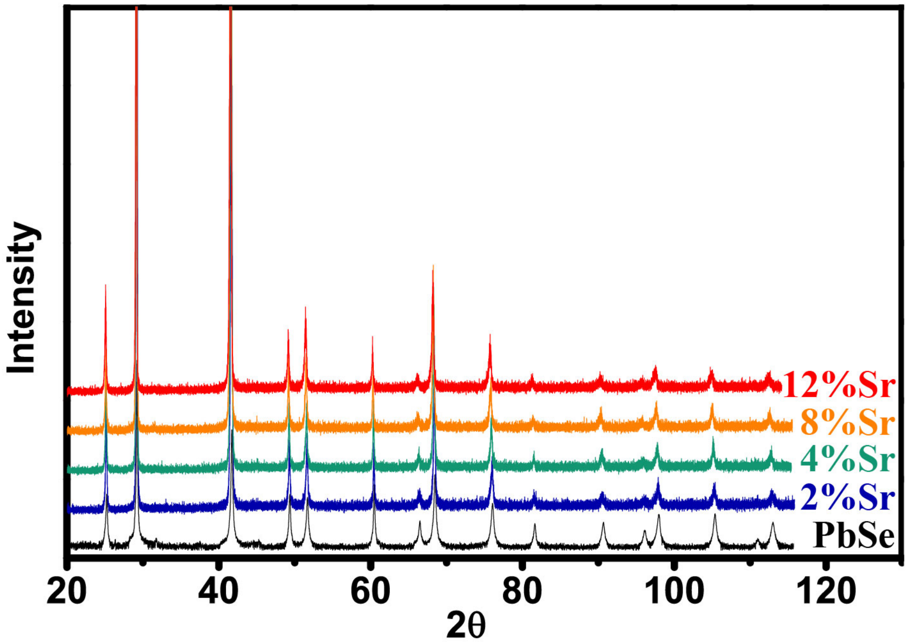
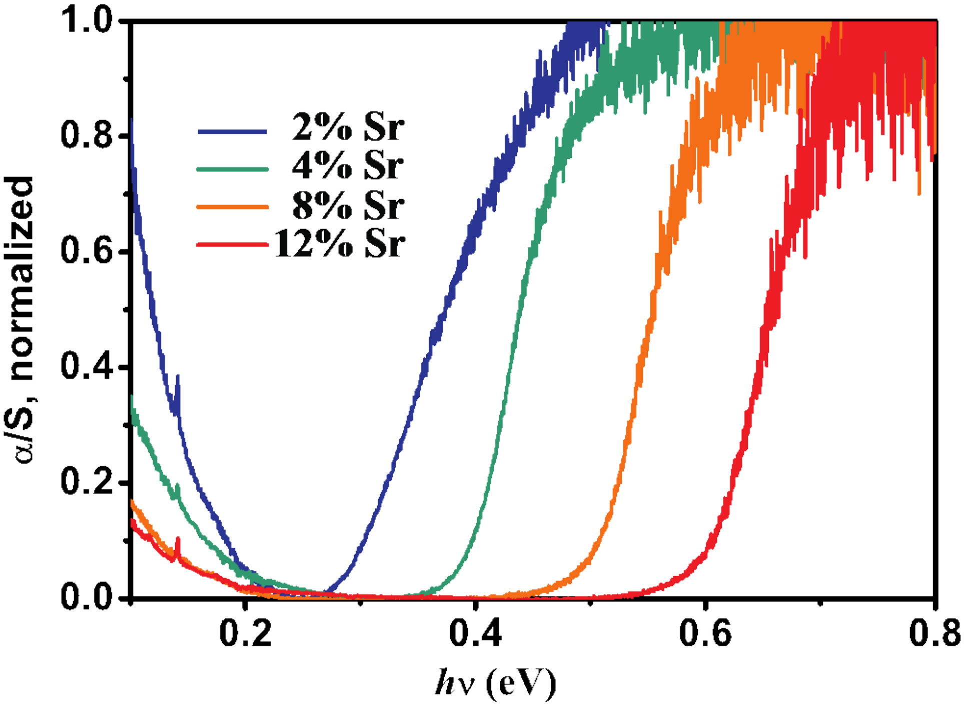
Electronic Supplementary Information

