High Thermoelectric Performance of n-type $\text{PbTe}_{1-y}\text{S}_y$ due to Deep Lying States Induced by Indium Doping and Spinodal Decomposition

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ABSTRACT

Good thermoelectric materials should have high engineering figure-of-merit $(ZT)_{\text{eng}}$, not peak ZT , to achieve high conversion efficiency. In this work, we achieved a good $(ZT)_{\text{eng}}$ by optimizing the carrier concentration to improve the room temperature ZT using deep lying dopant, indium, in $\text{PbTe}_{1-y}\text{S}_y$. It was found that a room temperature ZT as high as ~ 0.5 and a peak $ZT \sim 1.1$ at about 673 K were obtained in $\text{Pb}_{0.98}\text{In}_{0.02}\text{Te}_{0.8}\text{S}_{0.2}$ due to a lower thermal conductivity by alloy scattering and Spinodal decomposition. The calculated efficiency could be as high as $\sim 12\%$ at cold side 323 K and hot side 773 K. The approach is expected to work in other materials systems too.

KEYWORDS: thermoelectrics, deep lying doping, Spinodal decomposition, conversion efficiency

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INTRODUCTION

Thermoelectric (TE) materials converting waste heat into electricity is considered a promising way to increase energy conversion efficiency. The energy conversion efficiency is determined by the dimensionless figure of merit $ZT = [S^2\sigma/(\kappa_e + \kappa_L)]T$, where S , σ , κ_e , κ_L , and T are the Seebeck coefficient, electrical conductivity, electronic thermal conductivity, lattice thermal conductivity, and absolute temperature, respectively. The efficiency of the TE device depends on the average ZT , or precisely engineering ZT : $(ZT)_{\text{eng}}$, that takes into the consideration of the temperature dependence of all the individual properties over the whole temperature range of the cold and hot sides.¹ Most of the high ZT values achieved are attributed to the optimized carrier concentration by controlled doping,²⁻⁴ enhanced Seebeck coefficient because of resonant doping⁵⁻⁸ or band convergence,⁹⁻¹¹ enhanced Hall mobility due to weak electron-phonon coupling¹² or modulation doping,^{13, 14} and lowered thermal conductivity with intrinsic complex structures¹⁵⁻¹⁸ or artificial nanostructures.^{19, 20} Additional strategies to further increase the ZT values are always pursued. With intrinsic high valley degeneracy for high electrical properties⁹ and intrinsic phonon anharmonicity for low thermal conductivity,^{21, 22} lead chalcogenides have attracted much attention. Peak ZT s as high as ~ 2 have been obtained in p-type lead chalcogenides²³⁻²⁵ and ~ 1.5 in n-type lead chalcogenides.²⁶ However, we must point out that the $(ZT)_{\text{eng}}$ of most of the reported chalcogenides over the whole temperature range is still low due to the very low ZT s below 200 °C. Several recent studies show gradual progress on the improvement of the ZT below 200 °C, such as by combination of nanostructures and complex band structure,²⁷ alloying PbTe with MgTe to stabilize the optimal carrier concentration in a large temperature range,²⁸ and doping with Cr to effectively enhance the room temperature power factor and ZT .^{29, 30} It has been predicted that deep defect states in narrow band-gap semiconductors could lead to the enhancement of the TE properties by annihilating the minority carriers, which helps to keep the Seebeck coefficient high and the thermal conductivity low at higher temperatures.³¹⁻³⁷ Normally, the carrier concentration was optimized to achieve high peak ZT at higher temperature.²⁻⁴ If the carrier concentration is optimized to achieve higher ZT at lower temperature by deep lying doping, can higher $(ZT)_{\text{eng}}$ be expected in a wide temperature range?

In this paper, we report our success on improving the $(ZT)_{\text{eng}}$ by creating deep lying states in indium-doped PbTe.³⁴ Higher $(ZT)_{\text{eng}}$ was achieved with optimizing the carrier concentration to induce a higher room temperature $ZT \sim 0.5$ by alloying PbTe with PbS. The benefit from the deep

lying doping, together with lower thermal conductivity contributed by the point defects³⁸⁻⁴¹ and the Spinodal decomposition^{25, 42-45} simultaneously is for achieving a peak $ZT \sim 1.1$ at about 673 K and a higher $(ZT)_{\text{eng}}$ in $\text{Pb}_{0.98}\text{In}_{0.02}\text{Te}_{0.8}\text{S}_{0.2}$.

