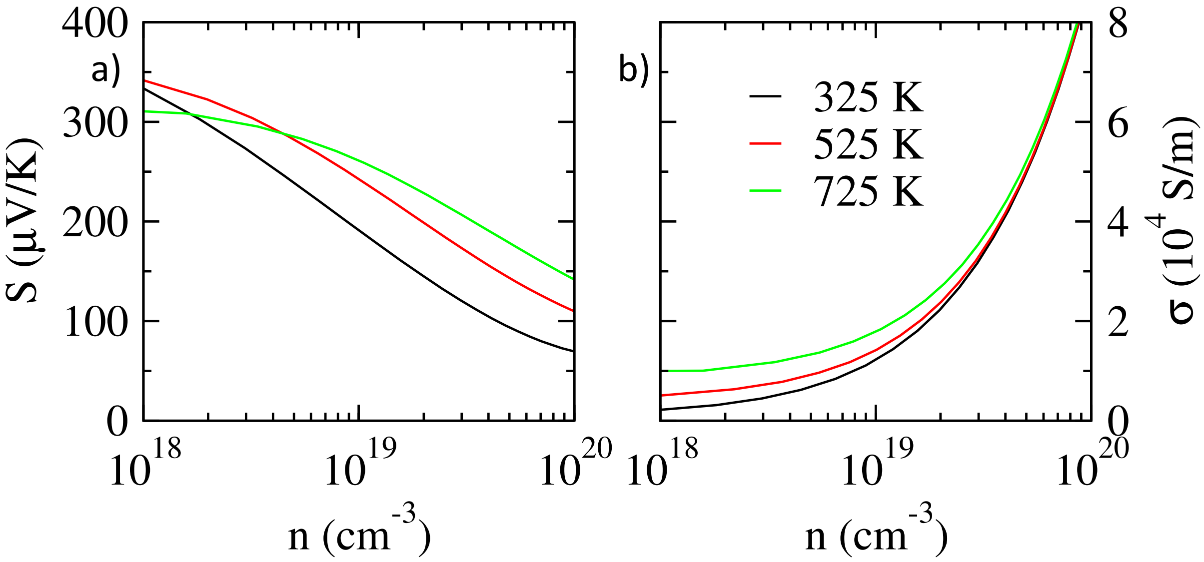


Figure S3. Theoretical DFT studies of (a) S *vs. n* and (b) σ *vs. n*.

