ADVANCED ENERGY MATERIALS

Supporting Information

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Subtle Roles of Sb and S in Regulating the Thermoelectric Properties of N-Type PbTe to High Performance

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Gangjian Tan,[1] Constantinos C. Stoumpos,[1] Si Wang,[2,3] Trevor P. Bailey,[2] Li-Dong Zhao,[4] Ctirad Uher,[2] and Mercouri G. Kanatzidis[1*]

[1]Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States

[2]Department of Physics, University of Michigan, Ann Arbor, Michigan 48109, United States

[3]State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China

[4]School of Materials Science and Engineering, Beihang University, Beijing, 100191, China

*Corresponding author: m-kanatzidis@northwestern.edu

Table S1. Densities of all the samples investigated in this study.

Compositions		Density (d, g/cm^3)	Relative density* (%)
$Pb_{1-x}Bi_xTe$	x=0.3%	8.00	98.0
	x=0.5%	8.01	98.1
	x=0.7%	7.94	97.3
	x=1.0%	7.98	97.7
	x=1.25%	7.94	97.3
	x=1.5%	8.02	98.2
$Pb_{1-x}Sb_xTe$	x=0.3%	8.01	98.1
	x=0.5%	7.97	97.6
	x=0.7%	7.91	96.9
	x=1.0%	7.95	97.4
	x=1.25%	7.90	96.8
	x=1.5%	7.92	97.0
$Pb_{0.9875}Sb_{0.0125}Te_{1-y}S_y$	y=0.04	7.89	96.9
	y=0.08	7.87	96.8
	y=0.12	7.85	96.8
	y=0.16	7.83	96.7

*The theoretical densities d(t) of the $Pb_{1-x}Bi_xTe$, $Pb_{1-x}Sb_xTe$, and $Pb_{0.9875}Sb_{0.0125}Te_{1-y}S_y$ samples were calculated using the law of mixtures in light of the volume fraction of each component.

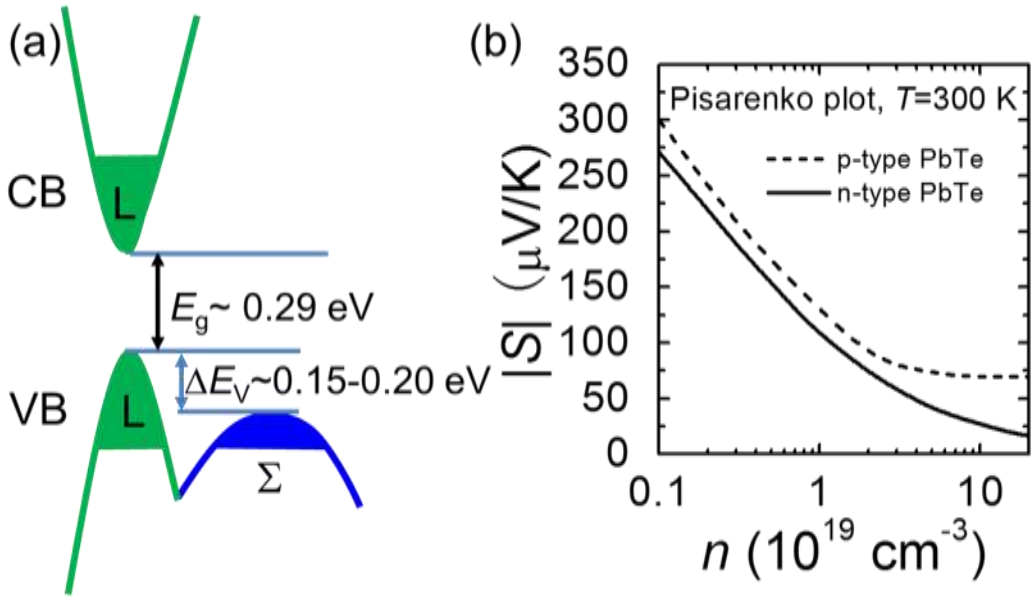

Figure S1. (a) A schematic diagram of the band structure of PbTe.[1-2] Both the conduction band (CB) minima and valence band (VB) maxima of PbTe occur at the L points of the Brillouin zone, separated by a direct band gap of ~0.29 eV at room temperature. Aside from the primary valence band at L band, there is a second lower-lying valence band with larger effective mass at Σ point. The energy separation of the two valence bands (ΔE_V) is ~0.15-0.20 eV at 300 K. (b) The comparison of theoretical Pisarenko plots of n- and p-type PbTe at room temperature.[3-4] P-type PbTe has higher absolute Seebeck coefficient than the n-type one, especially at high doping levels (n>2×10^{19} cm^{-3}) where the heavy valence band at Σ point is activated.