EXPERIMENTAL SECTION

Ingots with nominal compositions $\text{Pb}_{1-x}\text{In}_x\text{Te}_{1-y}\text{S}_y$ ($0 < x < 0.03$, $0 < y < 1$) were prepared by melting the raw materials (Pb granules, 99.99%, Te chunks, 99.999%, S pieces, 99.99%, and In powder, 99.99%) inside sealed quartz tube with carbon coating. The quartz tubes were slowly raised to 1100 °C and kept for 10 h, then quenched from 1100 °C into water. The obtained ingots were cleaned and hand milled in a glove box. The reason we used hand mill instead of ball mill is that samples made of the powders from ball milling often softens above 500 °C. The obtained powder was loaded into a graphite die and consolidated by hot pressing. X-ray diffraction spectra analysis was conducted on a PANalytical multipurpose diffractometer with an X'celerator detector (PANalytical X'Pert Pro). The microstructures were investigated by a scanning electron microscope (SEM, LEO 1525) and a high-resolution transmission electron microscope (HRTEM, JEOL 2100F). The electrical resistivity (ρ) and Seebeck coefficient (S) were simultaneously measured on a commercial system (ULVAC ZEM-3). The thermal conductivity κ was calculated using $\kappa = D\alpha C_p$, where D is volumetric density determined by the Archimedes method, α is the thermal diffusivity obtained on a laser flash apparatus (Netzsch LFA 457), and C_p is the specific heat measured on a differential scanning calorimetry thermal analyzer (Netzsch DSC 404 C) (shown in figure S1). The Hall carrier concentration n_H at room temperature was measured using the PPMS (Physical Properties Measurement System, Quantum Design). The Hall mobility μ_H was calculated using $\mu_H = \sigma/(qn_H)$. The uncertainty for the electrical conductivity is 3%, the Seebeck coefficient 5%, the thermal conductivity 6%, so the combined uncertainty for power factor is 10% and that for ZT value is 12%.

RESULTS AND DISCUSSION

Indium (In) can create deep defect states in PbTe, which is expected to lead to enhanced TE properties at higher temperature by keeping the higher Seebeck coefficient and lower thermal conductivity at higher temperature due to the suppressed bipolar effect.³¹⁻³⁷ However, it is difficult for the deep impurities to ionize to the conduction band, only a fraction of the impurities

contributed to the free carriers, so the carrier concentration is limited to only $\sim 2 \times 10^{18} \text{ cm}^{-3}$ at room temperature when prepared by melting and hot pressing, much lower than the I-doped PbTe,⁴⁶ which is shallow lying doping³⁶ (see figure 1). Figure 2 shows the TE properties of In-doped PbTe with different In concentrations compared with reported I-doped PbTe with lowest carrier concentration at $\sim 6 \times 10^{18} \text{ cm}^{-3}$ (inset). With increasing In content, the electrical conductivity increased, but was kept only at a low level of $\sim 1 \times 10^4 \text{ S m}^{-1}$ due to low confined carrier concentration, lower than that of I-doped PbTe. The Seebeck coefficient stabilized to be negative in the whole temperature range when $x \geq 0.01$, suggesting the n-type doping. All the lattice thermal conductivities were calculated by subtracting the electronic thermal conductivity from the total thermal conductivity ($\kappa_L = \kappa_{\text{total}} - \kappa_e = \kappa_{\text{total}} - L\sigma T$, where L is the Lorenz number calculated using a single Kane band model (SKB)^{4, 47}, see supporting information). A peak ZT value of ~ 0.65 was obtained at about 673 K because of the increased power factor ($S^2\sigma$) and the decreased thermal conductivity. The peak ZT of In-doped PbTe is lower than I-doped PbTe due to lower electrical conductivity. However, the peak ZT temperature is higher than that of I-doped PbTe (figure 2 (f)). This is consistent with the picture that In is deep levels in the band. At higher temperatures, more impurities are ionized, leading to more electrons in the conduction band and hence less minority-carrier excitation from the valence band. To get higher ZT , the carrier concentration needs to be further increased.