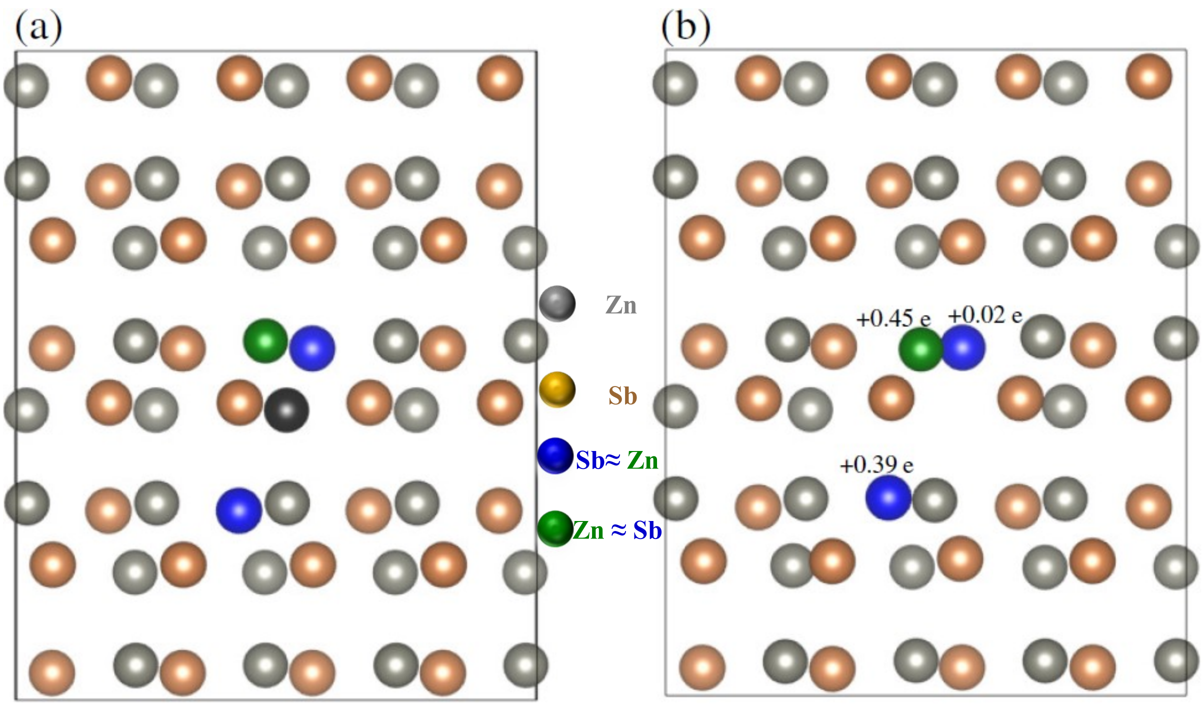
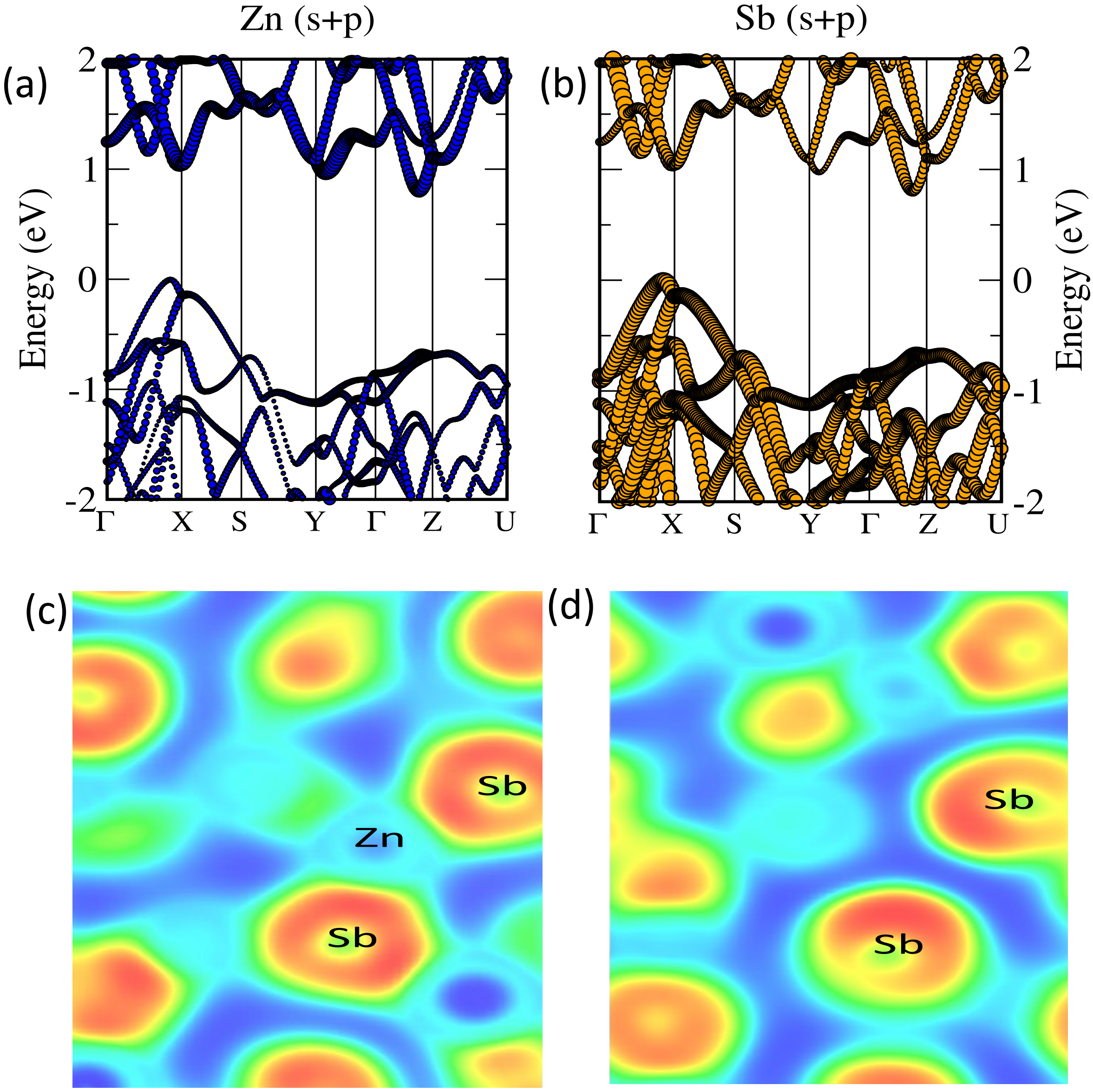


