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ORIGINAL REPORT

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Thermoelectric performance of PbSnTeSe high-entropy alloys

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ABSTRACT

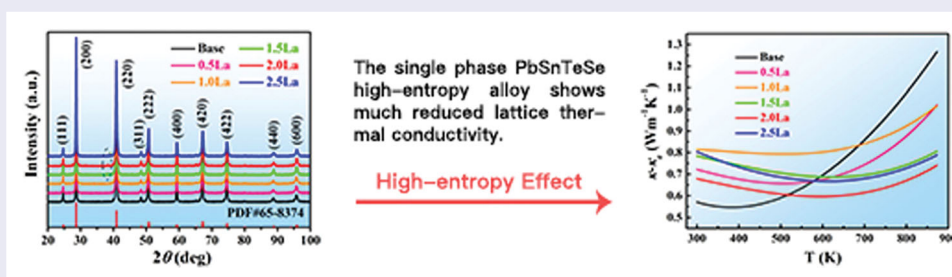
In our study, we designed the PbSnTeSe high-entropy alloy (HEA) and investigated its microstructure and thermoelectric properties. It was found that the PbSnTeSe HEA has a simple face-centered cubic structure and possesses quite low lattice thermal conductivity at low temperatures, which could be ascribed to the strong phonon scattering due to its severe lattice-distortion. Minor additions of La not only enhanced both Seebeck coefficient and electrical conductivity at high temperatures, but also suppressed the bipolar effect to some degree. Our results indicate that the HEA concept could be applied for developing promising thermoelectric materials, which merits further investigation.

ARTICLE HISTORY

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KEYWORDS

High-entropy alloys; thermoelectric; low thermal conductivity



IMPACT STATEMENT

The high-entropy alloy-design concept was employed to develop novel thermoelectric materials. Our findings indicate that this strategy effectively reduced the lattice thermal conductivity, which have important implications for the field.

Introduction

Thermoelectric materials, which are capable of direct conversion between heat and electricity,[1] have attracted worldwide attention over the past decades for engine exhaust heat recovery to improve fuel efficiency.[2] Ideal thermoelectric materials should possess a high dimensionless figure of merit, ZT , defined as $ZT = S^2 T / \rho(\kappa_e + \kappa_L)$, where S is the Seebeck coefficient, T is the absolute temperature, ρ is the electronic resistivity, and κ_e and κ_L are the carrier and lattice thermal conductivity, respectively.[1,3] Majority of IV–VI compounds tend to be dominant thermoelectric materials in the medium-temperature (500–900 K) range; these include most of lead chalcogenides (PbTe,[4–8] PbSe,[9,10] and PbS[11,12]), and tin chalcogenides (SnTe,[13,14] SnSe,[15–17] and SnS[18]). In addition, many mixtures composed of these compounds, such as PbTe–PbSe alloys,[19–21] PbTe–PbS alloys,[22,23]

PbSe–PbS alloys,[24,25] SnSe–SnS alloys,[26] and PbTe-rich quaternary alloys of PbTe–PbSe–PbS,[27,28] have been extensively studied for further improving their performance. However, solid solutions on a simple underlying lattice have been much less frequently considered for thermoelectric applications.

Recently, a brand-new method for designing alloys with multiple principal elements at equimolar or near equimolar ratios, called as high-entropy alloys (HEAs), has been proposed.[29–36] Because of the high-mixing entropy, these newly developed alloys often form random solid solutions with a simple body-centered cubic (BCC) or face-centered cubic (FCC) crystal structure during solidification, instead of intermetallic compounds or complex phases.[30,37–39] Due to the chemical complexity (e.g. large atomic size differences) and high configuration entropy, this novel class of alloys usually exhibits severe lattice-distortion and high-temperature