PbS has recently attracted much attention due to the advantage of abundance, inexpensiveness, and possible higher operation temperature.^{6, 47-49} Both n-type (Cl doping)⁴⁸ and p-type (Na doping)⁴⁹ PbS have ZT values higher than 1 at about 925 K with second phase nanostructures. Temperature dependence of (a) electrical conductivity, (b) Seebeck coefficient, (c) power factor, (d) thermal diffusivity, (e) total thermal conductivity and lattice thermal conductivity, and (f) ZT for $\text{Pb}_{1-x}\text{In}_x\text{S}$ ($x = 0.003, 0.005, \text{ and } 0.01$) is shown in figure 3. All the electrical conductivities monotonously decreased with increasing temperature, presenting typical behavior of degenerate semiconductors, different from the In-doped PbTe with confined doping concentration. In doping effectively increased the carrier concentration and the electrical conductivity of PbS with the room temperature Hall carrier concentration to an optimal value of $\sim 4 \times 10^{19} \text{ cm}^{-3}$ for the best peak ZT in $\text{Pb}_{0.995}\text{In}_{0.005}\text{S}$ (This is also the optimal Hall carrier concentration for the best reported n-type PbS with Cl doping.⁴⁷). Both In-doped PbTe (figure 2 (b)) and In-doped PbS have negative Seebeck coefficients, same with the reported In-doped PbSe,³

indicating consistent n-type doping. With increasing temperature, the band gap (~ 0.42 eV at 300 K) of PbS also increases,^{47, 50} so there is no obvious sign of bipolar effect in highly In-doped PbS. Since PbS is lighter than PbTe and PbSe, the lowest lattice thermal conductivity of ~ 1.0 W m⁻¹ K⁻¹ at about 873 K is higher than those of In-doped PbTe (~ 0.85 W m⁻¹ K⁻¹ at about 673 K) (figure 2 (e)) and the reported In-doped PbSe (~ 0.75 W m⁻¹ K⁻¹ at about 873 K),³ but consistent with the reported pristine Cl-doped PbS without nanostructures,⁴⁷ which has comparable lowest lattice thermal conductivity and highest ZT value shown in figure 3 (f) (bold line). The peak ZT is ~ 0.8 at about 873 K for Pb_{0.995}In_{0.005}S.

By alloying PbTe with PbS, we intended to increase the electrical conductivity of In-doped PbTe with fixed indium concentration. Many studies have shown the existence of a miscibility gap in the phase diagram of ternary PbTe_{1-y}S_y compound with possibility for Spinodal decomposition.^{25, 42-45} Figure 4 presents the XRD patterns for Pb_{0.98}In_{0.02}Te_{1-y}S_y ($y = 0.05, 0.10, 0.20, 0.30$, and 1.0). There is no impurity phase induced by In doping. Both Pb_{0.98}In_{0.02}Te ($y = 0$) and Pb_{0.995}In_{0.005}S ($y = 1$) are single phase crystallized in face-centered cubic Rocksalt structure (space group Fm $\bar{3}$ m). With increasing S content, all peaks gradually shift to right when $y \leq 0.2$, indicating the solid solution of PbS in PbTe, which is also confirmed by good fitting to Vegard's law (figure 4 (b)). A second phase (S-rich phase) was detected when $y \geq 0.1$ due to the Spinodal decomposition. For convenience, we still use Pb_{0.98}In_{0.02}Te_{1-y}S_y to represent the corresponding compounds.

Figure 5 shows the temperature dependence of (a) electrical conductivity, (b) Seebeck coefficient, (c) power factor, (d) thermal diffusivity, (e) total thermal conductivity and lattice thermal conductivity, and (f) ZT for Pb_{0.98}In_{0.02}Te_{1-y}S_y ($y = 0.05, 0.10, 0.20$, and 0.30) at fixed In concentration. With increasing y , the electrical conductivity increased as expected and the Seebeck coefficient decreased (figure 6 (a)), as a result of the increased Hall carrier concentration. The incorporation of PbS could move the impurity level from above the valence band maximum close to the bottom of the conduction band, with tendency to become shallow lying doping. The room temperature Pisarenko relation for Pb_{0.98}In_{0.02}Te_{1-y}S_y (figure 6 (b)) indicated the gradual band structure change from PbTe to PbS. No resonant state was found as discussed by the first principles calculation.³⁴ Due to deep lying doping, the n_H is difficult to reach that high when $y \leq 0.2$, but this relative low n_H is good for the higher ZT at room temperate in this system. Figure 7 shows the calculated power factor (a) and ZT (b) as a function of Hall carrier concentration for n-