Tuning bands of PbSe for better thermoelectric efficiency

Heng Wang[a*], *Zachary Gibbs*[b], *and G. Jeffrey Snyder*[a]*

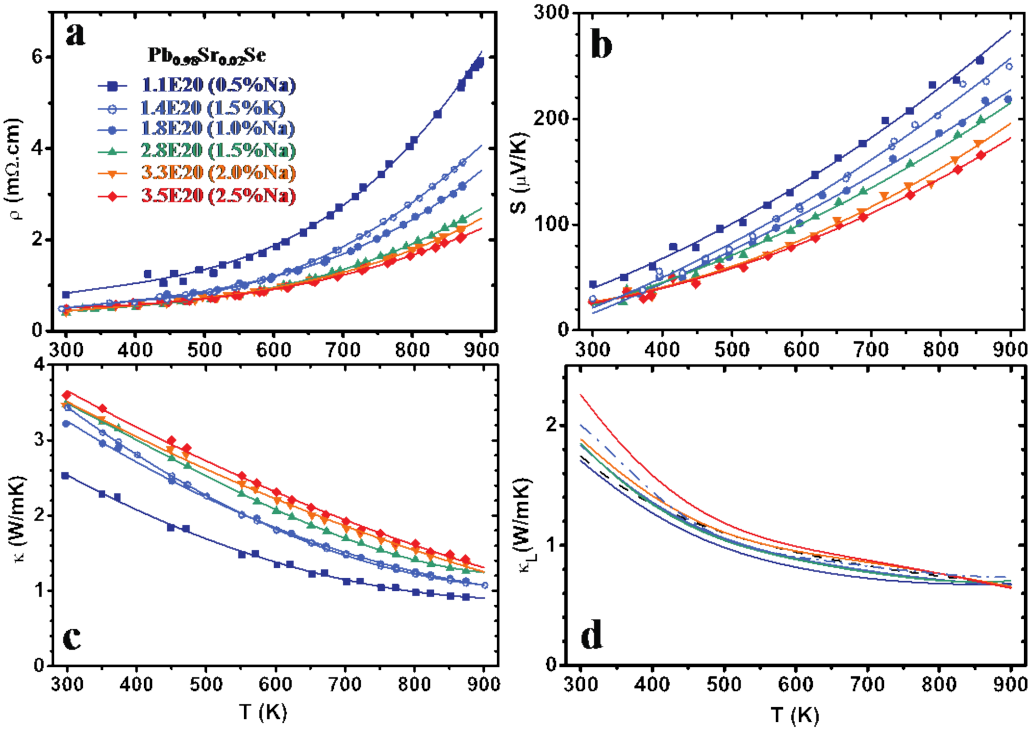
1. XRD and absorption spectrum result.