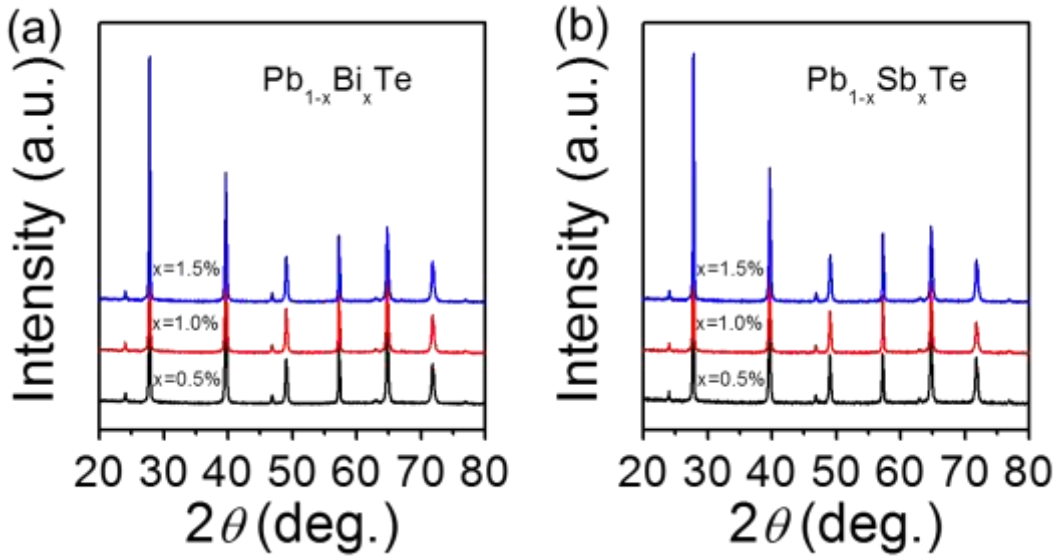

Figure S2. Powder X-ray diffraction patterns of (a) $Pb_{1-x}Bi_xTe$ and (b) $Pb_{1-x}Sb_xTe$ with selected compositions.