type PbTe and PbS at different temperatures (300 K and 600 K). The transport coefficients for PbTe and PbS were calculated using a non-parabolic single Kane band model (SKB) that includes deformation potential scattering of L-point conduction band electrons by acoustic phonons and polar scattering of electrons by optical phonons. The relaxation times for these two scattering mechanisms are given in the supporting information along with expressions used for the carrier density, Hall density, Hall mobility, electrical conductivity, Seebeck coefficient and Lorenz factor. The optimal carrier concentration for both peak power factor and peak ZT increased with increasing operation temperature and increasing PbS concentration. The experimental carrier concentration benefits the highest room temperature power factor, consistent with the calculation results, however, lower power factor values (figure 7 (a)) caused by alloy scattering induced lower Hall mobility. This lower Hall mobility also lowered the electronic thermal conductivity, leading to a peak room temperature $ZT \sim 0.5$ in $\text{Pb}_{0.98}\text{In}_{0.02}\text{Te}_{0.8}\text{S}_{0.2}$ with Hall carrier concentration at $\sim 8 \times 10^{18} \text{ cm}^{-3}$, just in between those of the calculated peak ZT s of n-type PbTe and PbS at room temperature (figure 7 (b)). At normal doping, the high temperature ZT will decrease dramatically due to the bipolar effect with this relative low n_H , like I-doped PbTe (solid line) shown in figure 5 (f).⁴⁶ However, in this case, electrons in deep lying states annihilated the minor carriers, which kept the high Seebeck coefficient, low thermal conductivity, and then still decent ZT at higher temperature, resulting in a $(ZT)_{\text{eng}}$, even comparable with the optimized composition with very high peak ZT by normal I doping (n_H is $\sim 4 \times 10^{19} \text{ cm}^{-3}$) (dashed line).⁴⁶ When $y = 0.3$, the carrier concentration increased to $\sim 1.1 \times 10^{19} \text{ cm}^{-3}$, whereas the bipolar temperature decreased (figure 5 (d)) in spite of the enlarged band gap by incorporation of PbS, which indicated the change of the deep lying doping to the shallow lying doping.

Incorporation of PbS not only increased the electrical conductivity, but also strongly decreased the lattice thermal conductivity of In-doped PbTe. All the lattice thermal conductivity of $\text{Pb}_{0.98}\text{In}_{0.02}\text{Te}_{1-y}\text{S}_y$ ($y = 0.05, 0.10, 0.20$, and 0.30) (figure 5 (e)) decreased compared with that of the In-doped PbTe. The lowest lattice thermal conductivity is $\sim 0.6 \text{ W m}^{-1} \text{ K}^{-1}$ at about 673 K for $\text{Pb}_{0.98}\text{In}_{0.02}\text{Te}_{0.8}\text{S}_{0.2}$. Figure 8 shows the calculated room temperature lattice thermal conductivity of $\text{Pb}_{0.98}\text{In}_{0.02}\text{Te}_{1-y}\text{S}_y$ ($0 \leq y < 1$) and $\text{Pb}_{0.995}\text{In}_{0.005}\text{S}$. Different from the $\text{PbTe}_{1-y}\text{Se}_y$ system, which has lowest lattice thermal conductivity at around $y = 0.5$ due to alloy scattering,^{30, 38} there are two inflection points ($y = 0.20$ and 0.95) in this $\text{PbTe}_{1-y}\text{S}_y$ system. According to the XRD patterns (figure 4 and figure S2), only four compositions ($y = 0, 0.05, 0.95$, and 1 , with open ovals in figure

