Chemical composition tuning in quaternary p-type Pb-chalcogenides – a promising strategy for enhanced thermoelectric performance†

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Recently a significant improvement in the thermoelectric performance of p-type ternary PbTe–PbSe and PbTe–PbS systems has been realized through alternating the electronic band structure and introducing nano-scale precipitates to bulk materials respectively. However, the quaternary system of PbTe–PbSe–PbS has received less attention. In the current work, we have excluded phase complexity by fabricating single phase sodium doped PbTe, alloyed with PbS up to its solubility limit which is extended to larger concentrations than in the ternary system of PbTe–PbS due to the presence of PbSe. We have presented a thermoelectric efficiency of approximately 1.6 which is superior to ternary PbTe–PbSe and PbTe–PbS at similar carrier concentrations and the binary PbTe, PbSe and PbS alloys. The quaternary system shows a larger Seebeck coefficient than the ternary PbTe–PbSe alloy, indicative of a wider band gap, valence band energy offset and heavier carriers effective mass. In addition, the existence of PbS in the alloy further reduces the lattice thermal conductivity originated from phonon scattering on solute atoms with high contrast atomic mass. Single phase quaternary PbTe–PbSe–PbS alloys are promising thermoelectric materials that provide high performance through adjusting the electronic band structure by regulating chemical composition.

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Introduction

Solid-state thermoelectric convertors are considered to be pioneer candidates for industrial waste heat recovery,¹ which has recently been driving the scientific interest on the mid-range temperature (600–900 K) thermoelectric materials.^{2–8} The search for high performance materials from naturally abundant elements has continued to improve the relatively low conversion efficiency of such materials, which is determined by the figure of merit, $zT = S^2T\sigma/(\kappa_E + \kappa_L)$, where, S , σ , T , κ_L , and κ_E are the Seebeck coefficient, electrical conductivity, absolute temperature, and the lattice and electronic components of the thermal conductivity, respectively.

Lead telluride stands out amongst the best thermoelectric materials and has been proven to possess a high zT value

of ~ 1.4 at ~ 750 K for both n-type⁹ and p-type¹⁰ compounds, and its high performance can be affected by tuning the electronic structure near the Fermi level, specifically: by introducing resonant states,^{5,11} manipulating and utilizing the material's multiple bands,^{10,12} and/or altering the band gap.^{13–16} Ternary PbTe-rich alloys of PbTe–PbSe^{4,17,18} show a higher figure of merit than individual binary PbTe and PbSe systems in the temperature range of 550–800 K, mainly due to alteration of the electronic band structure.^{4,18} In contrast, higher zT values of PbTe–PbS^{19–22} compared to the binary systems are credited to the reduction in lattice thermal conductivity, which originates from phonon scattering at the interfaces of secondary phases, as PbS shows very limited solubility in the PbTe matrix.²³ Here, we present a strategy to design single-phase quaternary alloys with high thermoelectric efficiency. We have extended the PbS solubility limit in the PbTe matrix by simultaneous alloying with PbSe and PbS. We show that the thermoelectric performance of heavily doped single-phase quaternary PbTe–PbSe–PbS alloys is superior to those of ternary PbTe–PbSe and PbTe–PbS, and binary PbTe, PbSe, and PbS alloys. The improved thermoelectric performance originates from an enhancement in the Seebeck coefficient through band structure tuning and lattice thermal conductivity reduction that is attributed to phonon scattering from the disorder arising from the introduction of solute atoms.

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Fig. 1 Experimentally derived quasi-binary PbS–PbTe phase diagram (data points extracted from ref. 24). The red curves show the upper limit of the miscibility gap and solidus curve for $\text{PbSe}_{0.1}\text{S}_x\text{Te}_{(0.9-x)}$ alloys, which indicates that addition of 10 at% PbSe to $\text{PbS}_x\text{Te}_{(1-x)}$ alloy (red curve) increases PbS solubility in the matrix and shifts the nucleation temperature of the secondary phase to lower temperatures.