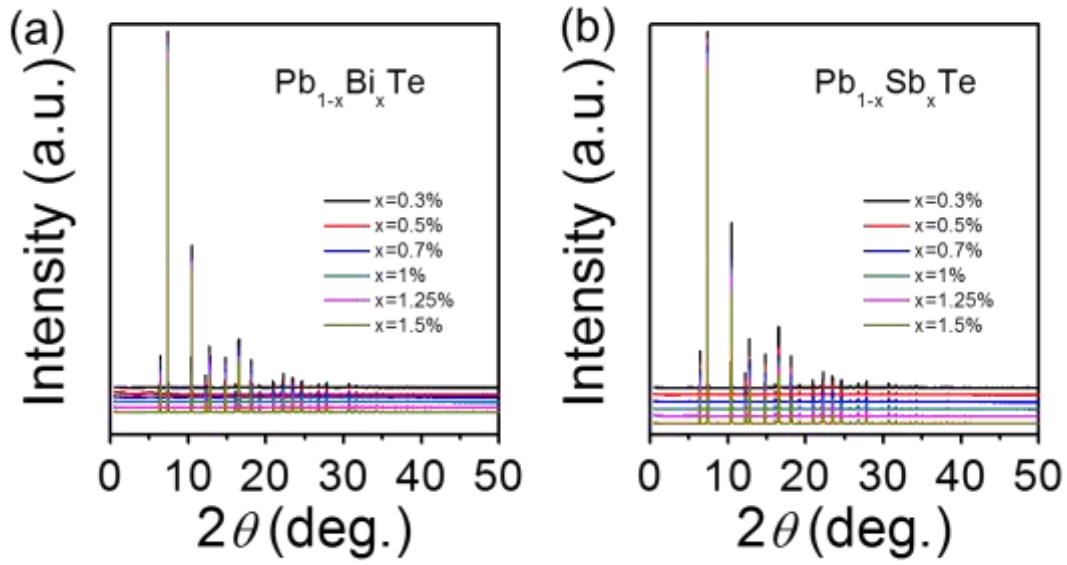

Figure S3. Synchotron powder XRD patterns for (a) $Pb_{1-x}Bi_xTe$ and (b) $Pb_{1-x}Sb_xTe$.

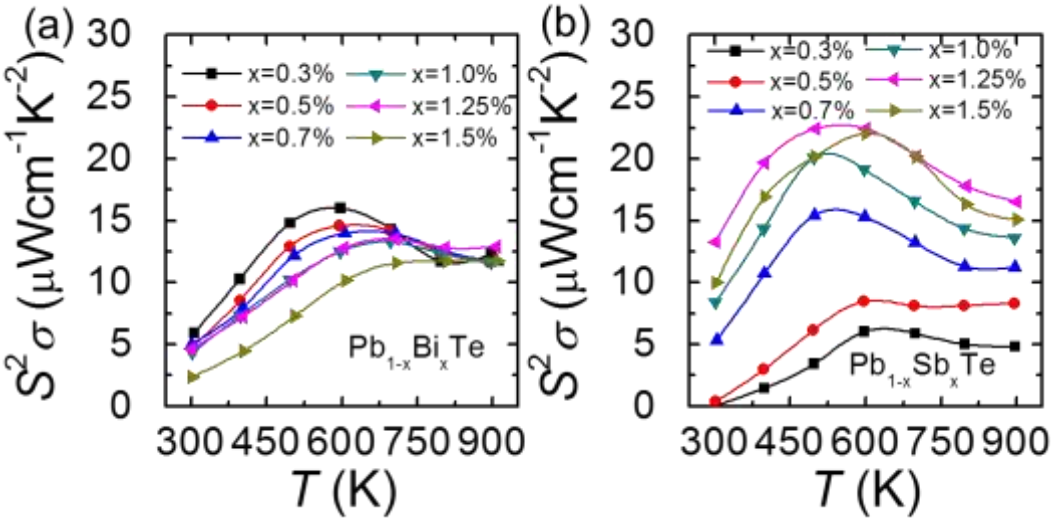

Figure S4. Temperature dependent power factors for (a) $Pb_{1-x}Bi_xTe$ and (b) $Pb_{1-x}Sb_xTe$, respectively.