phase stability,[33,34] which could effectively reduce its lattice thermal conductivity due to the enhancement of scattering of phonons.[1,21] Thus, it is reasonable to speculate that HEAs probably possess intrinsically low lattice thermal conductivity in a wide temperature range and may be a class of promising thermoelectric materials. Lately, $\text{Al}_x\text{CoCrFeNi}$ HEAs were studied for their thermoelectric properties at high temperatures.[40] However, these HEAs composed of only metal elements still exhibit the behavior typical of metal conductors and have a very small Seebeck coefficient due to high charge carrier concentration, and large thermal conductivity, leading to an ignorable ZT value. In our previous work,[41] we designed $\text{BiSbTe}_{1.5}\text{Se}_{1.5}$ high-entropy thermoelectric materials for uses in the near-room temperature range (300–500 K) with this concept and demonstrated that increasing configuration entropy is indeed beneficial for achieving low lattice thermal conductivity due to the severe lattice-distortion, and thus may be a novel approaching for developing promising thermoelectric materials.

In the present study, we simultaneously alloyed IV–VI elements in equimolar ratios to form a quaternary PbSnTeSe thermoelectric HEA for applications in the medium temperature range (500–900 K). We discovered that the PbSnTeSe HEA possesses quite low lattice thermal conductivity at room temperature, for example, less than $0.6 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K, and found that its thermoelectric property could be further enhanced by minor composition tuning. Our current results indicate that the PbSnTeSe HEA could be a promising thermoelectric material if some challenges can be resolved.

Experimental

Pure elements (Pb 99.9%; Sn 99.99%; Te 99.99%, Se 99.99%; La 99.5%) were weighed and mixed based on the nominal composition of $\text{Pb}_{1-x}\text{SnTeSeLa}_x$, where $x = 0, 0.02, 0.04, 0.06, 0.08$ and 0.10 , respectively. The mixtures were loaded into pyrolytic boron nitride crucibles within quartz ampoules, and the ampoules were then evacuated, sealed and heated up to 1373 K at a heating rate of $\sim 1 \text{ K/min}$ and stabilized at this temperature for 6 h. During this period, the ampoules were rocked several times to ensure good homogeneity of melts. After that, the ampoules were water-quenched and subsequently annealed at 873 K for 120 h. The annealed ingots were ground to powders with an agate mortar and the resultant powders were eventually consolidated at 823 K for 5 min in a 20 mm-diameter graphite die under a uniaxial pressure of 50 MPa by spark plasma sintering (SPS). The sintered samples are disk-shaped, 20 mm in diameter,

Table 1. Nominal composition, room temperature Hall carrier concentration (n_{H}), and Dulong-Petit heat capacity (C_{p}) for $\text{Pb}_{1-x}\text{SnTeSeLa}_x$ alloys.

$\text{Pb}_{1-x}\text{SnTeSeLa}_x$				
Label	x	La at. %	$n_{\text{H}} \text{ cm}^{-3}$	$C_{\text{p}} \text{ J g}^{-1} \text{ K}^{-1}$
Base	0	0	6.12×10^{19}	0.187
0.5 La	0.02	0.5	1.347×10^{20}	0.188
1.0 La	0.04	1.0	1.561×10^{20}	0.188
1.5 La	0.06	1.5	1.563×10^{20}	0.189
2.0 La	0.08	2.0	1.836×10^{20}	0.189
2.5 La	0.10	2.5	1.722×10^{20}	0.190

$\sim 7 \text{ mm}$ in thickness with a density no less than 97% of the theoretical value (i.e. 7.33 g cm^{-3}).

Differential thermal analysis was performed with a DSC 404 F1 Pegasus thermal analyzer (Netzsch, German) at a rate of 10 K/min using the $\alpha\text{-Al}_2\text{O}_3$ powder as reference. X-ray diffraction analysis was conducted on a D/max-RB diffractometer (Rigaku, Japan) using $\text{Cu K}\alpha$ radiation. Scanning electron microscopy (SEM) characterization of the bulk materials was carried out using a SUPPA-55 scanning electron microscope.