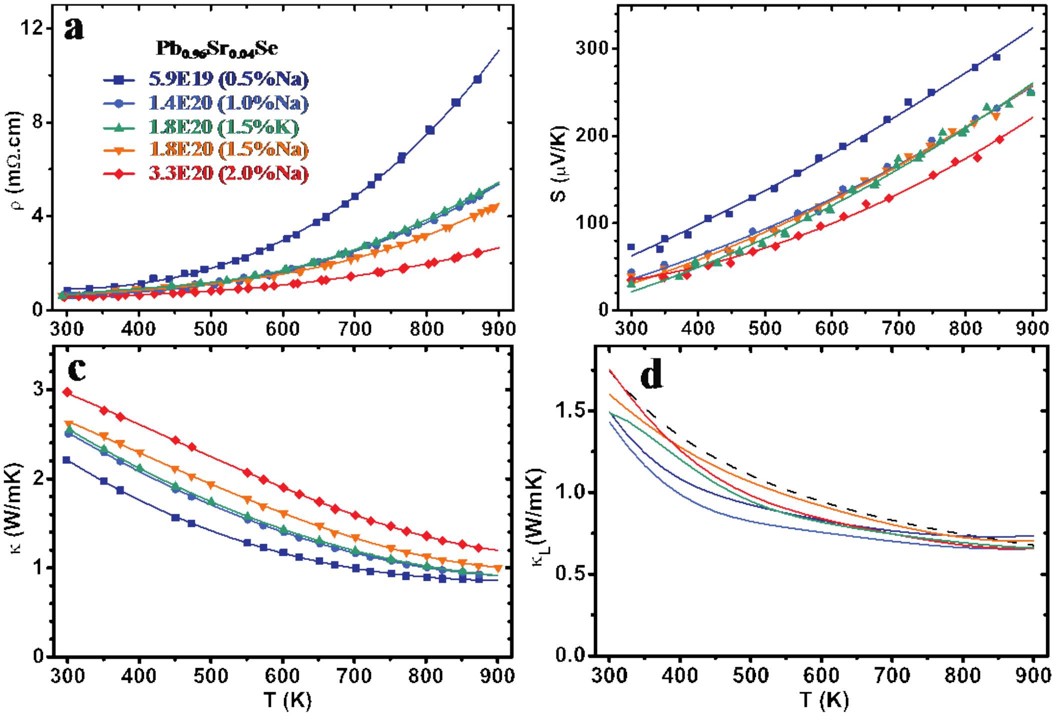


2. Transport properties for all samples studied.

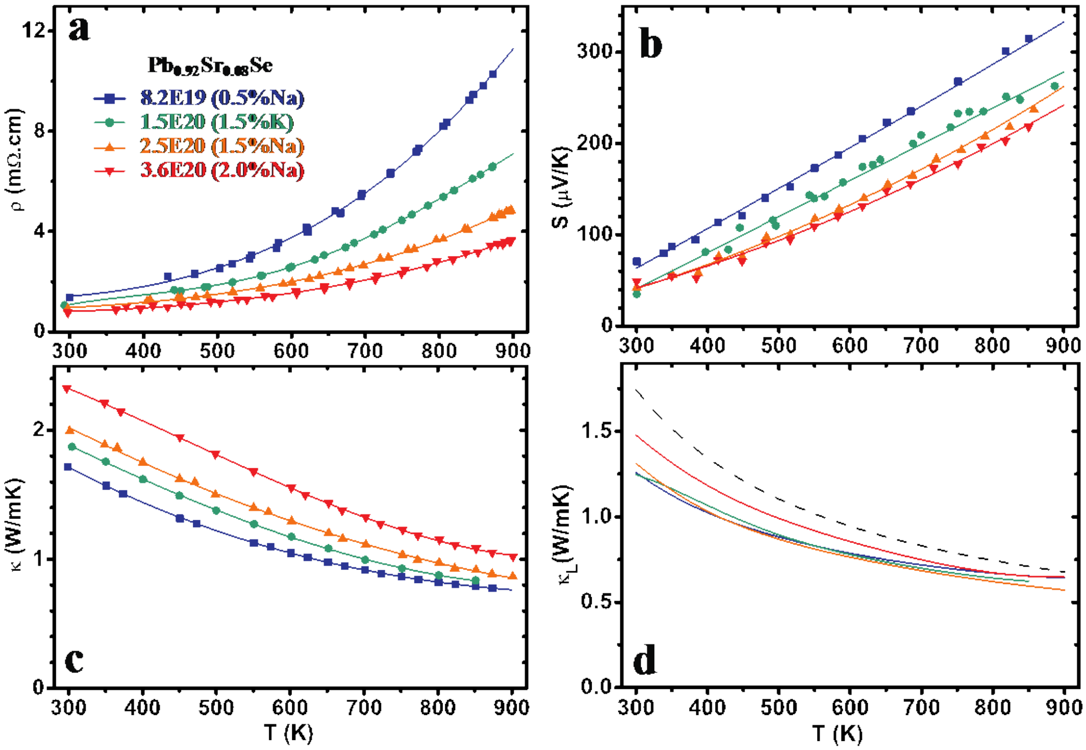
The 2%Sr alloys ($Pb_{0.98}Sr_{0.02}Se$):