8) are single phase. The dramatic κ_L decrease in $\text{Pb}_{0.98}\text{In}_{0.02}\text{Te}_{0.95}\text{S}_{0.05}$ and $\text{Pb}_{0.98}\text{In}_{0.02}\text{Te}_{0.05}\text{S}_{0.95}$ is the result of effective alloying. Other compositions are within the immiscible gap, having two phases (Te-rich phase and S-rich phase) confirmed by both XRD in figure 4 (a) and SEM images in figure 8 (a)-(f) (only show compositions with $y = 0.10, 0.20, 0.30, 0.50, 0.70$, and 0.90 (filled circles)) with the same naturally formed striped structure, but different width of the strips. All these compositions underwent the Spinodal decomposition without nucleation barrier, which continuously contributed to the decrease of the κ_L . The lowest room temperature κ_L is $\sim 0.68 \text{ W m}^{-1} \text{ K}^{-1}$ for $\text{Pb}_{0.98}\text{In}_{0.02}\text{Te}_{0.8}\text{S}_{0.2}$ with the thinnest strips ($\sim 30 \text{ nm}$ in width) (figure 8 (b)). Even thinner strips ($\sim 2 \text{ nm}$) coming from nanoscale compositional fluctuation in this composition were detected at many places by transmission electron microscopy (TEM) and are shown in figure 9 (a). More contributions for lower lattice thermal conductivity also comes from the partial nucleation and growth features in some regions, like the nanocrystals $\sim 30 \text{ nm}$ in figure 9 (b),^{44, 45} and many edge dislocations in figure 9 (c), where the variety of image contrast and the bend of atomic strings induced by the dislocations are remarkable, and the inserted half planes are clearly seen in the filtered image.^{29, 30} Figure 9 (d) is a [001] High-resolution TEM image for a grain boundary, the inserted fast Fourier transform (FFT) of the left area on the boundary showing the well crystallization as cubic structure $\text{Fm}\bar{3}\text{m}$ which is consistent with the XRD result. The clean boundaries and good crystallinity are beneficial to the transport of charge carriers.¹⁹

For considering the real application, we also calculated the $(ZT)_{\text{eng}}$ (that is a cumulative performance at a given T_h and T_c) and the efficiency of $\text{Pb}_{0.98}\text{In}_{0.02}\text{Te}_{0.8}\text{S}_{0.2}$ using the following formulas¹, compared with other reported n-type ternary and quaternary lead chalcogenides with even higher peak ZT s and presented in figure 10.

$$\eta_{\text{max}} = \eta_c \frac{\sqrt{1+(ZT)_{\text{eng}} \alpha_1 \eta_c^{-1}} - 1}{\alpha_0 \sqrt{1+(ZT)_{\text{eng}} \alpha_1 \eta_c^{-1} + \alpha_2}} \quad (1)$$

$$(ZT)_{\text{eng}} = \frac{\left(\int_{T_c}^{T_h} S(T) dT \right)^2}{\int_{T_c}^{T_h} \rho(T) dT \int_{T_c}^{T_h} \kappa(T) dT} \Delta T \quad (2)$$

where,

$$\alpha_i = \frac{S(T_h) \Delta T}{\int_{T_c}^{T_h} S(T) dT} - \frac{\int_{T_c}^{T_h} \tau(T) dT}{\int_{T_c}^{T_h} S(T) dT} W_T \eta_c - i W_J \eta_c \quad (i = 0, 1 \text{ and } 2) \quad (3)$$

$$W_J = \frac{\int_{T_c}^{T_h} \int_{T_c}^{T_h} \rho(T) dT dT}{\Delta T \int_{T_c}^{T_h} \rho(T) dT} \quad \text{and} \quad W_T = \frac{\int_{T_c}^{T_h} \int_{T_c}^{T_h} \tau(T) dT dT}{\Delta T \int_{T_c}^{T_h} \tau(T) dT} \quad (4)$$