Seebeck coefficient S and electrical resistivity ρ were measured simultaneously on the LSR-3 machine (Linseis, German). The total thermal conductivity κ is calculated from $\kappa = dDC_{\text{p}}$, where d is the density measured by the Archimedes method, D is the thermal diffusivity obtained by the laser flash method (LFA-457, Netzsch, German), and C_{p} is the specific heat. In the calculation of κ , C_{p} was regarded as a constant value estimated using the method of Dulong-Petit which was often employed in the calculation of C_{p} of PbTe-based materials.[4,8] Table 1 also lists the Dulong-Petit C_{p} of all the samples. Noted that the actual C_{p} value could be around 10% higher at 873 K and the corresponding ZT about 10% lower.[8] Hall coefficient R_{H} was measured by the Van der Pauw technique, and both the Hall carrier density $n_{\text{H}} = 1/eR_{\text{H}}$ and Hall mobility $\mu_{\text{H}} = R_{\text{H}}/\rho$ were then calculated based on the measured R_{H} .

Results and discussion

For simplicity, the $\text{Pb}_{1-x}\text{SnTeSeLa}_x$ alloys containing various nominal contents of La, that is, $x = 0, 0.02, 0.04, 0.06, 0.08$ and 0.10 , are designated hereafter as base, 0.5 La, 1.0 La, 1.5 La, 2.0 La and 2.5 La, respectively, as shown in Table 1 which also lists room temperature Hall carrier concentration and Dulong-Petit heat capacity of these samples. DTA curves for all the samples are shown in Figure 1(a). As can be seen, there is only one endothermic peak for the base alloy. The onset melting temperature of the PbSnTeSe HEA is about 1110 K and reduces slightly with the increase of the La content. In addition,

