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Supplementary Information for

Realizing High-efficiency Power Generation in Low-cost PbS-based

Thermoelectric Materials

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1. Elastic properties

Average sound velocity (v_a) is calculated from the sound velocity as follows.¹

$$\frac{1}{v_a} = \left[\frac{1}{3}\left(\frac{1}{v_l^3} + \frac{2}{v_t^3}\right)\right]^{1/3}, \qquad (1)$$

where v_l is the longitudinal sound velocity and v_t is the transverse sound velocity.

Young's modulus (E) is calculated by¹

$$E = \frac{\rho v_t^2 (3v_l^2 - 4v_t^2)}{(v_l^2 - v_t^2)}, \qquad (2)$$

where ρ is the sample density.

Poisson ratio (r) is calculated by²

$$r = \frac{1 - 2(\nu_t/\nu_l)^2}{2 - 2(\nu_t/\nu_l)^2},$$
 (3)

Shear modulus (G) is calculated by²

$$G = \frac{E}{2(1+r)}, \qquad (4)$$

The Gruneisen parameter (γ) is calculated by²

$$\gamma = \frac{3}{2} \left(\frac{1+r}{2-3r} \right)_{,} \tag{5}$$

Debye temperature (θ_D) is calculated by²

$$\theta_D = \frac{h}{k_B} (\frac{3N}{4\pi V})^{1/3} \nu_a \,, \qquad (6)$$

where *h* is Planck's constant, k_B is the Boltzmann constant, *N* is the number of atoms in the primitive unit cell (*N* = 8 for PbS) and *V* is the unit cell volume.

Bulk modulus (B) is calculated by²

$$B = \rho v_l^2 - \frac{4}{3}G, \quad (7)$$

The thermal expansion coefficient (α_V) is calculated by³

$$\alpha_V = \frac{\gamma C_V}{BV_m},\qquad(8)$$

where C_V is specific heat capacity at constant volume and V_m is the molar volume.

The specific heat capacity at constant pressure (C_p) is calculated by⁴

$$C_p = C_V + \alpha_V^2 B V_m T , \qquad (9)$$

where C_V is 24.943 Jmol⁻¹K⁻¹ (calculated by Dulong Petit law).

Table S1. Densities and sound velocities (longitudinal sound velocity v_l , transverse sound velocity v_t , average sound velocity v_a) of $Pb_{(0.99-1.5x)}Sb_{(0.01+x)}S_{(1-y)}Se_y$ samples. The elastic properties (Young's modulus *E*, Shear modulus *G*, Poisson ratio *r*), the Grüneisen parameter γ is derived using Eq. (1)-(6) based on the measured sound velocity.

Sample	ρ	V _l	V_t	V _a	E	G	r	Y
	(gcm ⁻³)	(ms ⁻¹)	(ms ⁻¹)	(ms ⁻¹)	(GPa)	(GPa)		

PbS	7.57	3429	1900	2117	69.9	27.4	0.278	1.647
$Pb_{0.99}Sb_{0.01}S$	7.51	3388	1856	2069	66.5	25.9	0.286	1.687
$Pb_{0.975}Sb_{0.02}S$	7.52	3391	1863	2077	67.0	26.1	0.284	1.677
$Pb_{0.96}Sb_{0.03}S$	7.45	3371	1841	2053	64.9	25.2	0.287	1.698
$Pb_{0.945}Sb_{0.04}S$	7.39	3362	1832	2043	64.0	24.8	0.289	1.707
$Pb_{0.93}Sb_{0.05}S$	7.37	3339	1812	2022	62.5	24.2	0.291	1.720
$Pb_{0.915}Sb_{0.06}S$	7.31	3309	1809	2017	61.6	23.9	0.287	1.694
$Pb_{0.93}Sb_{0.05}S_{0.9}Se_{0.1}$	7.47	3325	1801	2010	62.6	24.2	0.292	1.727
$Pb_{0.93}Sb_{0.05}S_{0.8}Se_{0.2}$	7.55	3314	1795	2003	62.9	24.3	0.293	1.728
$Pb_{0.93}Sb_{0.05}S_{0.7}Se_{0.3}$	7.60	3301	1784	1991	62.6	24.2	0.294	1.735
$Pb_{0.93}Sb_{0.05}S_{0.6}Se_{0.4}$	7.64	3302	1785	1993	62.9	24.3	0.293	1.732
$Pb_{0.93}Sb_{0.05}S_{0.5}Se_{0.5}$	7.74	3289	1776	1982	63.3	24.4	0.294	1.738
$Pb_{0.93}Sb_{0.05}S_{0.4}Se_{0.6}$	7.78	3288	1781	1987	63.8	24.7	0.292	1.727

2. Cost of thermoelectric materials



Fig. S1 Summary of cost (in \$/kg) of the best n- and p-type thermoelectric materials (price source: Shanghai metals market, SMM).