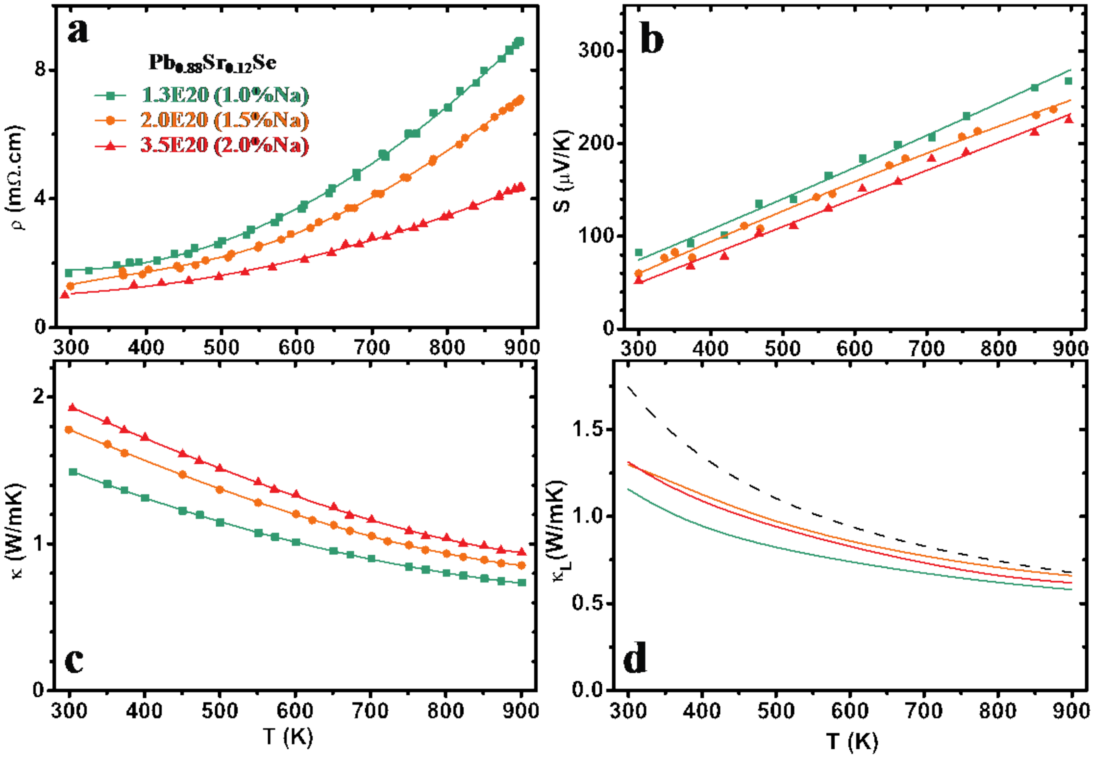
The 4%Sr alloys ($Pb_{0.96}Sr_{0.04}Se$):



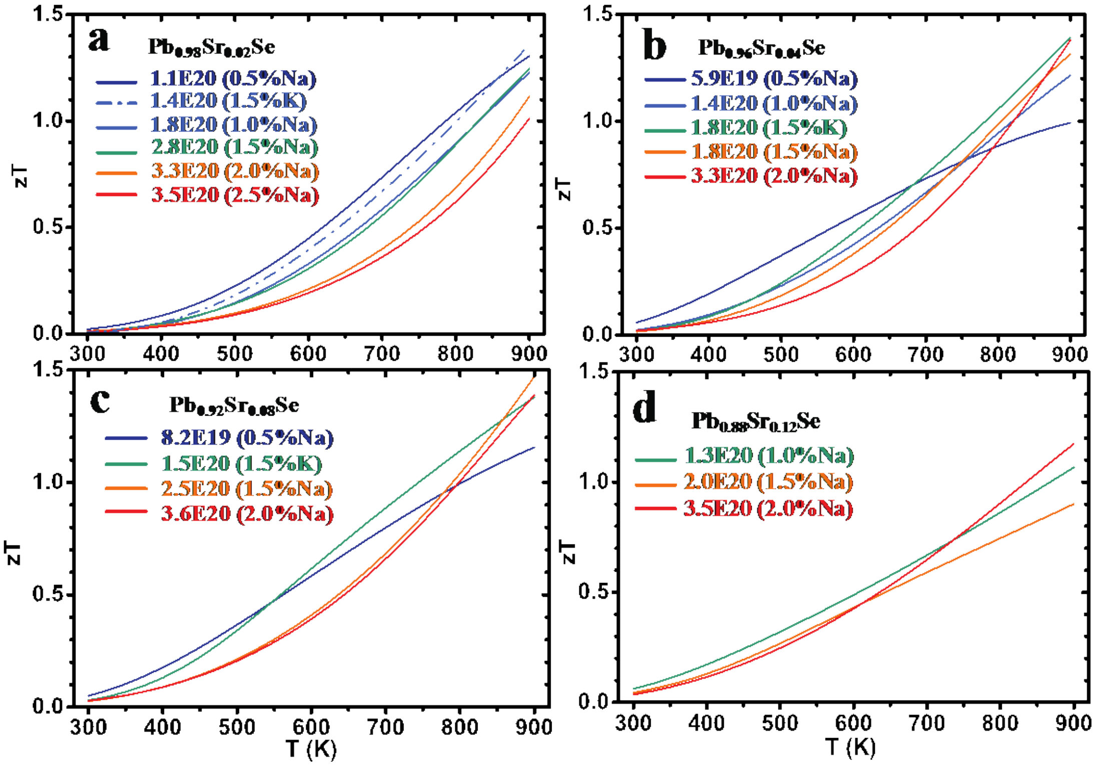
The 8%Sr alloys ($Pb_{0.92}Sr_{0.08}Se$):