Figure S4. The supercell of 2 x 2 x 1 for (a) ZnSb and (b) $Zn_{0.94}Sb$. Here, plus sign stands for the charge gain. Blue atoms represent the nearest Sb atoms and green is the nearest Zn atom to the vacancy.



Zn (s+p)
Sb (s+p)
(a)
(b)
Energy (eV)
2
1
0
-1
-2
Γ
X
S
Y
Γ
Z
U
(c)
(d)
Sb
Zn
Sb
Sb
Sb

Figure S5 (a) & (b) Electronic structure of Zn (s+p) and Sb (s+p) orbitals shown in E vs. k diagram, (c) Hole density mapping of orthorhombic ZnSb and (d) Hole density map of $Zn_{0.94}Sb$

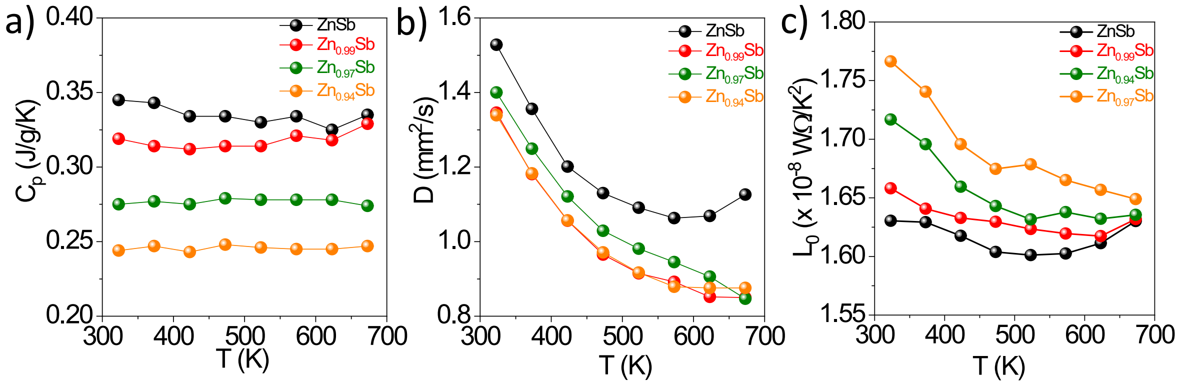


Figure S6. Temperature-dependent (a) Specific heat capacity; (b) Thermal diffusivity and (c) Lorentz number for $Zn_{1-x}Sb$ ($x =$ 0, 0.01, 0.03 and 0.06).