$(ZT)_{eng}$ is the engineering figure of merit as a direct indicator, representing overall performance of the material at given T_h and T_c . $S(T)$, $\rho(T)$, $\kappa(T)$, and $\tau(T)$ are temperature dependent Seebeck coefficient, electric resistivity, thermal conductivity, and Thomson coefficient, respectively. W_J and W_T are weight factors providing a practical contribution of Joule and Thomson heat, respectively, at the hot side. In spite of high peak ZT s in I-doped $\text{PbTe}_{1-y}\text{Se}_y$ (~ 1.5 at about 600 K),⁵¹ Cl-doped $\text{PbSe}_{1-y}\text{S}_y$ (~ 1.3 at about 900 K),⁵² and Cl-doped $\text{PbTe}_{1-x-y}\text{Se}_x\text{S}_y$ (~ 1.1 at about 800 K)⁵³ (figure 10 (a)), $(ZT)_{eng}$ (figure 10 (b)) and the efficiency (figure 10 (c)) of both $\text{Pb}_{0.99}\text{Cr}_{0.01}\text{Te}_{0.25}\text{Se}_{0.75}$ (previous work with high $(ZT)_{eng}$)³⁰ and $\text{Pb}_{0.98}\text{In}_{0.02}\text{Te}_{0.8}\text{S}_{0.2}$ are higher than others with T_h up to 773 K. It clearly shows that increase of $(ZT)_{eng}$ is more important than achieving high peak ZT . An $(ZT)_{eng}$ of ~ 0.7 and the efficiency of $\sim 12\%$ can be achieved for $\text{Pb}_{0.98}\text{In}_{0.02}\text{Te}_{0.8}\text{S}_{0.2}$ with T_h at 773 K and T_c at 323 K.

CONCLUSIONS

PbS was incorporated into In-doped PbTe to increase the electrical conductivity by band modification and to decrease the thermal conductivity by alloy scattering and Spinodal decomposition. With higher room temperature ZT achieved by deep lying doping, desirable average ZT and $(ZT)_{eng}$ are achieved in $\text{Pb}_{0.98}\text{In}_{0.02}\text{Te}_{0.8}\text{S}_{0.2}$, leading to an efficiency of $\sim 12\%$ with cold side at 323 K and hot side at 773 K. In-doped $\text{PbTe}_{1-y}\text{S}_y$ has higher $(ZT)_{eng}$ due to the deep lying doping for higher ZT at near room temperatures. This method could be applied to other material systems for higher TE efficiencies.

ACKNOWLEDGEMENT: This work is supported by “Solid State Solar Thermal Energy Conversion Center (S³TEC)”, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Science under award number DE-SC0001299.

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Figure Captions

Figure 1. Room temperature Hall carrier concentration as a function of In concentration x in $\text{Pb}_{1-x}\text{In}_x\text{Te}$ and I concentration x in $\text{PbTe}_{1-x}\text{I}_x$ (inset) ⁴⁶.

Figure 2. Temperature dependence of (a) electrical conductivity, (b) Seebeck coefficient, (c) power factor, (d) thermal diffusivity, (e) total thermal conductivity and lattice thermal conductivity, and (f) ZT for $\text{Pb}_{1-x}\text{In}_x\text{Te}$ ($x = 0, 0.01, 0.02$, and 0.03) compared with the reported I-doped PbTe having the lowest carrier concentration of $\sim 6 \times 10^{18} \text{ cm}^{-3}$.

Figure 3. Temperature dependence of (a) electrical conductivity, (b) Seebeck coefficient, (c) power factor, (d) thermal diffusivity, (e) total thermal conductivity and lattice thermal conductivity, and (f) ZT for $\text{Pb}_{1-x}\text{In}_x\text{S}$ ($x = 0.003, 0.005$, and 0.01). The TE properties of undoped PbS ⁴⁸ are included. The ZT value of the optimized Cl-doped PbS ⁴⁷ is plotted in (f) for comparison.

Figure 4. (a) XRD patterns for $\text{Pb}_{0.98}\text{In}_{0.02}\text{Te}_{1-y}\text{S}_y$ ($y = 0.05, 0.10, 0.20$, and 0.30) compared with $\text{Pb}_{0.98}\text{In}_{0.02}\text{Te}$ and $\text{Pb}_{0.995}\text{In}_{0.005}\text{S}$. The index is for the $\text{Pb}_{0.98}\text{In}_{0.02}\text{S}$ with face-centered cubic structure (space group $\text{Fm}\bar{3}\text{m}$). (b) The lattice parameter relation with S concentration y .

Figure 5. Temperature dependence of (a) electrical conductivity, (b) Seebeck coefficient, (c) power factor, (d) thermal diffusivity, (e) total thermal conductivity and lattice thermal conductivity, and (f) ZT for $\text{Pb}_{0.98}\text{In}_{0.02}\text{Te}_{1-y}\text{S}_y$ ($y = 0.05, 0.10, 0.20$, and 0.30). The ZT value of $\text{PbTe}_{1-x}\text{I}_x$ is plotted in (f) for comparison⁴⁶.