The 12%Sr alloys ($Pb_{0.88}Sr_{0.12}Se$):



The zT values (all samples):



3. The calculation of Pisarenko relation for $Pb_{1-x}Sr_xSe$ samples.

The model used to calculate Seebeck coefficient versus Hall carrier density for different Sr content takes into account the primary valence band (the light band, L band), the secondary valence band (the heavy band, Σ band) and the conduction band. The light band and the conduction band are Kane bands whereas the heavy band is parabolic. The carrier scattering mechanism takes into account the deformation potential scattering (acoustic phonon scattering), the polar scattering from optical phonons and the alloy scattering. The relaxation time of each mechanism is described in previous works[1-3]. The transport parameters for each single band is calculated using the equations described in ref. 2. The transport parameters for the multi-band system is calculated using equations given by Putley[4]. The parameters used in the calculation is determined based on the following considerations:

1. The density-of-state effective mass of the light band and the conduction band is taken as 0.27 m_e at 300 K and changes with temperature following $\frac{d\ln m_d^*}{d\ln T}=0.5$, the anisotropy factor K is taken as a constant 1.75. This result fits most published Pisarenko relations[1, 5-7] on PbSe at 300K, and when extrapolated to low temperatures matches well with effective mass determined using other techniques[1]. The deformation potential for the conduction band and the light band were determined as 25 and 35 eV[1].

2. Little is known for the parameters of the heavy band. Based on suggested values from Veis[8] and transport properties of p-type PbSe at high temperatures these parameters are determined as: DOS effective mass 4.2 m_e, $K = 1$, and the deformation potential 28 eV.

3. The band gap and the gap between two valence bands change with temperature and Sr content ($Pb_{1-x}Sr_xSe$) following:

E_g/eV = 0.17 + 3 × 10^{-4} T/K + 3x

ΔE/eV = 0.32 – 2.2 × 10^{-4} T/K – 1.5x

The temperature dependence of E_g is based on our optical band gap measurements on undoped PbSe from room temperature to 600 K. and its dependence on Sr content is from the measured band gap of undoped Sr alloys. The temperature dependence of ΔE is based on Veis' optical measurement result[8] and modeling of transport data of p-type PbSe at high temperatures, and its dependence on Sr content is taken assuming the band gap increase in $Pb_{1-x}Sr_xSe$ alloys is from the movement of two bands at L point simultaneously towards opposite directions.

4. The alloy scattering potential U due to Sr substitution, for the light valence band is taken as 3 eV, which is estimated from measured Hall mobility of undoped $Pb_{1-x}Sr_xSe$ alloys. The same U is taken for the conduction band because no data is available so far to estimate it more accurately. U for the heavy band is assumed to be 1.5 eV. A smaller U for the heavy band is consistent with the assumption that the heavy band position does not explicitly depend on Sr content. The value of 1.5 eV is used to provide the best overall fitting for all alloy compositions.

4. The point defect scattering model for lattice thermal conductivity in alloys

The general temperature dependent lattice thermal conductivities are calculated with Lorenz number L that are calculated from Seebeck coefficient values under the single parabolic band assumption. The p-type $Pb_{1-x}Sr_xSe$ is a multi-band system so L calculated this way is not exactly accurate (in some cases could have as much as ~40 % error). L is evaluated this way for convenience since more accurate evaluation requires complicated calculation from a multi-band model as well as detailed knowledge of the Σ valence band that has not been fully established.