3. XRD results

Fig. S2 XRD patterns of $Pb_{(0.99-1.5x)}Sb_{(0.01+x)}S$ samples.



Fig. S3 XRD patterns of Pb_{0.93}Sb_{0.05}S_{1-y}Se_y samples.



Fig. S4 DSC heat flow curves of four samples (Pb_{0.99}Sb_{0.01}S, Pb_{0.93}Sb_{0.05}S,

Pb_{0.87}Sb_{0.07}S and Pb₃SbS₄) in our experiments.



4. Thermoelectric performance

Fig. S5 Temperature dependences of (a) electrical conductivity (σ), (b) Seebeck coefficient (*S*), (c) power factor (*PF*), (d) thermal conductivity (κ), (e) lattice thermal conductivity ($\kappa_L + \kappa_b$), and (f) *zT* value for Pb_{0.99-x}Sb_{0.01+2x/3}S (x = 0-0.12) samples.



Fig. S6 Temperature dependences of (a) electrical conductivity (σ), (b) Seebeck coefficient (*S*), (c) power factor (*PF*), (d) thermal conductivity (κ), (e) lattice thermal conductivity ($\kappa_L + \kappa_b$), and (f) *zT* value for Pb_{0.93}Sb_{0.05}S_{1-y}Se_y (y = 0.1-0.6) samples.

5. Microstructure (TEM)



Fig. S7 Low-magnification TEM pictures of (a) PbS and (b) Pb_{0.93}Sb_{0.05}S samples.



Fig. S8 (a) Nanostructure and (b) dislocation arrays in Pb_{0.93}Sb_{0.05}S sample. The two pictures show high similarity, indicating that the zigzag nanostructure should be $_{9}$

formed around dislocations.



Fig. S9 The enlarged STEM images of a typical zigzag nanostructure line in $Pb_{0.93}Sb_{0.05}S$ sample. From (a) to (e), the magnification was increased.

6. Burgers vector

In order to determine the dislocation line direction in space we have carried out tilting experiments, imaging straight dislocations along different zone axes and analyzing the $\mathbf{g}\cdot\mathbf{b}$.



Fig. S10 Weak-beam dark-feld image of dislocations. (a-b) Using the (20^2) and (0^22) reflection at the [111] zone axis, respectively. (c-d) Using the (022) and (1^1) reflection at the [21¹] zone, respectively.

7. Structure and composition of zigzag nanostructure

Clarifying the elemental composition of the zigzag nanostructure is fundamental to evaluate its effect on thermoelectric transport properties of the material. We profiled the intensity of atoms along the arrowed direction based on the HAADF image (see **Figure S11a**), and the results are shown in **Figure S11c**. As indicated by the green arrows, the intensity of the two inner atomic planes are weaker than those of the two

outer atomic planes in the four-plane nanostructure, which indicates that a light element (Sb) should exist. Interestingly, some atoms in PbS matrix nearest to the nanostructure also show weaker intensity, indicating the enrichment of Sb element in the matrix. The difference between these two situations is that the atoms in the inner planes of the four-plane nanostructure show weaker intensities periodically, which corresponds to a periodic atomic arrangement of the second phase. While in the PbS matrix, only random atoms show weaker intensities, indicating the alloyed enrichment of Sb element rather than a new phase. The distribution of Sb element can be analyzed by the atomic EDS maps shown in Figure S11e. Sb atoms mainly locate inside the nanostructure and the existence of S atoms denies the possibility of pure Sb substance for the nanostructure. Through the analysis of atom intensity and EDS maps, the structure of the nanostructure can be described as a layer composed of four atom planes. The two outer atom planes are constituted by Pb and S atoms and the two inner atom planes are constituted by Pb, Sb and S atoms, forming a PbS-(Pb,Sb)S-(Pb,Sb)S-PbS layer. This layer has been found in Nagyagite mineral by Effenberger et al. (1999)⁵ and its structure is shown in Figure S10. Based on this structure, the standard XRD pattern is simulated and shown in Figure S2. Through indexing the peaks of second phase to simulated pattern, the second phase has been confirmed as PbS-(Pb,Sb)S-(Pb,Sb)S-PbS layer. The ratio of Sb: Pb in (Pb,Sb)S plane is 0.524:0.476 according to the single-crystal X-ray data and electron-microprobe analysis in Nagyagite's work.5



Fig. S11 Structure of layered Pb(Pb,Sb)S₂.



