Synergistically optimizing interdependent thermoelectric parameters of n-type PbSe through introducing a small amount of Zn

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ABSTRACT

In this work, we found that the interdependent thermoelectric parameters of n-type PbSe can be synergistically optimized through introducing a small amount of Zn. A record high power factor of 26.2 μW cm⁻¹K⁻² was achieved in PbZn0.01Se at 523 K, which is ascribed to the outstanding roles of Zn. We found that small Zn atoms first occupy Pb vacancies, which not only increases the carrier concentration but also improves the carrier mobility. When the content of Zn exceeds a certain level, the small Zn atoms will form interstitials and nanoprecipitates, which can enormously decrease the lattice thermal conductivity but slightly scatter carriers, thus maintaining a high carrier mobility. Combination of significantly enhanced power factor and remarkably reduced lattice thermal conductivity contributes to a high thermoelectric performance. A maximum ZT ~1.5 at 873 K and a high average ZT ~0.84 are achieved in PbZn0.01Se, which are superior to those of the most reported n-type PbSe systems. This work provides a strategy to synergistically optimize interdependent thermoelectric parameters through introducing small metallic atoms.

Keywords:
Thermoelectric
n-type PbSe
Lattice thermal conductivity
Pb vacancies
Zn interstitials

1. Introduction

Nowadays, global warming is getting worse because of using non-renewable energy sources, which causes the glacial melting and sea-level rising [1,2]; thus, the new green energy is highly sought. With more than 60% of input energy being lost as waste heat, there is a compelling need for high-performance thermoelectric materials that can directly and reversibly convert heat to electrical energy [3,4]. The conversion efficiency of the thermoelectric materials is determined by the dimensionless figure of merit, ZT = S²σT/(κele + κlat), where S, σ, κele, and κlat are the Seebeck coefficient, electrical conductivity, absolute temperature in Kelvin, electronic thermal conductivity, and lattice thermal conductivity, respectively [5–7]. Researchers have always been focusing on the designing of high-performance thermoelectric materials through converging electronic bands [8–10], flattening electronic bands [11–13], distorting electronic bands [14–16], improving carrier mobility through modulation doping [17,18], or reducing lattice thermal conductivity through nanostructuring [19–21].

Over past decades, lead chalcogenides PbQ (Q = Te, Se, S) have attracted much attention due to their complex band structure and low thermal conductivity [22–24]. To obtain excellent thermoelectric properties, the carrier concentration should be optimized in a temperature-dependent range [25,26]. Typically, a special behavior of metallic element inclusions has been widely researched in lead chalcogenides, which can realize a dynamic doping with rising temperature [28–30]. In our group, Ag and In are cointroduced in PbTe, AgₓPb₁₀₀₋ₓInₓTe₁₀₀₋₂ₓ (LIST), which features unique inherent electronic levels that can induce self-tuning carrier concentration [29]. Meanwhile, the excess of Ag forms spindle-shaped AgₓTe nanoprecipitates and atomic-scale interstitials, which can scatter phonons over a wide range of wavelengths and reduce the lattice thermal conductivity enormously [29]. Through introducing Cu in PbTe, a peak ZT ~1.5 at 723 K was realized in n-type PbTe by synergistically decreasing lattice thermal conductivity and improving carrier mobility [30].

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As a potential alternative candidate of PbTe, PbSe was focused and researched widely because of its abundance in the earth and lower price of Se than Te [31]. Recently, a peculiar behavior of Cu inclusion that can realize a dynamic doping in PbSe has been reported [28]. However, the mobile Cu in PbSe motivates us to explore other metallic elements whether can work as the roles of Cu, such as Zn, as the radius between Cu (1.28 Å) and Zn (1.37 Å) atoms is very comparable.