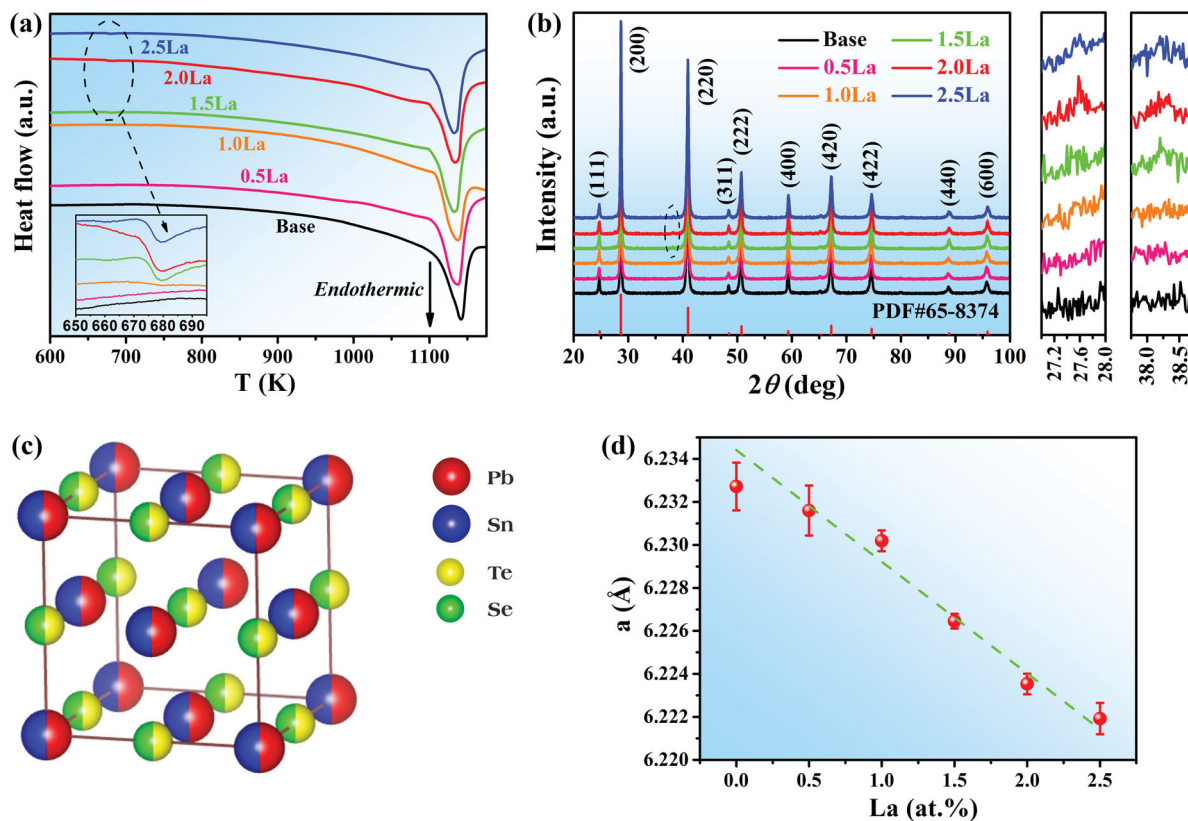


Figure 1. (a) Differential thermal analysis (DTA) curves, (b) XRD patterns of $\text{Pb}_{1-x}\text{SnTeSeLa}_x$ HEAs as well as (c) schematic illustration of the crystal structure of the PbSnTeSe HEA and (d) lattice parameter a as a function of the La content.

there is a small endothermic peak near 680 K on the DTA curves of the 1.5 La, 2.0 La and 2.5 La alloys, which should have resulted from the melting of precipitates. Figure 1(b) exhibits XRD patterns of all the samples subjected to the SPS process. All the crystalline peaks of the base alloy could be indexed to the single-phase PbSnTeSe with a NaCl-type face-centered cubic (FCC) crystal structure (PDF #65-8374), as indicated by vertical lines shown at the bottom. Based on these results, a schematic illustration of the crystal structure of the PbSnTeSe HEA can be obtained as shown in Figure 1(c). No appreciable difference on the XRD patterns among base, 0.5 La and 1.0 La alloys was observed, but there are two small extra diffraction peaks around 2θ of 27° and 38° for alloy 1.5 La, 2.0 La and 2.5 La, indicating the presence of precipitates in the alloys with a high La content, which is consistent with the result of the DTA curves. The lattice parameter a of all the samples, which was extrapolated from the high-angle XRD diffraction peaks, is shown in Figure 1(d). As can be seen, the lattice parameter reduces linearly with the increase of nominal La content. This observation is somewhat unexpected, given the fact that the atomic radius of La is larger than that of all of the other four principal elements. It seems that the doped La dissolved into the lattice with a limited amount, which may be associated with

the severe lattice distortion and complicated chemical environment of the PbSnTeSe HEA. The observed reduction of the lattice parameter could have resulted from the decrease in the Pb content which was substituted by La in the nominal compositions.

The corresponding back scattering electron (BSE) images of the polished surface are shown in Figure 2(a), which suggests that the PbSnTeSe HEA indeed is a complete solid solution without precipitate even doped with 0.5% La. However, a small amount of precipitates was already observed for the 1.0 La alloy and the amount of the precipitates apparently increased with the increase of La. The energy-dispersive X-ray spectroscopy (EDS) results confirm that the precipitates are mainly composed of Te, along with some Sn, Pb and Se, as shown in the inset of Figure 2(a). To further determine the chemical composition of the precipitate, EDS mapping was conducted and the results of alloy 2.5 La are exemplarily shown in Figure 2(b). As clearly seen, the precipitates are indeed enriched in Te. Since the La element is usually trivalent, its additions should contribute more electrons to the structure and induce excessive cation elements, that is, Pb or Sn, to precipitate out. In our case, however, the Te-rich precipitates were formed, which may have resulted from the decrease in the Pb content, further indicating that only