Ternary PbTe–PbSe and PbSe–PbS systems show solid solutions over the entire composition range.²⁴ However, the components of the PbTe–PbS system show very limited solubility with respect to each other, and phase separation of PbS precipitates in the PbTe matrix at the PbTe-rich side of the phase diagram occurs *via* nucleation and growth (Fig. 1). This behaviour is also well understood in the quaternary system of PbTe–PbSe–PbS, where addition of PbSe shifts the upper curve of the miscibility gap to lower temperatures,²⁵ as illustrated by the red line in Fig. 1 for 10 at% PbSe ($\text{PbSe}_{0.1}\text{S}_x\text{Te}_{(0.9-x)}$). The final composite contains two phases: Te-rich (matrix) and S-rich (precipitates) of $\text{PbTe}(\text{Se},\text{S})$ and $\text{PbS}(\text{Se},\text{Te})$, respectively, and the solubility limit of PbS-rich precipitates is increased in the matrix. Furthermore, PbS and PbSe have higher melting points of 1391 K and 1355 K, respectively compared with PbTe at 1197 K. Therefore, the solidus curve is slightly shifted to higher temperatures by addition of 10 at% PbSe to the alloy (Fig. 1); consequently, it is anticipated that the $\text{PbSe}_y\text{S}_x\text{Te}_{(1-x-y)}$ alloys can sustain higher temperatures than PbTe and $\text{PbTe}_x\text{S}_{(1-x)}$ composites.

Experimental

Fabrication

Polycrystalline samples of PbS and PbSe were synthesised by mixing high purity Pb (99.999%), Se (99.999%), and dried S (99.9%) in vacuum sealed quartz ampoules at a residual pressure of $\sim 10^{-4}$ Torr, and reacting them at high temperatures to produce high purity starting materials. The final polycrystalline $\text{Pb}_{0.98}\text{Na}_{0.02}\text{Se}_{0.1}\text{S}_x\text{Te}_{(1-x)}$ ($x = 0, 0.05, 0.1, 0.15, 0.2$) samples were synthesised by mixing stoichiometric quantities of high purity PbS, PbSe, Pb, and Te, with Na as a dopant, with a total mass of 10 g, sealing them in carbon-coated quartz tubes under vacuum, and then heating them to 1373 K. After homogenising at 1373 K for 10 hours, the samples were quenched in cold water, followed by annealing at 773 K for 48 hours. The resulting ingots were

hand-ground to powder and sintered at 773 K for 1 h at an axial pressure of 40 MPa under an argon atmosphere by induction hot pressing.²⁶

Transport property measurements

The electrical resistivity was measured using the van der Pauw method. Samples were loaded onto a heated BN substrate in vacuum, and four probes were attached to the edge of the sample. The Seebeck coefficients were obtained along the sample's cross-plane direction. The samples were placed in contact with a heater and thermocouple on each surface in a vacuum chamber. The heaters provide a temperature difference oscillation of $\pm 7^\circ\text{C}$ whilst maintaining a set average temperature. The thermoelectric voltage and the temperature on each surface were recorded, with the slope giving the Seebeck coefficient at the average temperature.²⁷ The thermal conductivity κ is calculated from $\kappa = \rho D_T C_p$. The laser flash method (Netzsch LFA457) was used to measure the thermal diffusivity, D_T , while the density, ρ , was calculated using the measured weight and dimensions, and the specific heat capacity, C_p , was estimated using:

$$C_p (k_B \text{ per atom}) = 3.07 + 4.7 \times 10^{-4} \times T/(K - 300)$$

The combined uncertainty for all measurements involved in zT determination is $\sim 20\%$.

Materials characterisation

The crystallographic structure and composition were determined using X-ray diffraction (XRD) using a PANalytical X'Pert Pro X-Ray diffractometer with Cu K_α radiation ($\lambda = 1.544 \text{ \AA}$, 40 kV, 30 mA).

Results and discussion

Samples with the composition $\text{PbSe}_{0.1}\text{S}_x\text{Te}_{(0.9-x)}$ ($x = 0, 0.05, 0.1, 0.15, \text{ and } 0.2$) doped with 1 mol% Na on the Pb sites ($\text{Pb}_{0.98}\text{Na}_{0.02}\text{Se}_{0.1}\text{S}_x\text{Te}_{(0.9-x)}$) were synthesised in ingots using melting, quenching, and annealing procedures, followed by hot pressing of hand-ground powders. These samples are referred to as S0, S5, S10, S15, and S20, respectively, based on the PbS percentage, from now on. The purity and crystal structure of the samples were distinguished by indexing the powder X-ray diffraction patterns in Fig. 2(a). The XRD patterns of samples with $x < 0.1$ show a single phase NaCl-type face centred cubic (FCC) structure, whereas samples with $x > 0.1$ reveal two distinct phases. The Fig. 2(a) inset shows that diffraction peaks are shifted to higher angles by increasing the PbS concentration up to 10 mol%, due to the alloying effect, whereas the diffraction peak angles remain almost constant upon PbS addition of over 10 mol%. Rietveld refinement was employed to accurately determine the lattice parameters of the matrix by extrapolating from high angle diffraction peaks. The lattice parameters are varied by PbS addition, which is in agreement with Vegard's law, which indicates that the samples are solid solutions with random atomic distribution, up to $x = 0.1$, as shown in Fig. 2(b). The microstructure of samples are discussed in detail in the ESI.†