In this work, we found that the interdependent thermoelectric parameters of \( n \)-type PbSe can be synergistically optimized through introducing a small amount of Zn. Different from the dynamic doping behavior of Cu/Ag, the small amount of Zn atoms will first occupy Pb vacancies, which not only increases the carrier concentration but also improves the carrier mobility. Therefore, the electrical conductivity can be remarkably magnified, boosting a record high power factor of 26.2 \( \mu W \cdot cm^{-1} \cdot K^{-2} \) at 523 K. Meanwhile, when the content of Zn exceeds 0.75%, the Zn interstitials and nanoprecipitates can be formed, which can decrease the lattice thermal conductivity enormously but slightly deteriorate carrier mobility. Consequently, a maximum \( ZT \) value of \(-1.5\) at 873 K and a high average \( ZT \) of \(-0.84\) are achieved in PbZn\(_{0.01}\)Se, which is comparable with that of \( n \)-type PbTe [30] and higher than those of the most reported \( n \)-type PbTe systems [32–35]. The present results clearly show that the thermoelectric performance of \( n \)-type PbSe can be significantly enhanced through decoupling of electron and phonon via introducing a small amount of metallic Zn.

2. Experimental

The PbZn\(_x\)Se samples were first prepared in the form of ingots through a melting method, subsequently ground into powders and densified by spark plasma sintering (SPS) method (SPS-211LX; Fuji Electronic Industrial Co., Ltd.) at 873 K for 5 min under an axial compressive stress of 50 MPa. The electrical resistivity and Seebeck coefficient were measured simultaneously in a helium atmosphere at 300–873 K using a CTA instrument (Cryoall, China). The total thermal conductivity was calculated using \( k = D \cdot C_p \cdot \rho \), where \( D \), \( C_p \), and \( \rho \) represent the thermal diffusivity, the specific heat capacity, and sample density, respectively. The thermal diffusivity (\( D \)) was measured using a Netzsch LFA457. The Hall carrier concentration and Hall carrier mobility were determined at 300–873 K using a Hall measurement system (model 8404; Lake Shore). The optical bandgap was measured by infrared diffuse reflectance method with a Fourier-transform infrared spectrometer (IRAffinity-1S). Powder X-ray diffraction (XRD) patterns for all samples were collected using a D/max 2500 PC X-ray diffractometer with Cu K\( \alpha \) (\( \lambda = 1.5418 \) Å) radiation in a reflection geometry on an Inel diffractometer operating at 40 KV and 20 mA and equipped with a position-sensitive detector. Scanning transmission electron microscopy (STEM) and transmission electron microscopy (TEM) were carried out using a JEOL ARM200F equipped with cold field emission gun and ASCOR probe corrector. More experimental details can be found in the Supplementary Material.

3. Results and discussion

The XRD indicates that all the samples of PbZn\(_x\)Se (\( x = 0 - 0.0125 \)) are single phase and can be indexed as a cubic structure (space group Fm-3m) [34], as depicted in Fig. 1(a). The infrared reflectance spectra of PbZn\(_x\)Se are exhibited in Fig. 1(b), and the slight change of optical bandgap indicates that Zn atoms are introduced into PbSe lattice.

3.1. Enhancing electrical transport properties through optimizing carrier concentration and carrier mobility

Interestingly, we found that the electrical conductivity was enormously improved with the increase of Zn content, as shown in Fig. 2(a). The electrical conductivity of PbZn\(_{0.01}\)Se and PbZn\(_{0.025}\)Se at room temperature can reach 4155 S cm\(^{-1}\) and 4326 S cm\(^{-1}\), respectively, which are much higher than that of reported Cu-containing PbSe [28]. The other thermoelectric transport parameters of PbZn\(_x\)Se at room temperature can be found in Table 1. To explore the origins of the huge improvement in electrical conductivity, the Hall measurement was conducted. The Hall carrier concentration and mobility for PbZn\(_x\)Se are depicted in Fig. 2(b). It was worth noting that both carrier concentration and mobility were increased simultaneously with rising Zn content. Because the undoped PbSe shows a p-type conducting behavior due to Pb vacancies [36,37], we believe that these Pb vacancies will scatter carriers and lower carrier mobility. In this work, when Zn atoms are introduced into PbSe matrix, they will first occupy Pb vacancies, which can reduce the vacancy scattering to carriers and improve carrier mobility. In addition, Zn atoms enter Pb vacancies as an electron donor, which can also increase carrier concentration. When the content of Zn exceeds 0.75%, Zn atoms will enter the tetrahexdral gap formed by Se atoms, which will result in a further increase in carrier concentration but a slight decrease in carrier mobility.