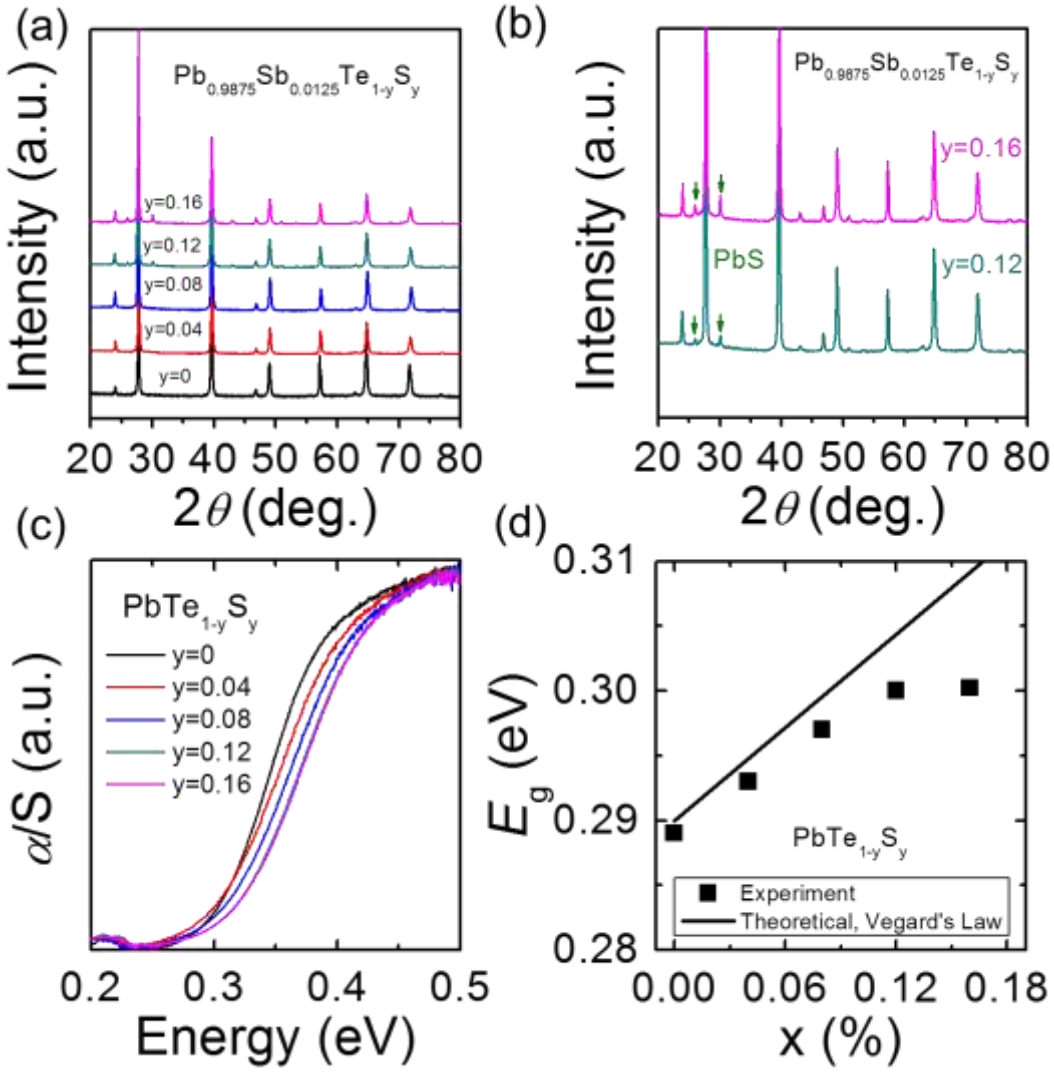

Figure S5. (a) Powder X-ray diffraction patterns for $Pb_{0.9875}Sb_{0.0125}Te_{1-y}S_y$. (b) Impurity phase of PbS is observable in the y=0.12 and y=0.16 samples. (c) Infrared absorption spectra for low carrier concentration $PbTe_{1-y}S_y$ samples. (d) Optical band gaps as a function of S alloying fraction y in PbTe, which depart from the Vegard's law (solid line) when y>0.04.

