Supporting materials

Role of Sodium Doping in Lead Chalcogenide Thermoelectrics

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A: Synthesis, characterization and DFT calculations

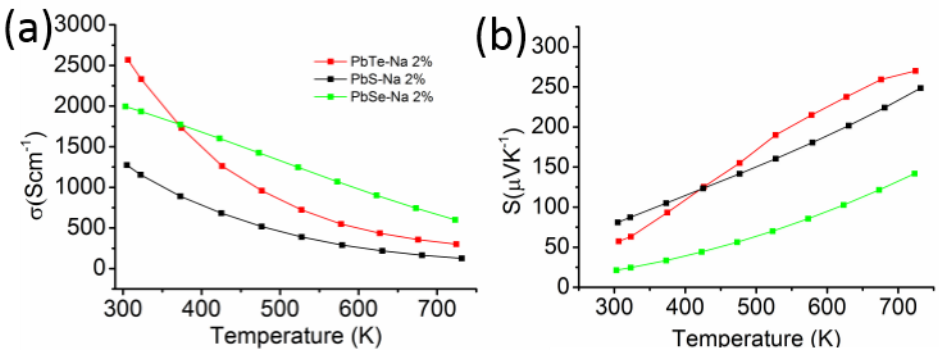
(1) Synthesis

Reagents chemicals were used as obtained: Pb wire (99.99%, American Elements, US), Te shot (99.999%, 5 N Plus, Canada), Se shot (99.999%, 5 N Plus, Canada), S shot or chunk (99.999%, Inc., Canada) and Na chunk (99.999%, Aldrich, US).

Samples $Pb_{1-x}Na_xQ$ (x=0.005, 0.01 or 0.02; Q = Te, Se and S) were prepared by a melting reaction using mixing elemental Pb, Q (Q=Te, Se, or S) and Na inside carbon-coated fused silica tubes, the tubes were then evacuated to a base pressure of ~10^{-4} torr, flame-sealed, slowly heated to 723 K in 12 h, and then heated to 1423 K in 7 h, soaked at this temperature for 6 h and subsequently air quenched to room temperature.

(2) Characterization:

Electrical properties: The obtained ingots were cut into bars with the dimension of 15 mm × 3 mm × 2 mm that were used for simultaneous measurements of the Seebeck coefficient and the electrical conductivity using an Ulvac Riko ZEM-3 instrument under a helium atmosphere from room temperature to 723 K.. Electrical properties obtained from different slices cut from the same pellets were similar attesting to the good homogeneity of the samples. The uncertainty of Seebeck coefficient and electrical conductivity measurements is within 5%.



FigureS1 (a) Electrical conductivity, and (b) Seebeck coefficient dependence of temperature of Na 2 mol% doped PbQ (Q=Te, S, Se) samples.

Thermal conductivity: Highly dense ingots were cut and polished into coins of Ø ~ 8 mm and 1~2 mm thickness for thermal diffusivity measurements. The samples were coated with a thin layer of graphite to minimize errors on the emissivity of the material. The thermal conductivity was calculated from $k = D\, C_p \rho$, where thermal diffusivity coefficient D was measured using laser flash diffusivity method in a Netzsch LFA457, the data were analyzed using a Cowan model with pulse correction, heating and cooling cycles give a repeatable diffusivity for a given sample. Thermal diffusivities obtained for different slices from the same pellet are similar; where C_p is the specific heat capacity, was indirectly derived using standard sample (Pyroceram 9606) in the range 300~923K, the C_p results show good agreement with the reported values, [1] where the density ρ of the sample was determined by using sample dimension and mass, the sample density was also reconfirmed by gas pycnometer (Micromeritics AccuPyc1340) measurements. The uncertainty of thermal conductivity is estimated to be within 8 % with considering the uncertainties for D, C_p and

ρ.

Transmission Electron microscopy: Transmission electron microscopy (TEM) investigations were carried out in a JEOL 2100F microscope at Xi'an Jiaotong University. The thin TEM specimens were prepared by conventional standard methods. The procedures include cutting, grinding, dimpling, polishing and Ar-ion milling on a liquid nitrogen cooling state subsequently.