Fig. S12 (a) A HAADF image shows the atomic structure of one zigzag nanostructure. The inset shows the atom simulation of Pb(Pb,Sb)S₂ nanostructure in PbS [110] direction with blue dots standing for Pb, whereas purple ones for (Pb,Sb). (b) The schematic diagram describing two connecting type of Pb(Pb,Sb)S₂ layers. (c) Line

scanning profiles of experimental image with corresponding color arrows in (a). (d) High-magnification atomic resolution image and (e) the EDS maps of part of one zigzag nanostructure. All the images are along [110] zone axes.



8. Reproducibility, isotropy and stability of transport properties

Fig. S13 (a) Electrical conductivity, (b) the Seebeck coefficient, (c) thermal conductivity and (d) zT values of one $Pb_{0.99}Sb_{0.01}S$, four $Pb_{0.93}Sb_{0.05}S$ and three $Pb_{0.93}Sb_{0.05}S_{0.5}Se_{0.5}$ samples



Fig. S14 Thermoelectric transport properties of another group of $Pb_{0.99-x}Sb_{0.01+2x/3}S$ samples. (a) Electrical conductivity (σ), (b) Seebeck coefficient (*S*), (c) total thermal conductivity (κ) and (d) figure of merit (*zT*).



Fig. S15 Scanning electron microscopy images of (a) PbS and (b) Pb_{0.93}Sb_{0.05}S samples.



Fig. S16 $Pb_{0.93}Sb_{0.05}S$ sample used to measure thermoelectric transport properties in both in-plane and cross-plane directions.



Fig. S17 Thermoelectric transport properties of $Pb_{0.93}Sb_{0.05}S$ sample in both in-plane and cross-plane directions.



Fig. S18 Thermoelectric transport properties of $Pb_{0.93}Sb_{0.05}S$ sample in in-plane directions for three circles.

9. Thermal conductivity modeling

The Callaway model is expressed as follows,⁶

$$\kappa_{L} = \frac{k_{B}}{2\pi^{2}v_{a}} (\frac{k_{B}T}{\hbar})^{3} \int_{0}^{\theta_{D}/T} \frac{x^{4}e^{x}}{\tau_{C}^{-1}(e^{x}-1)^{2}} dx$$
, (10)

where $x = \hbar \omega / k_B T$, ω , k_B , \hbar , θ_D and τ_C are reduced phonon frequency, phonon frequency, Boltzmann constant, reduced Planck constant, Debye temperature and the overall phonon scattering relaxation time, respectively. The overall phonon scattering relaxation time is expressed as⁷

$$\tau_{C}^{-1} = \tau_{I}^{-1} + \tau_{U}^{-1} + \tau_{PD}^{-1} + \tau_{GBDS}^{-1}$$
 (11)

For common grain boundaries, with perfect acoustic mismatch at the interface between the material and vacuum, the relaxation time of phonons is independent with phonon frequencies. Thus, the frequency-independent τ_I is given by

$$\tau_I^{-1} = \frac{\nu_a}{L}, \quad (12)$$

Where v_a is the average sound velocity and *L* is the experimentally determined grain size.

Umklapp scattering is the dominant process in material, describing the interaction of phonons, whose relaxation time is of the form

$$\tau_{U}^{-1} = A_{N} \frac{2 k_{B} V^{1/3} \gamma^{2} \omega^{2} T}{(6\pi^{2})^{1/3} M v_{a}^{3}}, \quad (13)$$

Where *V*, *M* are atomic volume and atomic mass, respectively. The parameter A_N is the ratio of Normal to Umklapp process, which can be estimated by the lattice thermal conductivity of a pure PbS sample. For a pure PbS sample, two phonon scattering mechanisms (interface and Umklapp scattering) will be included to calculate the lattice thermal conductivity. All the parameters used in the calculation are listed in **Table S2**. Based on the experimental parameters, the only unfixed parameter A_N is calculated and fixed to 3.7, which is close to the value ($A_N = 4$) of PbSe in literature.⁸ Then the variables in equation (13) are only average sound velocity (v_a) and Grunneisen parameter (γ), which affect the Umklapp scattering. The contribution of strengthened anharmonicity to lattice thermal conductivity can be quantified by v_a and γ . Similar to the situation of pure PbS sample with interface and Umklapp scatterings included, the practical lattice thermal conductivity of Pb_{0.93}Sb_{0.05}S sample using v_a and γ with strengthened anharmonicity introduced should be calculated. On the other hand, the alloyed Sb and Se atoms will also introduce mass and lattice constant fluctuations, resulting in point defect scattering for phonons.^{9,10} The relaxation time of point defect scattering can be written as

$$\tau_{PD}^{-1} = \frac{V\omega^4}{4\pi v_a^3} \Gamma$$
(14)

Where Γ is the scattering parameter related to mass (ΔM) and lattice constant (Δa) differences between two constituents of an alloy. The result indicates that the point defect scattering is a second reason for the largely depressed lattice thermal conductivity.