The temperature dependent Seebeck coefficient, electrical resistivity, and thermal transport properties of solid solution

Fig. 2 (a) Room temperature X-ray diffraction patterns for $\text{PbSe}_{0.1}\text{S}_x\text{Te}_{(0.9-x)}$ ($x = 0, 0.05, 0.1, 0.15, 0.2$) alloys. The inset shows shifting of the diffraction peaks to higher angles for x up to 0.1 due to the alloying effect: (b) lattice parameter of the matrix of $\text{PbS}_{0.1}\text{Se}_{0.9-x}\text{Te}_{(0.9-x)}$ alloys doped with sodium at room temperature as a function of the lead sulphide content, which is consistent with Vegard's law when $x < 0.1$, as expected for a solid solution.

$\text{PbSe}_{0.1}\text{S}_x\text{Te}_{(0.9-x)}$ ($x = 0, 0.05, 0.1$) samples in the temperature range of 300–850 K are given in Fig. 3. The transport properties of samples containing 5 and 10 at% PbS are compared to those of the sulphur-free compound (S0). All samples show the typical behaviour of strongly degenerate semiconductors, with the Seebeck coefficient and electrical resistivity increasing with temperature. The Seebeck coefficient at 800 K is increased from $220 \mu\text{V K}^{-1}$ for a sulphur-free sample to an approximate $240 \mu\text{V K}^{-1}$ upon sulphur addition. The origin of the high Seebeck coefficient values over a wide temperature range is discussed based on the contributions of the two valence bands in p-type PbTe.^{16,28} Results in the experimental literature show that the Seebeck coefficient of p-type PbTe deviates from the single band behaviour starting at a doping level in the mid- 10^{19} cm^{-3} range at room temperature, when carriers noticeably start to populate the heavy-hole band.^{16,28}

The band structure of PbTe is schematically shown in Fig. 4(a). The valence band structure of lead chalcogenides (PbTe, PbSe and PbS) is described by a non-parabolic Kane band at the L

point of the Brillouin zone (L band) and a parabolic band along the Σ line of the Brillouin zone (Σ -band).²⁸ Although the exact band structures of PbTe,²⁹ PbSe,³⁰ and PbS³¹ have been suggested to be more complicated than the proposed model, they have been able to explain the transport properties of PbTe,¹⁰ PbSe,³² and PbTe–PbSe^{4,33} very well. The energy gap, ε_g , at the L point is believed to linearly increase with the temperature by $d\varepsilon_g/dT = 4 \times 10^{-4} \text{ eV K}^{-1}$ for all three chalcogenides.²⁸ As the temperature rises, the energy of the light valence band is gradually reduced and reaches the Σ band edge. The density of states in the Σ band is much higher, and therefore, it provides a higher Seebeck coefficient than that with the L band alone, given the same carrier density. The higher effective band degeneracy results in higher thermoelectric efficiency at operating temperatures near 600 K in heavily doped materials where the Σ band contributes to the electronic properties of alloys.³⁴ At a given carrier concentration, a high Seebeck coefficient can be achieved due to the high density of states (DOS) effective mass ($m_d^* = N_v^{2/3} m_b^*$). A large total DOS can be due to either a large band degeneracy (N_v) or a

Fig. 3 Thermoelectric transport properties of $\text{PbSe}_{0.1}\text{S}_x\text{Te}_{(0.9-x)}$ ($x = 0, 0.05, 0.1$) sintered bulk samples doped with 1 at% Na: (a) temperature dependence of the Seebeck coefficient ($\mu\text{V K}^{-1}$), (b) the electrical resistivity (mΩ cm), (c) total thermal conductivity, κ ($\text{W m}^{-1} \text{ K}^{-1}$), and the lattice thermal conductivity κ_L , with Lorenz factor approximated using a single parabolic band model with acoustic scattering.