(3) DFT calculations:

Density functional theory (DFT) [2,3] calculations, which has been used to study phase stability in rocksalt-based thermoelectric materials with considerable success[4-7], have been carried out using projector-augmented wave (PAW) [8] pseudoptentials with the generalized gradient approximation (GGA) and exchange correlation of Perdew, Burke, and Ernzerhof (PBE) [9], as implemented in the Vienna Abinito Simulation Package (VASP) [10]. The pseudopotentials for Na, Pb, S, Se, and Te had as valence the $2p^6 3s1$, $6s^2 6p^2$, $3s^2 3p^4$, $4s^2 4p^4$, and $5s^2 5p^4$ electrons, respectively. DFT total energies of the elements Na, Pb, S, Se, and Te, as well as the compounds PbTe, PbSe, PbS, NaTe, NaSe, and NaS, were calculated using plane-wave energy cutoffs of 350 eV, and Monkhorst-Pack (MP) [11] k-point meshes with 8000 k-points per reciprocal atom (KPPRA) for metals and 2400 KPPRA for non-metals. The integration of electronic orbitals was performed with Gaussian smearing using a 0.1 eV smearing width. The crystal structures of the elements and compounds were taken from the inorganic crystal structure database (ICSD) [12], and their unit cell parameters and atomic positions were fully relaxed within DFT. The total energies of PbQ (Q=Te, Se, and S) containing one Pb atom replaced by Na were calculated using 216 atom supercells which were relaxed with respect to both unit cell parameters and atomic positions. The supercell calculations were carried out using 350 eV energy cutoffs, and 4x4x4 MP k-point meshes with 0.1 eV Gaussian smearing. Both pure supercells and supercells with 1 Na and 107 Pb atoms were calculated in this manner.

Table S1 shows the formation energies of the PbQ and NaQ compounds, the difference between the Na and Pb chemical potentials (with respect to their elemental standard states) found by assuming equilibrium between PbQ and NaQ [from eq. (4) in the main text], the 'raw' defect formation energy of Na in PbQ with respect to elemental standard states [the first term in eq. (3) of the main text], as well as the defect formation energy of Na in PbQ with respect to the compounds

PbQ and NaQ. There is no systematic trend in the chemical potential difference between Na and Pb – PbTe-NaTe has the lowest chemical potential difference, PbSe-NaSe has the highest, and PbS-NaS lies in between. On the other hand, the raw defect formation energies of Na in PbQ decrease as Q moves from Te to Se to S, with Na in PbS being twice as large as Na in PbTe. The trend in the defect formation energies with respect to the compounds PbQ-NaQ remains the same as the trend in the raw defect formation energies.

Table S1

PbQ and NaQ formation energies, chemical potential differences between Na and Pb, 'raw' Na defect formation energies, and Na defect formation energies calculated for the systems PbQ-NaQ with Q = Te, Se, S.

	Q		
	Te	Se	S
ΔE_F^{PbQ} (eV/atom)	-0.412	-0.578	-0.555
ΔE_F^{NaQ} (eV/atom)	-0.711	-0.834	-0.835
$\Delta\mu_{Na}$-$\Delta\mu_{Pb}$ (eV/2 atoms)	-0.598	-0.511	-0.560
$\Delta E_{F,raw}^{def}$ (eV/defect)	-0.33	-0.54	-0.66
ΔE_F^{def} (eV/defect)	0.27	-0.03	-0.10

B: The calculations of lattice thermal conductivity

The lattice thermal conductivity was calculated using the modified Callway's model [13];

$$\kappa_l = \frac{k_B}{2\pi^2 \upsilon}\left(\frac{k_B T}{\hbar}\right)^3 \int_0^{\theta_D/T} \tau_c(x) \frac{x^4 e^x}{(e^x - 1)^2} dx \qquad (1)$$

Where k_B is the Boltzmann's constant, $\hbar$ is the Plank constant, T is the absolute temperature, υ is an average phonon-group velocity, which can be calculated from $\upsilon^{-1} = \frac{1}{3}\left(\upsilon_{T,1}^{-1} + \upsilon_{T,2}^{-1} + \upsilon_L^{-1}\right)$, where υ_L and $\upsilon_{T,1,2}$ are the longitudinal- and transverse-sound velocity, respectively; $x = \hbar\omega / \kappa_B T$, and τ_c is the relaxation time. The latter is obtained by integrating the relaxation times from various processes. In the TEM studies, at a certain frequency, relaxation time mainly is related to scattering from the boundaries, dislocations, strains, nanoscale precipitates, and the phonon-phonon interactions [13];

$$\frac{1}{\tau_c} = \frac{1}{\tau_U} + \frac{1}{\tau_N} + \frac{1}{\tau_B} + \frac{1}{\tau_{PD}} + \frac{1}{\tau_D} + \frac{1}{\tau_P} + \frac{1}{\tau_S} \quad (2)$$