The relaxation time of GBDS is written as two parts: cores τ_{DC} and strain $\tau_{DS,7,11}$

$$\tau_{DC}^{-1} = N_d \frac{V^{4/3}}{v^2} \omega_{,(15)}^3$$
$$\tau_{DS}^{-1} = 0.6B_D^2 N_d (\gamma + \gamma_1)^2 \omega \left[\frac{1}{2} + \frac{1}{24} \left(\frac{1 - 2r}{1 - r} \right)^2 \{1 + \sqrt{2} \left(\frac{\nu_l}{\nu_t} \right)^2 \}^2 \right]_{.(16)}$$

Where B_D , r, γ and γ_1 are the magnitude of effective Burgers vector, the Poisson ratio, Gruneisen parameter and change in Gruneisen parameter, respectively. Based on equation (15) and (16), the contribution of GBDS to lattice thermal conductivity can be calculated.

Table S2. Parameters of lattice thermal conductivity modeling for PbS.

Parameters	Notes	Values
V _a	Average sound velocity	2117 ms ⁻¹
L	Average grain size	10 μm
A_N	Ratio of Normal to Umklapp process	3.7

V	Average atomic volume	$2.615 \times 10^{-29} \text{ m}^3$
Μ	Average atomic mass	$1.986 \times 10^{-25} \text{ kg}$
γ	Gruneisen parameter	1.647

Table S3. Parameters of lattice thermal conductivity modeling for Pb_{0.93}Sb_{0.05}S.

Parameters	Notes	Values
Va	Average sound velocity	2022 ms ⁻¹
L	Average grain size	5 μm
A_N	Ratio of Normal to Umklapp process	3.7
V	Average atomic volume	$2.615 \times 10^{-29} \mathrm{m}^3$
M	Average atomic mass	1.951×10 ⁻²⁵ kg
γ	Gruneisen parameter	1.72
N _D	Density of GBDS	$5 \times 10^{10} \mathrm{cm}^{-2}$
B _D	Effective Burgers vector	0.4 nm
<i>γ</i> 1	Change of Gruneisen parameter	0.05
r	Poisson ratio	0.291

10.Electrical transport modeling

The electrical transport properties can be fitted by the single parabolic band (SPB) model, which assume a single, parabolic, and rigid band. The details of SPB model can be found everywhere.^{12,13} Using this model, the Seebeck coefficient (*S*), carrier concentration (*n*), carrier mobility (μ) can be calculated by the basic parameter

(reduced chemical potential η , the mobility parameter m_0 and density of states effective mass m^*). These transport quantities are calculated by the following equations:

$$S = \frac{k_B}{e} \left(\frac{2F_1(\eta)}{F_0(\eta)} - \eta \right), \quad (17)$$

$$n = 4\pi \left(\frac{2m^* k_B T}{h^2} \right)^{1.5} F_{0.5}(\eta), \quad (18)$$

$$n_H = \frac{n}{r_H}, \quad (19)$$

$$r_H = \frac{1.5F_{0.5}(\eta)(0.5)F_{-0.5}(\eta)}{F_0^2(\eta)}, \quad (20)$$

$$\mu_{H} = \mu_{0} \frac{F_{-0.5}(\eta)}{2F_{0}(\eta)}, \qquad (21)$$

$$\sigma = \frac{\mu_H}{R_H}, \quad (22)$$

Here, $k_{\rm B}$ is the Boltzmann's constant, $F_j(\eta)$ is the Fermi integral of order *i*, and the reduced chemical potential η is given by $\eta = E_F/(k_B T)$, where E_F is the Fermi energy. Because it is hard to confirm μ_0 , $\mu_{\rm H}$ is usually fitted using experimental mobility data based on the following equations:

$$\frac{1}{\mu_{H}} = \frac{1}{\mu_{H}^{AP}} + \frac{1}{\mu_{H}^{AS}}, \quad (23)$$
$$\mu_{H}^{AP} = \frac{\sqrt{8\pi}e\hbar^{4}\rho v_{l}^{2}\psi(\eta)}{3E_{def}^{2}(m_{s}^{*})^{2.5}(k_{B}T)^{1.5}}, \quad (24)$$

$$\mu_{H}^{AS} = \frac{64e\hbar^{4}N_{0}\psi(\eta)}{9(2\pi)^{1.5}x(1-x)E_{AS}^{2}(m_{s}^{*})^{2.5}(k_{B}T)^{0.5}},$$
 (25)