Fig. 4 (a) Schematic temperature dependencies of the relative energies of different bands of PbTe: the conduction band (CB), the light valence band at the L point, and the heavy valence band at the Σ line. ϵ_g shows the room temperature band gap, and $\Delta\epsilon_v$ demonstrates the energy offset between the L and Σ valence bands, with the red and blue lines showing that the valence bands shift to lower energy levels when alloyed with PbS. (b) Room temperature band-gap width as a function of composition of PbTe–PbSe and PbSe–PbS alloys.²⁸ The dashed red line shows the band gap width of $\text{PbSe}_{0.1}\text{S}_x\text{Te}_{(0.9-x)}$ alloys, and the continuous red line illustrates the secondary band gap for $\text{PbSe}_{0.6}\text{S}_x\text{Te}_{(0.4-x)}$ alloys if the linear relationship between composition and band gap is assumed for PbTe–PbS alloys.

high single-valley density of states effective mass of the degenerate valleys (m_b^*).^{28,35} The density of states effective mass for PbS is shown to be larger than that for PbTe.²⁸ Therefore, the higher Seebeck coefficient of alloys containing sulphur (S5 and S10) in Fig. 3(a) should be expected from the increase in the density of states.

The energies of the two valence band have been shown to also be adjustable in PbTe when alloying with PbSe,⁴ MgTe^{12,14} and (Zn, Cd, Hg)Te.³⁶ Alloying of PbTe with MgTe^{12,14} and MnTe¹³ increases the room temperature band gap (ϵ_g) and therefore reduces the energy of the L band, which consequently reduces the temperature at which the L and Σ bands are aligned. The alloying with PbSe has an opposite effect on the alignment because the energy levels of the Σ band in PbTe are reduced by alloying with PbSe.⁴ The band gap ϵ_g at the L point at 300 K for PbTe, PbSe, and PbS is 0.31, 0.28, and 0.41 eV, respectively. There is infinite solubility of PbTe–PbSe and PbSe–PbS alloys, where the band gap to the first order is correlated linearly with the alloying ratio as shown in Fig. 4(b) by the blue lines.²⁸ Therefore, alloying

PbTe with 10 at% PbSe reduces the band gap at room temperature to the red point in Fig. 4(b) for the S0 alloy. However, alloying with PbS increases the band gap along the dashed red line in Fig. 4(b) up to solubility limit (red star point), where a linear relationship between the band gap and the chemical composition is supposed for the PbTe–PbS alloy. This predicts that the L-band is shifted to lower energy (red line in Fig. 4(a)) for samples containing sulphur. The increased band gap slows the degradation of the Seebeck coefficient through the contribution of minority carriers, which are thermally excited across the band gap at high temperatures.³⁵ Therefore, the increase in the density of states, combined with the larger band gap (ϵ_g), should lead to a higher Seebeck coefficient at high temperature, as shown in Fig. 3(a).

The electronic band structure calculation shows that the Σ -band exists in both PbSe and PbS, but it lies at a lower energy level than in PbTe.³¹ The simultaneous alloying of PbTe with PbSe and PbS in the current samples increases the energy gap between the light and heavy valence bands, $\Delta\epsilon_v$ (blue line in Fig. 4(a)). Therefore, the doping level at room temperature, where carriers start to occupy the heavy-hole band, will be increased.

Fig. 3(b) shows that the electrical resistivity is increased by sulphide addition, which is presumably due to scattering of carriers from disordered atoms³³ and the increase in the L band effective mass, which reduces carrier mobility.³⁵ The electronic transport properties of samples are discussed in detail in the ESI.†

The total thermal conductivity, κ_{tot} , values for $\text{Pb}_{0.98}\text{Na}_{0.02}\text{S}_x\text{Se}_{0.1}\text{Te}_{(0.9-x)}$ ($x = 0, 0.05$, and 0.1) samples as a function of temperature are shown in Fig. 3(c). The lowest room temperature thermal conductivity of $2.2 \text{ W m}^{-1} \text{ K}^{-1}$ is observed for the sample containing 10% PbS. This value is decreased to $1 \text{ W m}^{-1} \text{ K}^{-1}$ at 650 K. A considerable reduction in thermal conductivity has been observed in samples that are alloyed with PbS compared to the $\text{PbSe}_{0.1}\text{Te}_{0.9}$ compound. The phonons are scattered on point defects in solid solutions and at grain boundaries. In order to fully visualize this effect, the lattice thermal conductivity, κ_L , was obtained by subtracting the electronic component, κ_e . The value of the charge carrier thermal conductivity κ_e can be determined via the Wiedemann–Franz relation, $\kappa_e = LT/\rho$ where ρ is the resistivity, and L is the Lorenz number estimated as a function of temperature, assuming a parabolic band with acoustic phonon scattering.³⁷ This rough estimation has been shown to be reasonably consistent with a more detailed model calculation taking the band non-parabolicity and multiband conduction effects into account⁴ (see ESI†).