The Lorenz number was calculated using simple parabolic band model with function temperature using following relation,

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

Here, κ_B, η and e for Boltzmann constant, the reduced chemical potential and charge of an electron respectively. Specifically this model assumes that the carriers are scattered by acoustic phonons. The L values can be measured using the Seebeck coefficient values and the relation between the reduced chemical potential and S is given below

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

$$F_i(\eta) = \int_0^{\infty} \frac{\xi^i d\xi}{1 + e^{\xi - \eta}}$$

Where $F_i(\eta)$ fermi integrals of i^{th} order and ξ denotes the reduced carrier energy. Here Figure S6 (c) , depicts the Lorentz number as a function of temperature as calculated from κ_{ele} values.

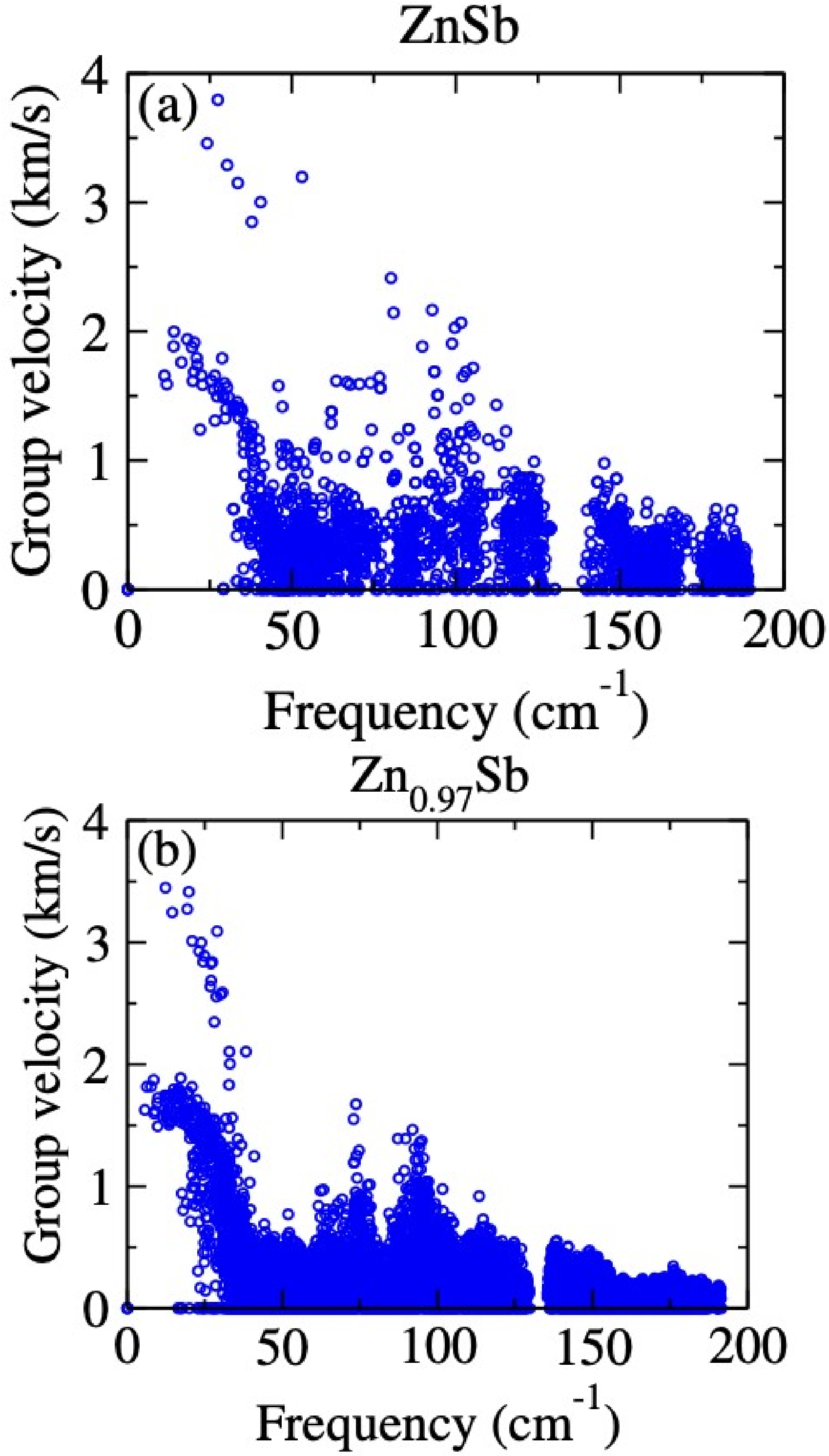


Figure S7. The calculated phonon group velocities (a) ZnSb and (b) $Zn_{0.94}Sb$ as a function of phonon frequency.

The calculation for ZT_{eng}, PF_{eng}, P_d, and η_{max}

The figure of merit, zT, of thermoelectric material is an indefinite indicator for determining the conventional thermoelectric conversion efficiency (η_{max}) because it assumes temperature-independent behavior of S, $\rho = 1/\sigma$, and κ_{total} in the calculations. H. S. Kim et al.[1] recently proposed the term ZT_{eng}, a quantitative measure that assesses the effectiveness of thermoelectric (TE) conversion. ZT_{eng} takes into account the temperature-dependent properties of TE materials. This metric is especially valuable for precisely