To further verify this assumption, the carrier concentration and mobility as a function of temperature are measured, as displayed in

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**Fig. 1.** (a) Powder XRD patterns and (b) bandgaps of PbZn\(_x\)Se (\( x = 0 - 0.0125 \)) at room temperature. XRD, X-ray diffraction.
Fig. 2. Thermoelectric transport properties as a function of temperature for PbZn$_x$Se: (a) Electrical conductivities; (b) Room-temperature carrier concentration and mobility; (c) Carrier concentration; (d) Carrier mobility; (e) Seebeck coefficient; (f) Power factor. The reported PbCu$_{0.005}$Se [28] was also plotted for comparison.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>$n_H$ (10$^{19}$ cm$^{-3}$)</th>
<th>$\mu_H$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$\sigma$ (S cm$^{-1}$)</th>
<th>$S$ (µV K$^{-1}$)</th>
<th>$\kappa_{lat}$ (W m$^{-1}$ K$^{-1}$)</th>
<th>$ZT_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbSe</td>
<td>0.62</td>
<td>29</td>
<td>29</td>
<td>−174</td>
<td>1.99</td>
<td>0.76</td>
</tr>
<tr>
<td>PbZn$_{0.0025}$Se</td>
<td>1.39</td>
<td>18</td>
<td>28</td>
<td>−126</td>
<td>2.17</td>
<td>0.81</td>
</tr>
<tr>
<td>PbZn$_{0.005}$Se</td>
<td>2.80</td>
<td>321</td>
<td>1436</td>
<td>−77</td>
<td>2.06</td>
<td>1.36</td>
</tr>
<tr>
<td>PbZn$_{0.0075}$Se</td>
<td>3.22</td>
<td>754</td>
<td>3884</td>
<td>−67</td>
<td>1.05</td>
<td>1.44</td>
</tr>
<tr>
<td>PbZn$_{0.01}$Se</td>
<td>3.42</td>
<td>758</td>
<td>4155</td>
<td>−64</td>
<td>0.96</td>
<td>1.50</td>
</tr>
<tr>
<td>PbZn$_{0.0125}$Se</td>
<td>4.15</td>
<td>651</td>
<td>4326</td>
<td>−68</td>
<td>0.84</td>
<td>1.17</td>
</tr>
</tbody>
</table>

$n_H$, carrier concentration; $\mu_H$, carrier mobility; $\sigma$, electrical conductivity; $S$, Seebeck coefficient; $m^*(m_e)$, the effective mass; $\kappa_{lat}$, lattice thermal conductivity; $ZT_{\text{max}}$, maximum $ZT$ value.

Fig. 2(c) and (d). The carrier concentration of PbZn$_x$Se has little changed with increasing temperature. It is well known that carrier mobility and carrier concentrations are two competing parameters. However, it is worth noting that present carrier concentration of PbZn$_x$Se is much higher than that of PbCu$_{0.005}$Se [28] but maintains a comparable carrier mobility in PbZn$_x$Se. Moreover, the carrier
mobilities of PbZnxSe are significantly improved at low temperature range with the increase of Zn content, which results from the compensation of Pb vacancies. The carrier scattering mechanism can be clearly revealed by temperature-determined carrier mobility to further certify this explanation. The reciprocal of the mobility as a function of temperature considering several scattering mechanisms determined from the Boltzmann transport equation can be given by [30,38].

\[
\frac{1}{\mu} = a_l T^{-3/2} + a_i T^{-3/2} + a_v T^{-1}
\]  