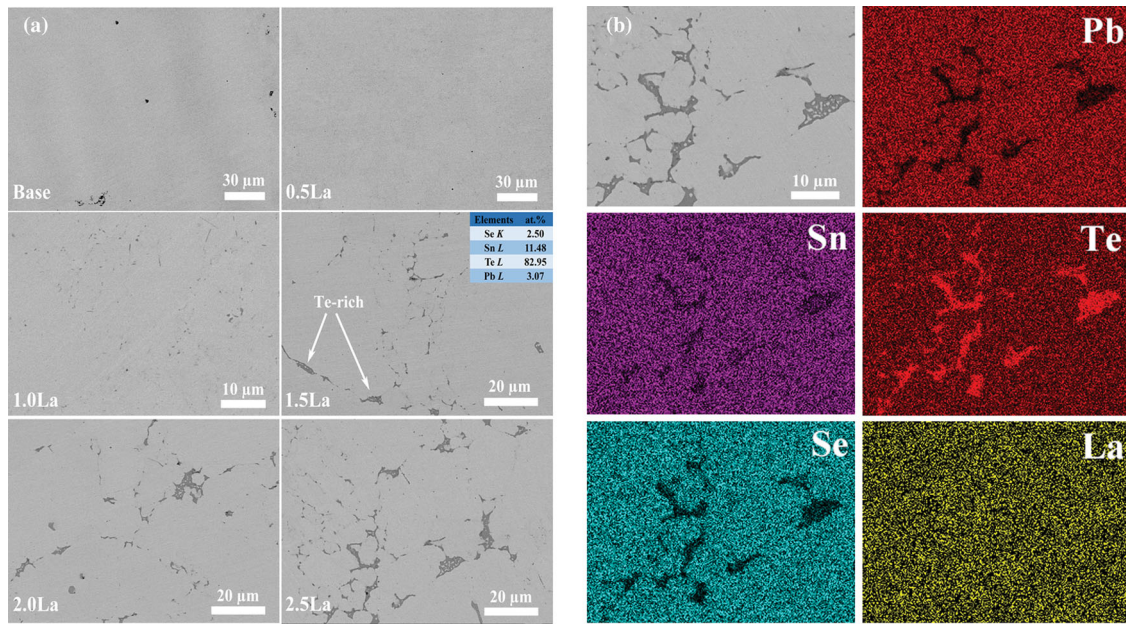


Figure 2. (a) BSE images of the polished surface of all the samples and (b) energy-dispersive X-ray spectroscopy (EDS) elemental maps of alloy 2.5 La.

a limited amount of La dissolved into the lattice of the HEA.

As can be seen in Figure 3(a), the sign of Seebeck coefficient is positive over the entire measured temperature range for the PbSnTeSe HEA, indicating that the base alloy is a p-type semiconductor and its dominant charge carriers are holes. The Seebeck coefficient S of the base alloy increases from $\sim 15 \mu\text{V/K}$ at 300 K to $\sim 175 \mu\text{V/K}$ at 750 K, after which it starts to reduce with the further increase of temperature due to the onset of thermal excitation of minority carriers (i.e. the bipolar effect). The Seebeck coefficient of all the La-doped alloys increases with temperature, a behavior typical of degenerate semiconductors. The peak value of the Seebeck coefficient of alloy 0.5 La is around $180 \mu\text{V/K}$ at 873 K and slightly higher than that of the samples added with a higher La content. Compared to that of PbTe,[7] PbSe,[9] and SnSe,[16] the maximum Seebeck coefficient of the PbSeTeSe HEAs doped with La is relatively lower, which leaves more room for further optimization. According to the formula for calculating the band gap E_g developed by Goldsmid,[42] $E_g = 2eS_{\text{max}} T$, where S_{max} and T are the peak Seebeck coefficient and corresponding temperature, respectively, the band gap of the base alloy was estimated to be about 0.26 eV, and that of the alloys doped with La is in the range of between 0.29 and 0.32 eV, indicating that the minor compositional change increases the band gap of the PbSnTeSe HEA to some degree, which is consistent with the bipolar effect being suppressed to some extent.

The electrical resistivity ρ of all the samples as a function of temperature is shown in Figure 3(b). The electrical

resistivity of the base alloy increases monotonically from $\sim 0.6 \text{ m}\Omega \text{ cm}$ at room temperature to $\sim 5.5 \text{ m}\Omega \text{ cm}$ at 873 K, which is lower than that of PbSe[9] and comparable with PbTe.[7] At temperatures below 500 K, there is almost no difference in the electrical resistivity between all La-doped alloys and the base alloy. However, above 500 K the electrical resistivity reduces gradually with the La addition. Compared with that of the base alloy, the hole concentration of the 0.5 La alloy at room temperature increased appreciably, which could have resulted from the increase of the concentration of cation vacancies due to the reduction of the Pb content. However, the hole concentration just increases slightly once the La content is above 1.0%, which could be related to the appearance of the rich-Te precipitates. The deficiency of Te created donor defects, thus reducing the hole concentration and compensating the effects of the reduction in Pb. Figure 3(d) exhibits Hall mobility as a function of La at room temperature. As can be seen, the Hall mobility of the 0.5 La alloy decreases drastically compared to that of the base alloy. With the further increase of La, the Hall mobility just decreases slightly, which is associated with the formation of the Te-rich precipitates.