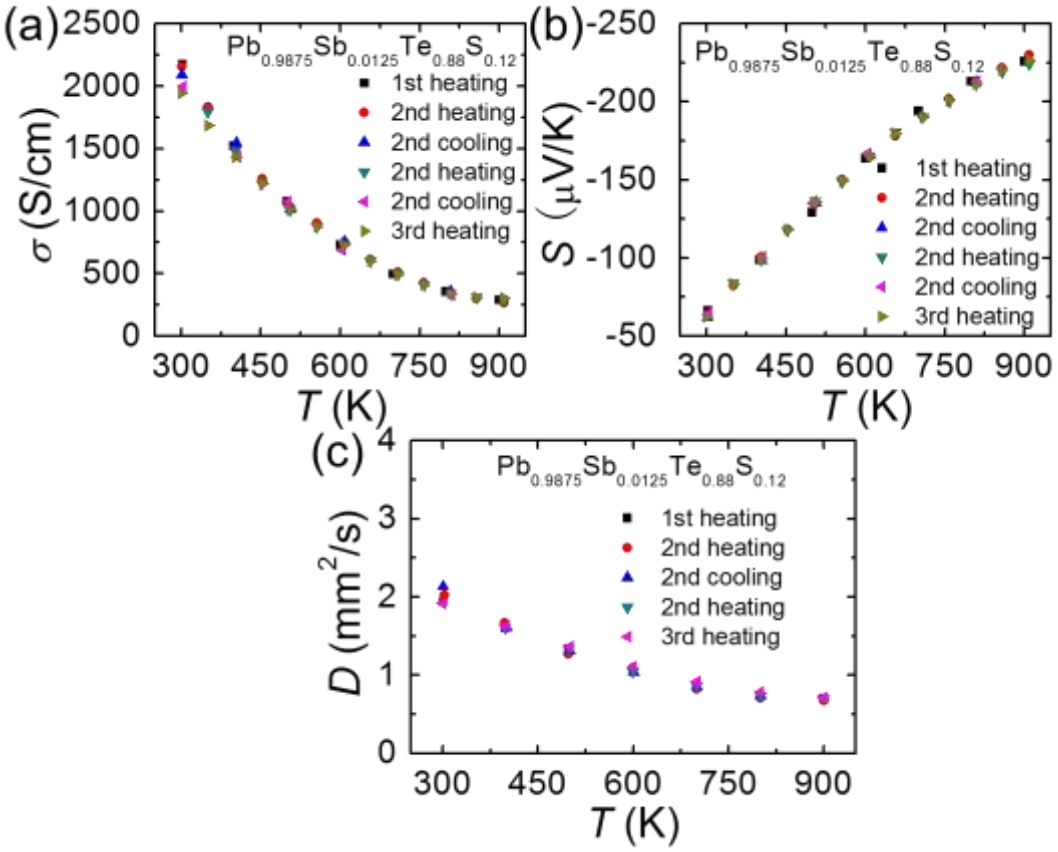

Figure S6. Comparison of thermoelectric properties for $Pb_{0.9875}Sb_{0.0125}Te_{0.88}S_{0.12}$ during the first measurement (1st), second measurement with multiple heating-cooling cycles (2nd) and after vacuum annealing at 773 K for 48 hours (3st): (a) Electrical conductivity; (b) Seebeck coefficient and (c) thermal diffusivity.

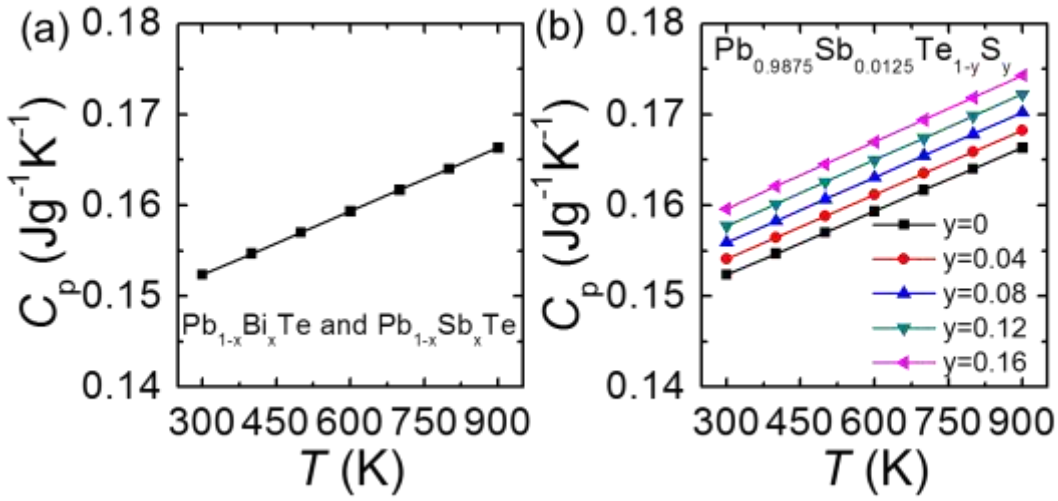

Figure S7. Temperature dependent heat capacities (C_p) for (a) $Pb_{1-x}M_xTe$ (M=Bi, Sb) and (b) $Pb_{0.9875}Sb_{0.0125}Te_{1-y}S_y$.