(1)

where \(a\) is a temperature-independent parameter and subscripts \(l\), \(i\), and \(v\) represent the contributions to the scattering from the lattice, impurities, and vacancies, respectively. The exponents \(m\) of \(-3/2\), \(3/2\), and \(-1\) indicate that acoustic phonon scattering, ionized impurity scattering, and vacancy scattering are the predominant carrier scattering mechanism, respectively. It can be clearly noted from Fig. 2(d) that the vacancy scattering is the predominated scattering mechanism in Zn-free PbSe at 300-600 K. As the Pb vacancies are compensated by Zn atoms, the vacancy scattering is substituted by acoustic phonon scattering.

The Seebeck coefficients of PbZnxSe decrease sharply with rising Zn content because of the increased carrier concentration, as depicted in Fig. 2(e). The Seebeck coefficients of PbZnxSe are higher than that of PbCu0.005Se [28] at higher temperatures, which indicate that the carrier concentration of PbZnxSe is optimized in a reasonable range at the higher temperatures. The power factors of PbZnxSe as a function of temperature are shown in Fig. 2(f); on account of the significant increase of carrier concentration and carrier mobility, the power factors are enhanced tremendously with the increase of Zn content. The fantastic power factors of 25.1 \(\mu\)W/cm\(^{-1}\)K\(^{-2}\) and 26.2 \(\mu\)W/cm\(^{-1}\)K\(^{-2}\) for PbZn0.075Se and PbZn0.01Se at 523 K are achieved, which are much higher than that of PbCu0.005Se [28].

To well understand the complex roles of Zn, we calculated the formation energies for possible defects in PbZn\(_x\)Se system, including Pb vacancy (\(V_{Pb}\)), Zn-filled Pb vacancy (\(ZnPb\)), Zn interstitials (\(Zn_i\)), etc. The defect formation energies as a function of Fermi energy are shown in Fig. 3 for both Pb-rich and Se-rich conditions. The \(E_F = 0\) is set at the valence band maximum (VBM), and the position of the dashed line is the conduction band minimum (CBM). In this work, as an \(n\)-type degenerate semiconductor, the Fermi level of PbSe has entered the conduction band. Therefore, we only consider the situation of the dashed area. It is obvious that for both Pb-rich and Se-rich conditions, the formation energy of Pb vacancy is lower than those of Zn-generated defects, which indicates that the Pb vacancies exist in the PbZn\(_x\)Se system.

Besides, the formation energy of ZnPb is lower than that of \(Zn_i\), which manifests that Zn will prefer to occupy Pb vacancies and then form Zn interstitials. The calculation of formation energies theoretically proves our assumption, and then we will experimentally observe these analyses through microstructure characterizations.

The annular bright-field scanning transmission electron microscopy (ABF-STEM) images taken from PbSe and PbZn0.01Se along their [100] zone axis are shown in Fig. 4(a) and (b), respectively. It is obvious that in the Zn-free PbSe, the atoms are in the lattice position, and no interstitial atoms are found. However, in the PbZn0.01Se sample, the presence of interstitial atoms can be clearly observed. To analyze the composition of this interstitial atom, we carried out the intensity-scan profiles obtained from the ABF images, as indicated by blue and red hollow arrows shown in Fig. 4(a) and (b). The additional Zn peak can be clearly found in PbZn0.01Se, as depicted in Fig. 4(c), which well proves the existence of Zn interstitials. As shown in the atomic structure diagram in Fig. 4(d), the Zn interstitials occupy the Wyckoff 8c sites.