A low room temperature lattice thermal conductivity of $\sim 1.3 \text{ W m}^{-1} \text{ K}^{-1}$ is observed for the S5 and S10 samples, respectively, and it is reduced to less than $\sim 0.6 \text{ W m}^{-1} \text{ K}^{-1}$ at temperatures above 650 K. The solute atom scattering is the dominant phonon scattering process for $\text{PbSe}_x\text{Te}_{(1-x)}$ alloys.^{4,38} Further alloying of $\text{PbSe}_{0.1}\text{Te}_{0.9}$ with sulphur reduces the lattice thermal conductivity even further. As discussed in a previous study,³⁹ replacing matrix atoms with solid solution atoms with the largest mass contrast can introduce considerable thermal conductivity reduction into the solid solution alloy. Therefore, the large mass contrast between the sulphur atoms and the

Fig. 5 (a) Temperature dependence of the thermoelectric figure of merit, zT , for Na doped $\text{PbSe}_{0.98}\text{S}_x\text{Te}_{(0.9-x)}$ ($x = 0, 0.05$, and 0.1) sintered bulk samples. The improvement in zT is attributed to the high Seebeck coefficient due to the wide band gap and larger effective mass of PbS relative to the matrix, as well as the reduction of the lattice thermal conductivity via disorder arising from solute atoms. (b) Comparison of the thermoelectric efficiency of the quaternary system in the present study with maximum reported values for binary p-type PbSe,³² p-type strontium-added PbS,⁴⁰ strontium-added PbTe⁶ and p-type PbTe-12 at% PbS¹⁹ and PbTe-16 at% PbS,¹⁹ indicating larger efficiency over a wide temperature range.

tellurium matrix atoms is considered to be responsible for the significant reduction in the thermal conductivity of sulphur-containing alloys.

Fig. 5 shows measured zT values up to 850 K. A 20% error bar can be considered as an estimate of the uncertainty of figure of merit values. The maximum zT value of 1.6 was achieved at 750 K for the $\text{Pb}_{0.98}\text{Na}_{0.02}\text{Se}_{0.1}\text{S}_{0.05}\text{Te}_{0.85}$ sample, which is higher than 1.4 for the sulphur-free alloy, $\text{Pb}_{0.98}\text{Na}_{0.02}\text{Se}_{0.1}\text{Te}_{0.9}$. Although the electrical resistivity of the samples containing sulphur has been increased due to the high effective mass of PbS, as well as the alloy scattering of carriers, the thermal conductivity reduction, together with the higher Seebeck coefficient, results in a high figure of merit. The beneficial effect of alloying with PbS is compensated by higher electrical

resistivity in the sample with 10% PbS, where the thermoelectric efficiency has been reduced to 1.2.

The thermoelectric efficiency of the current samples is compared with the maximum values reported for p-type PbSe,³² strontium-added PbS,⁴⁰ PbTe,¹⁰ strontium-added PbTe,⁶ and PbTe-12 at% PbS¹⁹ and PbTe-16 at% PbS¹⁹ composites with identical dopant concentration in Fig. 5(b). The higher thermoelectric performance has been obtained at lower temperatures compared to the binary and ternary chalcogenides, which can enhance the power generation efficiency of thermoelectric devices. The thermoelectric efficiency of $\text{PbS}_{0.05}\text{Se}_{0.1}\text{Te}_{0.85}$ is only lower than strontium-added PbTe⁶ at high temperatures, while it has much lower tellurium content and is not alloyed with strontium that provides a high performance, cost-effective alternative for PbTe alloys. These findings leave open the possibility of achieving a high figure of merit, zT , in alloys with more than 10 at% PbS through the contribution of PbS secondary phase in the composite alloys and/or nanostructuring through hierarchical architecture, in a similar manner to a previous study on the PbTe-PbS system¹⁹ strontium-added PbTe.⁸

Conclusions

In summary, we demonstrate that the thermoelectric efficiency of p-type solid solution quaternary Pb-Te-Se-S alloys is enhanced compared to binary PbTe, PbSe, and PbS, and ternary PbTe-PbSe and PbTe-PbS systems by increasing the solubility of PbS in PbTe in the presence of PbSe, which results in a wider band gap and larger DOS effective mass, where, the lattice thermal conductivity is reduced considerably due to phonon scattering at point defects. The maximum zT value of 1.6 has been achieved in an alloy where 15 at% tellurium is replaced by the abundant elements selenium and sulphur. The high thermoelectric performance of solid solution quaternary Pb-Te-Se-S alloys can potentially start a new research direction in Pb-chalcogenides, based on adjusting the band gap and the energy separation between the upper and the lower valence bands to enhance the Seebeck coefficient, where low thermal conductivity is guaranteed due to scattering of long wavelength phonons at point defects.

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