Here, $\mu_{\rm H}{}^{\rm AP}$ and $\mu_{\rm H}{}^{\rm AS}$ are acoustic phonon and alloying scattering mobility, respectively. $E_{\rm def}$ is the deformation potential which characterizes the interaction between charge carriers and phonons and $E_{\rm AS}$ is the alloying scattering potential. \hbar is the reduced Planck constant, ρ is the density of sample, μ is the longitudinal velocity of sound, x is the fraction of alloyed element, and N_0 is the number of atoms per unit volume. m_s^* is the single valley effective mass, which can be calculated by $m_s^* = m^* N_v^{-2/3}$ with $N_v = 4$, where N_v is valley degeneracy. $\psi(\eta) = \frac{3\sqrt{\pi}F_{-0.5}(\eta)}{16}$ is

a combination of constants.

Sample	300 K			800 K			
	n	μ	S	n	μ	S	
	(10^{19}cm^{-3})	$(cm^2V^{-1}s^{-1})$	(µVK ⁻¹)	(10^{19}cm^{-3})	$(cm^2V^{-1}s^{-1})$	(µVK ⁻¹)	
Pb _{0.99} Sb _{0.01} S	6.6	80.2	-57.3	7.1	37.4	-187.4	
Pb _{0.975} Sb _{0.02} S	6.2	81.4	-56.4	5.8	39.6	-185.5	
Pb _{0.96} Sb _{0.03} S	5.5	76.5	-73.3	4.2	43.6	-191.2	
Pb _{0.945} Sb _{0.04} S	4.3	74.7	-83.9	3.9	47.9	-193.3	
Pb _{0.93} Sb _{0.05} S	3.3	78.4	-91.2	3.6	51.7	-189.9	
Pb _{0.915} Sb _{0.06} S	3.0	80.2	-92.1	3.6	50.4	-192.0	

Table S4. Electron concentration, mobility and the Seebeck coefficient of $Pb_{(0.99-x)}Sb_{(0.01+2x/3)}S_{(1-y)}Se_y$ samples at 300 K and 800 K.

Pb _{0.93} Sb _{0.05} S _{0.9} Se _{0.1}	3.4	90.4	-81.5	3.4	62.2	-195.9
Pb _{0.93} Sb _{0.05} S _{0.8} Se _{0.2}	3.5	103.5	-80.0	3.4	65.0	-192.8
Pb _{0.93} Sb _{0.05} S _{0.7} Se _{0.3}	3.9	116.7	-75.2	3.8	59.6	-183.9
Pb _{0.93} Sb _{0.05} S _{0.6} Se _{0.4}	4.9	122.4	-65.8	4.5	63.3	-168.3
Pb _{0.93} Sb _{0.05} S _{0.5} Se _{0.5}	4.5	134.3	-69.9	3.8	71.2	-175.1
Pb _{0.93} Sb _{0.05} S _{0.4} Se _{0.6}	4.0	140.4	-71.5	3.5	75.4	-178.0

11.Mechanical properties

Table S5 Fracture toughness K_{IC} determined using Vickers indentation for $Pb_{0.93}Sb_{0.05}S_{0.5}Se_{0.5}$ sample. *E* is Young's modulus, *P* is the applied indentation load, *d* is the length of the diagonal of the resultant impression and *c* is the radial crack length for Vickers indentation.

Indentation	E (GPa)	P (N)	<i>d</i> (µm)	<i>с</i> (µm)	$K_{\rm IC}$ (MPam ^{1/2})
1	74.82	0.49	28.2	23.5	0.56
2	74.82	0.49	28.0	16.8	0.91
3	74.82	0.49	29.5	18.0	0.87
4	74.82	0.98	42.5	29.2	0.86
5	74.82	0.98	41.5	30.0	0.80
6	74.82	0.98	40.1	32.0	0.70
average					0.78



Fig. S19 Micrographs of Vickers indentations at (a) 0.49 N, (b) 0.49 N, (c) 0.49 N, (d) 0.98 N, (e) 0.98 N, and (f) 0.98 N for $Pb_{0.93}Sb_{0.05}S_{0.5}Se_{0.5}$ sample.

12.Thermoelectric module



Fig. S20 Internal resistance of single and segmented modules.

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