Figure 3(c) shows the power factor PF as a function of temperature for all the samples. The maximum PF of the base alloy is reached at a relatively lower temperature (i.e. 700 K) and about $7.7 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$. Since the minor compositional tuning not only improved the Seebeck coefficient, but also reduced the electrical resistivity at high temperatures, the peak value of PF

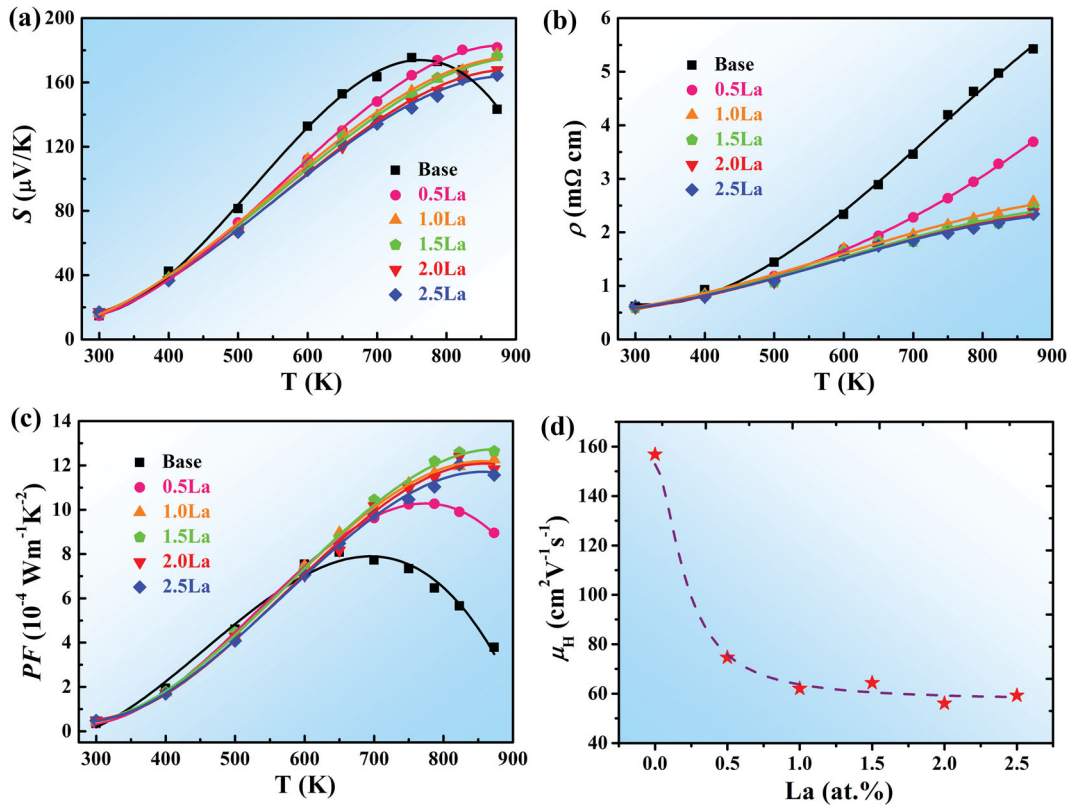


Figure 3. (a) Seebeck coefficient S , (b) electrical resistivity ρ and (c) power factor PF as a function of temperature for all the HEAs and (d) Hall mobility μ_H at room temperature as a function of the La content.

was achieved at relatively high temperatures for the La-doped alloys. Among all the samples, the highest PF is about $12.6 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$ in the temperature range of 823–873 K for alloy 1.5 La.

Temperature dependence of thermal diffusivity D and thermal conductivity κ is plotted in Figure 4(a) and (b), respectively. The thermal conductivity of the base alloy at room temperature is less than $1.8 \text{ W m}^{-1} \text{ K}^{-1}$, which is lower than that of both SnTe[13] and PbTe,[5,7] and comparable with that of PbSe.[9] Upon heating, it shows a reducing trend before 650 K where an upturn occurs due to the bipolar effect. The thermal conductivity of La-doped alloys in the range of 300–700 K is slightly higher than that of the base alloy due to the increased electronic contribution.