With the potential error in mind the most accurate κ_L can be found at 300 K from measured total thermal conductivity of undoped samples that have high electrical resistivity (> 10 mΩ.cm) and negligible κ_e. κ_L evaluated at high temperatures are also relatively accurate because the resistivities are the highest at these temperatures and κ_e reaches minimum, which means the absolute error in κ_e evaluation also reaches minimum. Thus, in Fig. 2 c) κ_L at 300 K and 850 K are discussed.

In materials without boundary scattering that has nano-scale mean-free-path, the most essential phonon scattering mechanism that affects thermal conductivity is the Umklapp process. In alloys assuming this and the point defect scattering are the only scattering mechanisms Callaway and Klemens has proposed the following model describing the lattice thermal conductivity of alloys and that of a defect-free system:

$$\frac{\kappa_{L,alloy}}{\kappa_{L,pure}} = \frac{arc\tan(u)}{u}\ , \quad u^2 = \frac{\pi\theta_D\Omega}{2\hbar v^2}\kappa_{L,pure}\Gamma$$

$\kappa_{L,alloy}$, $\kappa_{L,pure}$ are the lattice thermal conductivity of the alloy and the system without atomic disorder, respectively. v is the averaged speed of sound, θ_D is the Debye temperature, Ω is the volume per atom. The scattering parameter Γ for pseudo-binary ($(AB)_{1-x}(AC)_x$ type) systems can be written as[9, 10]:

$$\Gamma = x(1-x)[(\frac{\Delta M}{M})^2 + \varepsilon(\frac{\Delta a}{a})^2]$$

ΔM and $\Delta \alpha$ are the difference in mass and lattice constants between two constituents, M and α are the molar mass and lattice constant of the alloy. The parameter ε is generally considered an adjustable parameter determined by experiment result for each system[10, 11]. It has also been suggested by Klemens[12] that ε can be estimated using the Grüneisen parameter γ and elastic properties of the material:

$$\varepsilon = \frac{2}{9}[(G+6.4\gamma)\frac{1+r}{1-r}]^2$$

r is the Poisson ratio which for most semiconducting compounds is found between 0.15 and 0.3. G is a ratio between the contrast in bulk modulus (ΔK/K) and that in the local bonding length (ΔR/R), for cubic crystals with covalent bonding (IV elements, III-V compounds) G = 4 and with ionic bonding (II-VI, I-VII compounds) G = 3[13]. No other experimental data is available for the PbSe-SrSe system, so the value of ε has to be calculated. Using parameters for PbSe: r = 0.25[14], γ = 1.65[15], G = 3, ε is calculated to be 110. This value is used in the modeling. For the properties ($\kappa_{L,pure}$, v, θ_D) of the system without point defect, the simple rule of mixing is used, with parameters for PbSe θ_D = 190 K[16], κ_L = 1.7 W/mK at 300 K and 0.75 W/mK at 850 K; for SrSe θ_D = 290 K[17]. No thermal conductivity data is available for SrSe so this value is assumed 2.5 W/mK at 300 K and 1 W/mK at 850 K.

5. The mobility reduction from alloy scattering in undoped samples

For p type PbSe at 300 K, the influence of the secondary valence band is negligible, so is the bipolar contribution from the conduction band. Thus the system can be regarded as a single K band system. For the scattering mechanisms the influence of polar scattering from optical phonons is seen in non-degenerate lead chalcogenides[18], however, the deformation potential of L valence band in PbSe is large[1] so that the strong acoustic phonon scattering overwhelms the polar scattering. As a result, the single Kane band model with acoustic phonon scattering assumption is found adequate to explain the observed mobility in p-type PbSe[16, 19]:

$$\tau_{ac} = \frac{\pi\hbar^4 C_l N_V}{2^{1/2} m_d^{*3/2}(k_B T)^{3/2}\Xi^2}(\varepsilon+\varepsilon^2\alpha)^{-1/2}(1+2\varepsilon\alpha)^{-1}[1-\frac{8\alpha(\varepsilon+\varepsilon^2\alpha)}{3(1+2\varepsilon\alpha)^2}]^{-1}$$

$\alpha = k_BT/\varepsilon_g$, ε_g being the gap between conduction band and valence band at L point. Ξ is the effective deformation potential coefficient and C_l is the averaged longitudinal elastic constant. $m_b{}^*$ is the density-of-state effective mass for a single valley and ε is the reduced carrier energy $\varepsilon = E/k_BT$. All this parameters have be determined for PbSe.