3.2. Decreasing lattice thermal conductivity via introducing Zn interstitials and nanoprecipitates

To observe Zn interstitials, aberration-corrected scanning transmission electron microscopy (Cs-corrected STEM) was used.
High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) produces contrast interpretable by mass thickness (the number of atoms) or Z contrast, while ABF-STEM has weaker Z-dependence, which is useful for revealing lighter atoms [39, 40]. Fig. 5(a) and (b) are low-magnification ABF images showing a high density of nanostructures. These nanostructures are obvious in ABF imaging mode, while almost invisible in HAADF imaging mode, which suggests that the composition difference is quite small, and the contrast is mainly from the strain effect. The high-magnification ABF image in Fig. 5(b) clearly reveals the details of these nanostructures, i.e., having plates in the core and strain field in the shell. The platelet-like cores are possibly formed from the ordered aggregation of interstitial atoms, which may be related to the non-equilibrium intercalation of Zn. Such interstitial clusters induce strong lattice distortions to the PbSe matrix. As expected, strain analysis in Fig. 5(c) derived from Fig. 5(b) by geometric phase analysis (GPA) clearly show the strains along the <200> directions. The strains induced by the platelet-like interstitial clusters exhibit an anisotropic behavior, and they are mainly distributed along the direction perpendicular to the platelets. When observing along [110] directions, the aforementioned nanostructures appear as elliptical, as shown in Fig. 5(e). The atomically resolved ABF image in Fig. 5(f) clearly shows the plane view of the interstitial cluster, which is similar to those observed in Cu-/Mn-doped PbTe or SnTe [30, 41, 42]. Such atomic-scale interstitial clusters could contribute much to the phonon scattering, and lowering lattice thermal conductivity of PbSe.

The total thermal conductivities (\(\kappa_{\text{tot}}\)) of PbZn\(_{x}\)Se are displayed in Fig. 6(a). It can be easily found that the total thermal conductivities are increased with rising Zn content, which is because the total thermal conductivity is the sum of the electronic and lattice thermal conductivities (\(\kappa_{\text{tot}} = \kappa_{\text{ele}} + \kappa_{\text{lat}}\)) [43, 44]. The electronic thermal conductivity is in proportion to the electrical conductivity according to the Wiedemann-Franz law [45, 46], \(\kappa_{\text{ele}} = LsT\), where the \(L\) is the Lorenz number estimated using a single parabolic band (SPB) model and assuming acoustic phonon scattering [47, 48]. The Lorenz number and electronic thermal conductivity of PbZn\(_{x}\)Se can be found in Fig. 1. Owing to the enormously increased electrical conductivity resulting from the increase of carrier concentration and carrier mobility, the total thermal conductivity keeps the same tendency.
Fig. 6(b) shows that the lattice thermal conductivity of PbZnₓSe is decreased through introducing metallic Zn atoms, which further proves that the Zn interstitials could effectively scatter phonons.

The slightly increased lattice thermal conductivity in PbSe with 0.25% Zn indicates that the Pb vacancies are compensated by Zn. When the Zn content exceeds 0.75%, excess Zn atoms will enter the

Fig. 6. Thermoelectric transport properties of PbZnₓSe: (a) Total thermal conductivity; (b) Lattice thermal conductivity; (c) ZT values; (d) Average ZT values.
tetrahedral gap sites and form Zn interstitials and nanoprecipitates. The interstitial Zn clusters and nanoprecipitates can enhance the scattering of phonons tremendously and reduce the lattice thermal conductivity, especially in low temperature range, precisely from ~2.0 W m$^{-1}$K$^{-1}$ at 300 K and ~0.96 W m$^{-1}$K$^{-1}$ at 873 K in Zn-free PbSe to ~0.84 W m$^{-1}$K$^{-1}$ at 300 K and ~0.65 W m$^{-1}$K$^{-1}$ at 873 K in PbZn$_{0.0125}$Se.

The temperature-dependent $ZT$ values of PbZn$_x$Se are shown in Fig. 6(c). The $ZT$ values of PbZn$_x$Se are increased with the rise of Zn content, which results from the increased power factor and decreased lattice thermal conductivity. The superior $ZT$ of ~1.5 can be achieved in PbZn$_{0.01}$Se at 873 K, increased by 75% compared with the maximal $ZT$ of ~0.8 for Zn-free PbSe. Moreover, the improved carrier mobility and reduced lattice thermal conductivity contribute to the increase of $ZT$ over the whole temperature range of 300–873 K, especially in the low temperature range. The average $ZT_{\text{ave}}$ values of PbZn$_{0.01}$Se at 300–873 K are shown in Fig. 6(d), and the $ZT_{\text{ave}}$ of ~0.84 for PbZn$_{0.01}$Se is achieved.