The combined lattice and bipolar thermal conductivity, that is, $\kappa_L + \kappa_b$, was obtained through subtracting the electronic contribution κ_e from the total thermal conductivity κ . The electronic thermal conductivity was determined according to the Wiedemann–Franz relation, $\kappa_e = LT/\rho$, where ρ is the resistivity and L is the Lorenz number which was estimated as a function of temperature, as shown in Figure 4(c), assuming a single parabolic band with acoustic phonon scattering.[43] This rough estimate has been shown to be reasonably

consistent with the calculation based on the detailed model taking into account the band nonparabolicity and multiband conduction effects.[19,27,28] As can be seen in Figure 4(d), the lattice thermal conductivity of the PbSnTeSe HEA with a highly symmetric NaCl structure is less than $0.6 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature, which is far lower than that of binary compounds with the same crystal structure, for example, SnTe,[13] PbTe,[5,7] and PbSe,[9] also lower than that of PbTe–PbSe[21] and PbTe–PbSe–PbS[27] solid solutions with the same crystal structure, and even lower than that of SnSe[16] with a layered orthorhombic structure. This phenomenon should be ascribed to the strong phonon scattering that resulted from the severe lattice-distortion of the PbSnTeSe HEA. Unfortunately, the lattice thermal conductivity of the base alloy starts to surge when the testing temperature exceeds 400 K due to the strong bipolar effect. For all the La-doped alloys, the bipolar effect was suppressed to a certain degree but still exists.

To analyze the lattice thermal conductivity without the bipolar contribution, $\kappa - \kappa_e$ vs. $1000/T$ was plotted in the inset of Figure 4(d). As can be seen, the lattice thermal conductivity at 873 K would be lower than $0.5 \text{ W m}^{-1} \text{ K}^{-1}$ for the base alloy if the bipolar effect were entirely eliminated. The lattice thermal conductivity of all