For $Pb_{1-x}Sr_xSe$ alloys, the alloy scattering of carriers[16, 20, 21] needs to be added besides the acoustic phonon scattering:

$$\tau_{alloy} = \frac{8\hbar^4}{3\sqrt{2}\pi\Omega x(1-x)U^2 m_b^{*3/2}(k_BT)^{1/2}}(\varepsilon+\varepsilon^2\alpha)^{-1/2}(1+2\varepsilon\alpha)^{-1}[1-\frac{8\alpha(\varepsilon+\varepsilon^2\alpha)}{3(1+2\varepsilon\alpha)^2}]^{-1}$$

Ω is the volume per atom, x is the concentration ratio of the alloy atom, U is the alloy scattering potential. U was undetermined fort the $Pb_{1-x}Sr_xSe$ system. Its value is estimated here by fitting the calculated ratio of Hall mobility of $Pb_{1-x}Sr_xSe$ and that of PbSe with same carrier density (the energy dependence of two scattering mechanisms are the same so only the pre-factors need to be counted). The number of data points in Fig. 2 d) is limited thus it is possible that U is overestimated a bit, nonetheless, this value should be much larger than 1 eV.

1. H. Wang, Y. Pei, A. D. LaLonde and G. J. Snyder, Proc. Natl. Acad. Sci. U. S. A. **109** (25), 9705-9709 (2012).
2. H. Wang, E. Schechtel, Y. Pei and G. J. Snyder, Advanced Energy Materials **3** (4), 488-495 (2013).
3. H. Wang, A. D. LaLonde, Y. Z. Pei and G. J. Snyder, Adv. Funct. Mater. **23** (12), 1586-1596 (2013).
4. E. H. Putley, Journal of Physics C: Solid State Physics **8** (12), 1837 (1975).
5. M. N. Vinogradova, I. M. Rudnik, L. M. Sysoeva and N. V. Kolomoets, Soviet Physics Semiconductors-Ussr **2** (7), 892-893 (1969).
6. J. Androulakis, D. Y. Chung, X. L. Su, L. Zhang, C. Uher, T. C. Hasapis, E. Hatzikraniotis, K. M. Paraskevopoulos and M. G. Kanatzidis, Phys. Rev. B **84** (15), 155207 (2011).
7. H. Wang, Y. Pei, A. D. Lalonde and G. J. Snyder, Adv. Mater. **23** (11), 1366-1370 (2011).
8. A. N. Veis, V. I. Kaidanov, R. F. Kuteinikov, S. A. Nemov, S. A. Rudenko and Y. I. Ukhanov, Soviet Physics Semiconductors-Ussr **12** (2), 161-163 (1978).
9. G. T. Alekseeva, B. A. Efimova, L. M. Ostrovskaya, O. S. Serebryannikova and M. I. Tsypin, Soviet Physics Semiconductors-Ussr **4** (7), 1122-& (1971).
10. B. Abeles, Physical Review **131** (5), 1906 (1963).
11. J. Yang, G. P. Meisner and L. Chen, Appl. Phys. Lett. **85** (7), 1140 (2004).
12. P. G. Klemens, Proceedings of the Physical Society. Section A **68** (12), 1113 (1955).
13. O. L. Anderson and J. E. Nafe, Journal of Geophysical Research **70** (16), 3951-& (1965).
14. T. Seetawan and H. Wattanasarn, Procedia Engineering **32** (0), 609-613 (2012).

15. Y. I. Ravich, B. A. Efimova and I. A. Smirnov, *Semiconducting lead chalcogenides*. (Plenum Press, New York, 1970).
16. H. Wang, A. D. LaLonde, Y. Pei and G. J. Snyder, Adv. Funct. Mater., n/a-n/a (2012).
17. K. P. Thakur, Austr J Phys **30**, 325-334 (1977).
18. H. Wang, E. Schechtel, Y. Pei and G. J. Snyder, Advanced Energy Materials, n/a-n/a (2012).
19. Y. I. Ravich, B. A. Efimova and V. I. Tamarchenko, Phys. Status Solidi B-Basic Res. **43** (1), 11-33 (1971).
20. J. W. Harrison and J. R. Hauser, Phys. Rev. B **13** (12), 5347 (1976).
21. L. Makowski and M. Glicksman, J. Phys. Chem. Solids **34** (3), 487-492 (1973).