3.3. Origins of high thermoelectric performance for PbZn$_x$Se

To clarify the origins of the enhancement in power factor and final $ZT$ values, the theoretical calculations on the Seebeck coefficient and carrier mobility as a function of carrier concentration are investigated. The relaxation time for the Kane band model with acoustic phonon scattering can be expressed by the following equations [32,49]:

![Thermoelectric properties as a function of temperature for PbZn$_{0.01}$Se and their comparisons: (a) Pisarenko relationship with effective masses $m^* = 0.27 m_e$; (b) Carrier mobility as a function of carrier concentrations; (c) Power factor; (d) Lattice thermal conductivity; (e) $ZT$ values; and (f) Average $ZT$ values at 300-873 K. Reported X-doped PbSe (X = Cl, Br, Cr, B, Ga, In, Al, Bi, Sb, Cu), PbSe-SiO$_2$, and PbSe-Ag-Sb are also plotted for comparisons [15,32-35,53-55].](image_url)
\[
\tau = \frac{\hbar C_l N_v}{\pi^2 k_B T Z} g(e) \left[ 1 - \frac{8\alpha (e + e^2 \alpha)}{3(1 + 2e\alpha)^2} \right]^{-1}
\]

\[
g(e) = \frac{\sqrt{2m^*} k_B T^{1/2}}{\pi^2 h^3} \left( e + e^2 \alpha \right)^{1/2} (1 + 2e\alpha)
\]

where \(k_B\) is the Boltzmann constant, \(\hbar\) is the reduced Plank’s constant, \(m^*\) is the density-of-state effective mass considering band degeneracy, \(C_l\) [9.1 \times 10^{10} \text{ Pa}\] for PbSe [50] is a parameter determined by the combination of the elastic constants [51], \(Z\) is a combination of deformation potentials for multivalley systems [50,51], which describes the carrier scattering strength by acoustic phonons, \(N_v\) is the band degeneracy (\(N_v = 4\)), \(e\) is the reduced energy, and \(\alpha\) is defined by \(\alpha = k_B T \varepsilon_g\) where \(\varepsilon_g\) is the bandgap of PbSe at \(T = 0\) (in Brillouin zone) which changes with temperature according to \(\varepsilon_g/\text{eV} = 0.17 + 3 \times 10^{-4} T / K\) [52].

Based on the Kane model, the transport parameters are expressed as follows:

The carrier concentration [32]:

\[
n = \frac{(2m^* k_B T)^{3/2}}{3\pi^2 k_B^3} 0 F_0^{3/2}
\]

(4)

The Seebeck coefficient [30,32]:

\[
S = \frac{k_B}{e} \left[ \frac{1}{m^*} \frac{1}{F_0^{3/2}} - \eta \right]
\]

(5)

where \(\eta\) is the reduced chemical potential \(\eta = E_F/k_B T\).

The mobility [32]:

\[
\mu = \frac{2\pi^4 e^4 C_l}{m^* (2m^* k_B T)^{3/2}} \frac{3^{9/2}}{\alpha F_0^{3/2}}
\]

(6)

\[
The Hall factor \(A\) \(n = A_{\text{Hall}} = A(e\text{RH})\) [32]:

\[
A = \frac{3(K + 2)}{2(K + 1)^2} \frac{0 F_0^{1/2} F_0^{3/2}}{4 F_0^{1/2}} \frac{0 F_0^{1/2}}{(0 F_0^{1/2})^2}
\]

(7)

where \(K = m^*_c / m^*_v\) (\(K = 1.75\), assumed \(T\) independent).