evaluating the thermoelectric efficiency of material when there is a substantial temperature difference between the cold and hot side of the thermoelectric legs. Here, $(PF)_{eng}$, $(ZT)_{eng}$, P_d, and η_{max} are calculated using the following relations,

(i) $$zT_{avg} = \frac{\frac{S^2(T)}{\rho(T)}}{\kappa(T)} * T$$

(ii) $$(⟦PF)⟧_{eng} = \frac{\left(\int_{T_C}^{T_H} S(T)dT\right)^2}{\int_{T_C}^{T_H} \rho(T)dT} \Delta T$$ in W/mK^2

Where ρ(T) represents the resistivity, S(T) represents the Seebeck coefficient, κ(T) represents the total thermal conductivity, η_C represents the Carnot efficiency, and α represents a dimensionless intensity component of the Thomson coefficient.

(iii) $$(ZT)_{eng} = \frac{(⟦PF)⟧_{eng}}{\int_{T_C}^{T_H} \kappa(T)dT}$$

(iv) $$P_d = \frac{(PF)_{eng}\Delta T}{L} \quad \frac{m_{opt}}{(1+m_{opt})^2}$$ in W/cm^2; $$m_{opt} = \sqrt{1 + (ZT)_{eng}\left({}^{\alpha}/_{\eta_C} - {}^{1}/_{2}\right)}$$

Where $(PF)_{eng}$ and m_{opt} are the engineering power factor and optimum ratio of external electrical load (R_L) and internal resistance (R_{int}).

(iv) $$\eta_{max} = \eta_C \cdot \frac{\sqrt{1 + (ZT)_{eng}\left({}^{\alpha}/_{\eta_C} - {}^{1}/_{2}\right)} - 1}{\alpha\sqrt{1 + (ZT)_{eng}\left({}^{\alpha}/_{\eta_C} - {}^{1}/_{2}\right)} - \eta_C}$$; $$\eta_C = \frac{\Delta T}{T_H}$$ and $$\alpha = \frac{S(T_H)\Delta T}{\int_{T_C}^{T_H} S(T)dT}$$

References:

(1) H. S. Kim, W. Liu, G. Chen, C.-W. Chu, and Z. Ren, Relationship between

thermoelectric figure of merit and energy conversion efficiency, Proceedings of the National Academy of Sciences, 2015, 112, 8205–8210.