Where τ_U, τ_N, τ_{PD}, τ_S, τ_P, τ_B and τ_D, are the relaxation times [14-22] corresponding to scattering from Umklapp processes, normal processes, point defects (solid solution), strains, precipitates, boundaries and dislocations, respectively. In principle, more mechanisms may further contribute to the relaxation time, such as electron-phonon interactions. In our treatment, however, we consider only the contributors mentioned above.

From the second–order perturbation theory, the relaxation time for Umklapp scattering is given by [14]

$$\tau_U^{-1} \approx \frac{\hbar\gamma^2}{M\upsilon^2\theta_D}\omega^2 T \exp(-\theta_D / 3T) \quad (3)$$

Wherein γ is the Gruneisen anharmonicity parameter, M is the average mass of an atom in the crystal, and θ_D is the Debye temperature.

For normal phonon-phonon scattering, several models were proposed [14-16]. For the appropriate form of group IV or III-V semiconductors can be written as [14]

$$\tau_N^{-1} \approx B_N \omega^a T^b \quad (4)$$

Where (a, b) = (1, 4) or (2, 3), depending on the type of phonons, for longitudinal phonons, (a, b) = (1, 4), and transverse phonons (a, b) = (2, 3); B_N is a constant independent of ω and T, $B_N(1,4) \approx \frac{k_B^4\gamma^2 V_0}{M\hbar^3\upsilon^5}$, $B_N(2,3) \approx \frac{k_B^3\gamma^2 V_0}{M\hbar^2\upsilon^5}$; V_0 is the volume per atom. τ_N also can be by [15,16]

$$\tau_N^{-1} \approx \beta\tau_U^{-1} \quad (5)$$

Where β is the ratio of normal phonon scattering to umklapp scattering, which is assumed to be temperature–independent. Here we used equation (5) to calculate normal phonon scattering of our study. The value of parameter β will be determined by fitting experimental data of pure PbQ.

The term, τ_{PD}, describing the contribution of point defects from solid solution part, is given by: [17]

$$\tau_{PD}^{-1} = A\Gamma = \frac{\omega^4\delta^3}{4\pi\upsilon^3}\Gamma \quad (6)$$

$$\Gamma = \Gamma_S + \Gamma_M \qquad (7)$$

In the above equation, δ is the radius of the impurity atom in the host lattice, υ is the average lattice sound velocity and Γ is the disorder scaling parameter, which depends on mass and strain field fluctuations. Both types of fluctuations are taken to have an additive effect on Γ.[18, 20] The mass fluctuations are quantified by Γ_M that takes into account the average mass of each of the sublattices and the strain field fluctuations by Γ_S that is a value weighted by the average sublattice mass, the average sublattice ionic radius and a phenomenological parameter ε. [19] The parameter ε is a function of the Grüneisen parameter and hence is a measure of the anharmonic contributions to the lattice.[18] he explicit relations of Γ_M and Γ_S are given by Yang et al.[18] as:

$$\Gamma_M = \frac{\sum_{i=1}^{n} c_i (\frac{< M_i >}{M^*})^2 f_i^1 f_i^2 (\frac{M_i^1 - M_i^2}{< M_i >})^2}{\sum_{i=1}^{n} c_i} \qquad (8)$$

$$\Gamma_S = \frac{\sum_{i=1}^{n} c_i (\frac{< M_i >}{M^*})^2 f_i^1 f_i^2 \varepsilon (\frac{r_i^1 - r_i^2}{< r_i >})^2}{\sum_{i=1}^{n} c_i} \qquad (9)$$

where the symbols in equation (8) and (9) are as following: c_i is the degeneracy (here c_1=c_2=1), f_i is the fractional occupation, $<r_i>$ the average radius, $<M_i>$ the average mass of each sublattice and M^* is the average atomic mass of the compound.