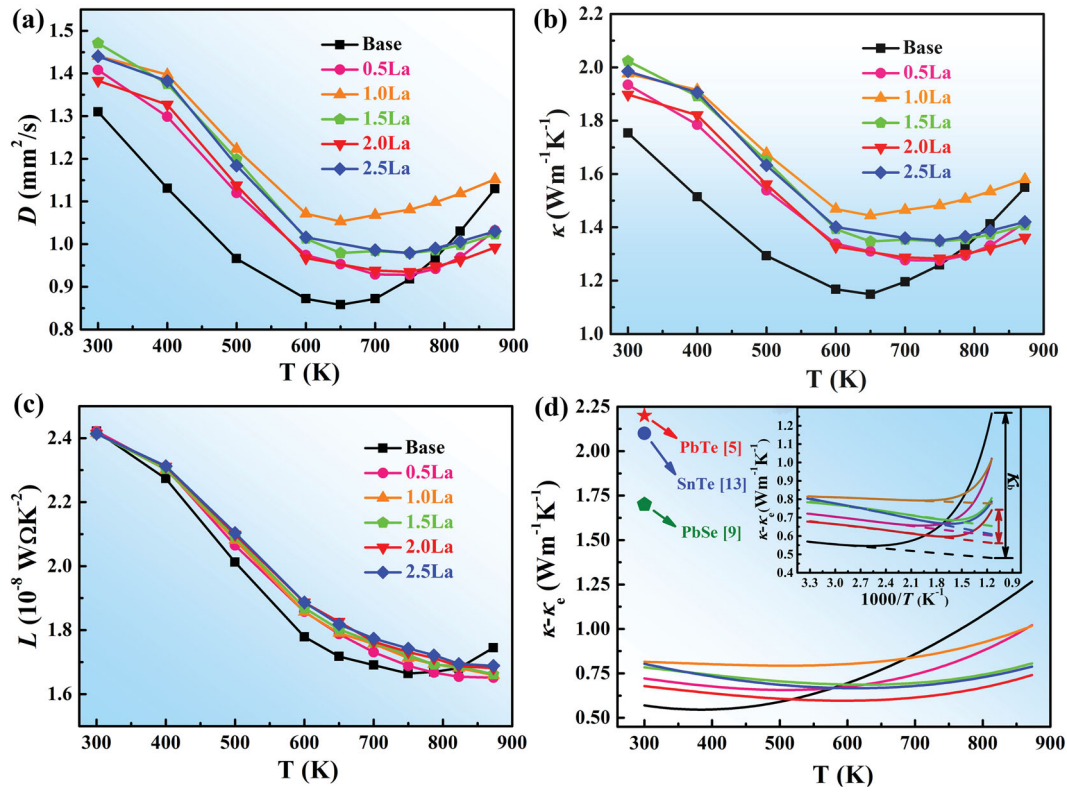


Figure 4. Thermal transport properties as a function of temperature. (a) thermal diffusivity, (b) thermal conductivity, (c) Lorenz number and (d) the combined lattice and bipolar thermal conductivity for all the samples. The lattice thermal conductivity of PbTe, PbSe and SnTe at 300 K was also shown in (d). The inset in (d) shows $\kappa - \kappa_e$ as a function of $1000/T$.

the La-doped alloys was slightly higher than that of the base alloy, which may have resulted from the contribution of the Te-rich precipitates and/or the errors introduced from the Lorenz numbers estimated with ignoring the presence of the Te-rich precipitates.

Figure 5 shows the figure of merit, ZT , calculated from the above data for all the samples as a function of temperature. The peak value of ZT of the base alloy is up to 0.4 at a relatively low temperature, that is, 650 K, due to the strong bipolar effect. The minor compositional change not only improved both Seebeck coefficient and electrical conductivity at high temperatures, but also alleviated the bipolar thermal conductivity to some extent, which results in the increasing of both the peak value of ZT and the corresponding peak temperature. The maximum ZT value of ~ 0.8 was obtained at 873 K in the 1.5 La alloy. Based on the above discussion, the maximum ZT value of the PbSnTeSe HEA could be greatly improved if the Seebeck coefficient is further enhanced and/or the bipolar effect is entirely suppressed through searching for more ideal dopants or/and applying proper band structure engineering.

In summary, polycrystalline high-entropy PbSnTeSe alloys with minor additions of La substituted for Pb were prepared by melting, followed by SPS. The base PbSnTeSe HEA possesses very low lattice thermal conductivity at

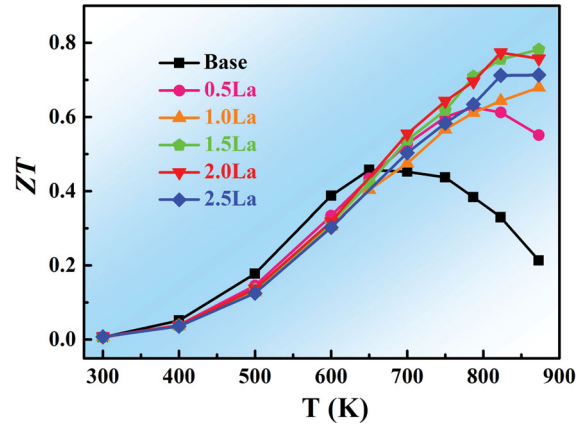


Figure 5. Figure of merit ZT as a function of temperature for all the samples.

low temperature, for example, less than $0.6 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K. The minor compositional change not only improved both the Seebeck coefficient and electrical conductivity of the PbSnTeSe HEA at high temperatures, but also alleviated its bipolar thermal conductivity to some extent, resulting in the increment in the maximum ZT value. For the PbSnTeSe HEA doped with 1.5% La, its ZT value was found to be around 0.8 at 873 K. The PbSnTeSe HEA could be a promising thermoelectric

material, provided that some remaining challenges mentioned above can be resolved, which merits further investigation. Our work also demonstrates that the HEA concept is indeed a potential strategy for designing novel thermoelectric materials with desirable properties.

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Disclosure statement

No potential conflict of interest was reported by the author.

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