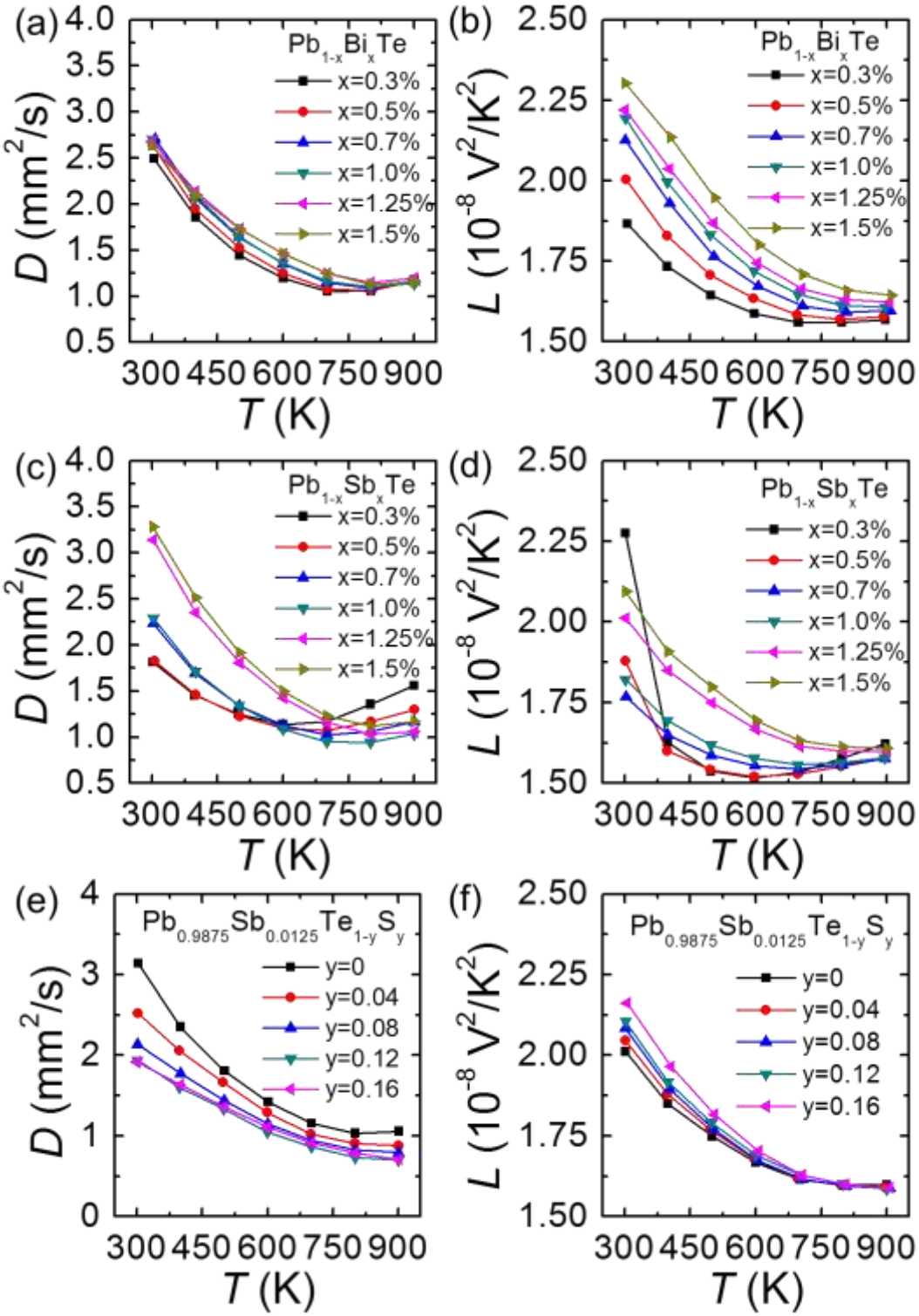

Figure S8. Temperature dependent thermal diffusivities (a, c, e) and Lorenz numbers (b, d, f) for $Pb_{1-x}Bi_xTe$, $Pb_{1-x}Sb_xTe$ and $Pb_{0.9875}Sb_{0.0125}Te_{1-y}S_y$, respectively.

Supporting references

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