Figure 6. (a) Room temperature Hall carrier concentration as a function of S concentration y in $\text{Pb}_{0.98}\text{In}_{0.02}\text{Te}_{1-y}\text{S}_y$, and (b) Room temperature Pisarenko plots for $\text{Pb}_{0.98}\text{In}_{0.02}\text{Te}_{1-y}\text{S}_y$ ($y = 0, 0.05, 0.10, 0.20, 0.30, 0.40, 0.50$, and 1). Red curve is based on single Kane model (SKB) with the electron effective mass of PbTe $m^* = 0.25 m_e$. Blue curve is based on single Kane model (SKB) with the electron effective mass of PbS $m^* = 0.39 m_e$.

Figure 7. Room temperature power factor (a) and ZT (b) as a function of Hall carrier concentration for $\text{Pb}_{0.98}\text{In}_{0.02}\text{Te}_{1-y}\text{S}_y$ ($y = 0.05, 0.10, 0.20, 0.30, 0.40, \text{ and } 0.50$). Black curve is calculated power factor (a) and ZT (b) as a function of Hall carrier concentration for n-type PbTe, blue curve is calculated power factor (a) and ZT (b) as a function of Hall carrier concentration for n-type PbS. The dashed lines represent the power factor at 600 K. All the calculations are based on the single Kane model (SKB). We used the fitted lattice thermal conductivity of $\text{Pb}_{0.98}\text{In}_{0.02}\text{Te}_{1-y}\text{S}_y$ for the calculation of the room temperature ZT .

Figure 8. Room temperature lattice thermal conductivity for $\text{Pb}_{0.98}\text{In}_{0.02}\text{Te}_{1-y}\text{S}_y$ ($0 \leq y \leq 1$). The SEM images for different compositions (filled circles) are shown in figure (a)-(f), respectively. The scale bar is 200 nm for (a), (b), (c), (e), and (f), and 2 μm for (d).

Figure 9. TEM images for $\text{Pb}_{0.98}\text{In}_{0.02}\text{Te}_{0.8}\text{S}_{0.2}$, showing Spinodal decomposition (a), nanograins (b), many edge dislocations, and the extra half planes marked by $\perp$ in magnified filtered image of the circular area (c), and clean grain boundary (d). FFT of the left area of the boundary is presented in inset to show the good crystallization. The scale bars are 10 nm for (a), and (b), and 2 nm for (c), and (d).

Figure 10. Temperature dependence of (a) ZT , (b) $(ZT)_{\text{eng}}$, and (c) Device efficiency for $\text{Pb}_{0.98}\text{In}_{0.02}\text{Te}_{0.8}\text{S}_{0.2}$ in comparison with the other reported n-type ternary and quaternary lead chalcogenides: Cr-doped $\text{PbTe}_{1-y}\text{Se}_y$,³⁰ I-doped $\text{PbTe}_{1-y}\text{Se}_y$,⁵¹ Cl-doped $\text{PbSe}_{1-y}\text{S}_y$,⁵² Cl-doped $\text{PbTe}_{1-x-y}\text{Se}_x\text{S}_y$,⁵³ Cl-doped $\text{PbS}_{1-y}\text{Te}_y$,⁵⁴ and In-doped $\text{PbTe}_{1-y}\text{Se}_y$,⁵⁵ with cold side temperature 323 K.

Figure 1 Qian Zhang *et al.*

$\text{Pb}_{1-x}\text{In}_x\text{Te}$

Figure 2 Qian Zhang *et al.*

$\text{Pb}_{1-x}\text{In}_x\text{S}$

Figure 3 Qian Zhang *et al.*

Figure 4 Qian Zhang *et al.*

Figure 5 Qian Zhang *et al.*

Figure 6 Qian Zhang *et al.*

Figure 7 Qian Zhang *et al.*

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Figure 9 Qian Zhang *et al.*

Figure 10 Qian Zhang *et al.*

Graphic Abstract

We have achieved increased average ZT and high conversion efficiency $\sim 12\%$ at cold side 323 K and hot side 773 K by optimizing the carrier concentration to improve the room temperature ZT using deep lying dopant, indium, in $\text{PbTe}_{1-y}\text{S}_y$ and lowered the lattice thermal conductivity through alloy scattering and Spinodal decomposition.