In addition to the boundary scattering mechanism, scattering due to dislocations are incorporated into the relaxation time according to our observations. We use here the following simplified dislocations: [21]

$$\tau_D^{-1} = N_D \frac{V_0^{4/3}}{\upsilon^2} \omega^3 + 0.06 N_D \gamma^2 B_D^2 \omega \left\{ 1/2 + \frac{1}{24} \left(\frac{1-2\nu}{1-\nu} \right)^2 \left[1 + \sqrt{2} \left(\frac{\upsilon_L}{\upsilon_T} \right)^2 \right]^2 \right\} \qquad (10)$$

Where N_D is the dislocation density, r is the core radius, B_D is the magnitude of the Burgers vector of the dislocation, γ is the Gruneisen number, and ω the phonon angular frequency. The first term in this equation is the contribution of the dislocation core, and the secondary term is due to the surrounding strain field. Since PbQ is anisotropic structure, we use the approximation of averaged elastic constants with the anisotropic factor, H, defined over the elastic coefficients c_{ij} by $H=2c_{44}+c_{12}-c_{11}$, the averaged elastic constant λ, and shear modulus μ for a cubic crystal are

$\lambda = c_{12} - (1/5)H$ and $\mu = c_{44} - (1/5)H$, correspondingly. The Poisson's ratio ν is equal to $\frac{\lambda}{2(\lambda+\mu)}$.

To simplify our calculation, the relaxation time due to elastic strain field, τ_S, is given by Peter Carruthers [22]

$$\tau_s^{-1} = \frac{1}{4}\sigma\left(\frac{gA'}{\rho}\right)^2\left(\frac{q^2}{\upsilon^3}\right) = \frac{144\sigma\gamma^2\varepsilon^2 r_0^4}{\upsilon}\omega^2 \qquad (11)$$

Where $g = 24\gamma\rho\upsilon^2$, $A' = \varepsilon r_0^2$, $q = \frac{\omega}{\upsilon}$, σ is the scatter density, r_0 is radius of the sphere and ε is the misfit between the sphere and the matrix. The misfit has a dependence of temperature, which can be written as:

$$\varepsilon = \varepsilon_0 + \left[\alpha_P - \alpha_M\left(1-\varepsilon_0\right)\right]\left(T - 300\right) \qquad (12)$$

Where ε_0 is misfit at room temperature (300K) which can be obtained from TEM study, α_P and α_M are the thermal expansion coefficient of precipitate and matrix, respectively.

Relaxation time of phonon scattering due to the nanoscale precipitates is given by a Mathiessen-type interpolation between the short- and long-wavelength scattering regimes [23-26]

$$\tau_P^{-1} = \upsilon(\sigma_s^{-1} + \sigma_l^{-1})^{-1}V_p \qquad (13)$$

Where $\sigma_s = 2\pi R^2$; $\sigma_l = \pi R^2 \frac{4}{9}(\Delta D/D)^2(\omega R/\upsilon)^4$, here R is particle average radius; D is medium density, and ΔD is the difference between the particle and matrix materials; V_p is the density of the nanoscale particles.

Table S2

Key parameters used to calculate the lattice thermal conductivity.

Parameters		PbTe	PbSe	PbS
Lattice constant	a (Å)	6.460	6.125	5.936
	c_{11} (GPa)	105.3	123.7	127
Elastic coefficients	c_{12} (GPa)	7.0	19.2	29.8
	c_{44} (GPa)	13.2	15.9	24.8
	H (GPa)	-71.9	-72.7	-47.6
	λ (GPa)	21.4	33.74	39.32
	μ (GPa)	27.6	30.44	34.32
	ν	0.218	0.263	0.267
Volume per atom	V_0 (Å^3)	33.69	28.72	26.15
Gruneisen parameter	γ	1.96	1.65	2.52
Sound velocity	υ(m/s)	1770	1926.3	2040
Debye temperature	θ_D (K)	136	125	145
Density of mass	ρ(g/cm^3)	8.242	8.270	7.597

Table S3

Parameters used to calculate the lattice thermal conductivity.

Parameters	**Symbol**	**Value**
Mass of an atom Pb	M_{Pb} [amu]	207.2
Te	M_{Te}	127.6
Se	M_{Se}	78.96
S	M_S	32.065
Na	M_{Na}	22.99
Radius of an atom Pb	r_{Pb} [pm]	175
Te	R_{Te}	140
Se	R_{Se}	115
S	R_S	100
Na	R_{Na}	186

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