The Lorenz number [32]:

\[
L = \left( \frac{ka}{e} \right)^2 \left[ \frac{2 F_0^{1/2}}{0 F_0^{1/2}} - \frac{1 F_0^{3/2}}{0 F_0^{3/2}} \right]^2
\]

(8)

The integral \(n F_1^n\) in the aforementioned equations is defined by [32]:

\[
n F_1^n = \int_0^\infty \left( \frac{df}{de} \right)^n (e + a e^2)^m \left[ 1 + 2a e^2 \right]^{1/2} d e
\]

(9)

Owing to the anisotropy of both conduction and valence bands at the \(L\) point, the inertial effective mass \(m^*_i\) and the density-of-state effective mass \(m^*\) are determined by the effective band mass of a single pocket along two directions \(m^*_i\) and \(m^*_v\) [32]:

\[
m^*_i = \frac{3}{5} \left( \frac{2}{m^*_i} + 1 + \frac{1}{m^*_v} \right)^{-1}
\]

(10)

\[
m^* = N_v^{2/3} m^*_v = N_c^{2/3} \left( m^*_v m^*_i \right)^{1/3}
\]

(11)

For PbSe, \(m^* = 0.27 m_0\) at 300 K, which changes with temperature according to \(m^*/m_0 = 0.5\) in this work [32].

The Pisarenko relationship corresponding to a single parabolic band (SBP) with the assumption of acoustic phonon scattering is depicted in Fig. 7(a) [48,56,57]. The results illustrate that the effective mass has no obvious enhancement in \(n\)-type PbZnSe system, which indicates that the super high power factor is predominantly attributed to the improvement from carrier mobility. Room-temperature carrier mobility as a function of carrier concentration is shown as the black solid line [32] in Fig. 7(b). Experimental carrier mobility data of PbZnSe are very close to the theoretical line and indicate that acoustic phonon scattering is the predominant scattering mechanism. Apparently, the carrier mobilities of PbZnSe are higher than those of the other \(n\)-type PbSe system with additional scattering, such as Pb1-xBixSe [53] and Pb1-xSb1-xSe [53] with point defects, Pb1-xSb2xSe [33] with dislocations, and AgPb18SbSe20-xClx [58] with nanostructures. Therefore, in this work, the improved carrier mobility contributes to an outstanding power factor through compensating Pb vacancies.

As depicted in Fig. 7(c) and (d), the power factor of PbZn0.01Se is higher than that of the other \(n\)-type PbSe systems [15,28,34,35,53]. Meanwhile, because the Zn interstitials and nanoprecipitates can enhance the phonon scattering enormously, the lattice thermal conductivity of PbZn0.01Se is the lowest compared with other \(n\)-type PbSe systems [32,34,35,53,54]. As a result, decoupling of electron and phonon leads to a high \(ZT\) value. As shown in Fig. 7(e) and (f), the maximum \(ZT_{\text{max}}\) and average \(ZT_{\text{ave}}\) of PbZn0.01Se are all higher than those of the most reported \(n\)-type PbSe systems [15,32–35].

4. Conclusion

The thermolectric properties of \(n\)-type PbSe were boosted via introducing small amount of additional Zn atoms. The carrier concentration and mobility of PbSe were improved by compensating Pb vacancies, and the lattice thermal conductivity was decreased through forming Zn interstitials and nanoprecipitates. Decoupling electrons and phonons contributed to a significant improvement in thermolectric performance. The superior maximum \(ZT_{\text{max}}\) of ~1.5 at 873 K and a high average \(ZT_{\text{ave}}\) of ~0.84 at 300-873 K were achieved in \(n\)-type PbZn0.01Se. Our results indicate that the thermolectric performance of lead chalcogenides PbQ (Q = Te, Se, S) can be enhanced through introducing small amount of metallic Zn atoms and that the present strategy can be extended to other thermolectric systems.

Conflicts of interest

There are no conflicts of interest to declare.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mtphys.2019.100102.

References


