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Cite as: APL Mater. 8, 010901 (2020); https://doi.org/10.1063/1.5144097
Submitted: 29 December 2019. Accepted: 07 January 2020. Published Online: 23 January 2020

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ABSTRACT
Excellent thermoelectric materials need both high carrier transport properties and low phonon transport properties simultaneously, which make it challenging to enhance thermoelectric performance. However, recent progress shows that sub-nanostructures can strongly intensify phonon scattering but scarcely impede carrier mobility, thus effectively contributing to high thermoelectric performance in PbTe/Se-based systems. In this perspective, we summarize the thermoelectric transport properties and internal atomic-scale structures in these PbTe/Se-based systems with sub-nanostructures. Then, their thermoelectric properties are comprehensively compared with other massively nanostructured PbTe/Se-based systems, revealing the favorable role of sub-nanostructures in achieving high carrier mobility. Finally, several other potential strategies to further maintain carrier transport properties and enhance thermoelectric performance are proposed, which might be extended to other thermoelectric systems.

INTRODUCTION
Thermoelectric materials are capable of directly and reversibly converting heat into electricity, and thus have drawn increasing attention in recent decades. The efficiency of thermoelectric materials and devices is characterized by the dimensionless figure of merit (ZT), defined as $ZT = (S^2\sigma/(\kappa_{\text{ele}} + \kappa_{\text{lat}}))T$, where $S$, $\sigma$, $\kappa_{\text{ele}}$, $\kappa_{\text{lat}}$, and $T$ are the Seebeck coefficient, the electrical conductivity, the electronic thermal conductivity, the lattice thermal conductivity, and the absolute temperature in Kelvin, respectively. Among these thermoelectric parameters, $\kappa_{\text{lat}}$ is the independent parameter, which can be manipulated using nanostructure engineering. Therefore, nanostructure engineering is extensively implemented to suppress lattice thermal conductivity due to intensified phonon scattering, such as PbTe-MgTe, PbSe-GeSe, PbS-SrS/CaS, SnSe-GeSe, and SnTe-SrTe. However, nanostructure engineering will also enhance carrier scattering, thus simultaneously reducing carrier mobility and the power factor ($S^2\sigma$), and finally lead to a limited enhancement of the net ZT value.

As is known, high-performance thermoelectric materials require good carrier transport properties and low phonon transport properties, and the ideal thermoelectric materials are regarded as “phonon glass-electron crystals.” As noted in recent progress in n-type PbTe/PbSe-based systems, the sub-nanostructures can reduce lattice thermal conductivity while maintaining carrier mobility simultaneously. Compared with other massively nanostructured n-type PbTe/PbSe-based systems, the thermoelectric materials with sub-nanostructures present much higher carrier mobility and a larger power factor especially in a low temperature range. As a result, this favorable role of sub-nanostructures can obviously enhance the maximum $ZT$ and $ZT_{\text{ave}}$ in the entire working temperature range.

The origin of this particular role of sub-nanostructures in thermoelectric materials to balance carrier and phonon transport properties is systematically investigated by estimating phonon and carrier mean free paths. In this perspective, phonon mean free path ($l_p$) is calculated by the following equation:

$$\kappa_{\text{lat}} = \frac{1}{3}c_v\nu_a/l_p,$$

where $\kappa_{\text{lat}}$ is the measurement lattice thermal conductivity, $\nu_a$ is the average sound velocity, $c_v$ is the heat capacity at constant volume ($c_v = C_{\text{vp}} + C_p$ is the heat capacity at constant pressure, and $p$ is the sample density), and $l_p$ is the mean free path. The estimated
phonon mean free path in PbTe/Se is in the range of 0.1–10 nm, which is comparable to the size of sub-nanostructures. While the carrier mean free path \( (l_c) \) can be obtained using following equation:\(^{19}\)

\[
l_c = \frac{\pi h c_l}{k_B T^2 \rho m^*},
\]

where \( h \) is the reduced Planck constant, \( c_l \) is the longitudinal elastic modulus \( (c_l = \rho v_l^2) \), \( v_l \) is the longitudinal speed of sound, and \( \rho \) is the sample density, \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature in Kelvin, \( \epsilon_d \) is the effective deformation potential, \(^{23-25}\) and \( m^* \) is the transport effective mass.\(^{24,26,27}\) The calculated carrier mean free path of PbTe/Se is around \( 10^2–10^3 \) nm, which is much larger than the size of sub-nanostructures. Therefore, it is found that phonons can be strongly scattered due to the comparable sizes between sub-nanostructures and phonon mean free path, while the carrier mobility is well maintained because the carrier mean free path is larger than the size of sub-nanostructures in PbTe/Se. The mechanism of this favorable role of sub-nanostructures to scatter phonon and transport carrier in the matrix is schematically presented in Fig. 1. To present the high thermoelectric performance in sub-nanostructured PbTe/Se, their carrier mobility, power factor, the calculated ratio of carrier mobility to lattice thermal conductivity \( (\mu/\kappa_{lat}) \), and final \( ZT \) values are systematically compared with massively nanostructured PbTe/Se systems. Additionally, the different types of sub-nanostructured PbTe/Se systems are summarized with transmission electron microscope (TEM) observations. Finally, some other strategies to maintain high carrier mobility in thermoelectric materials are further proposed.

**DISCUSSION**

Comparisons of carrier mobility and power factor in \( n \)-type sub-nanostructured and nanostructured PbTe/Se systems. In this perspective, \( n \)-type PbTe and PbSe systems are the paradigms to interpret the advantages of maintaining carrier mobility. In Fig. 2, the carrier mobility and power factor are compared in the PbTe/Se-based systems with sub-nanostructures and nanostructures.

As presented in Fig. 2(a), the carrier mobility in PbTe with nanostructures [such as PbTe with Ag\(_{2}\)Te and AgPb\(_{100}\)InTe\(_{102}\) (LIST) with extra Ag systems] significantly decreases compared to the theoretical value of PbTe. However, the sub-nanostructures containing...
point defects in PbTe-MnTe, interstitials in PbTe-Cu and clusters in PbTe-Cu₂Te, which can maintain large carrier mobility. For example, the maximum carrier mobility in $n$-type sub-nanostructured PbTe can achieve $\sim 1450$ cm² V⁻¹ s⁻¹ in the PbTe-Cu system with carrier density at $\sim 2.6 \times 10^{18}$ cm⁻³, which is much higher than the carrier mobility $\sim 683$ cm² V⁻¹ s⁻¹ in the LIST-Ag system with carrier density at $\sim 3.1 \times 10^{18}$ cm⁻³. Therefore, this well-maintained carrier mobility in $n$-type sub-nanostructured PbTe systems can contribute to obviously enhanced power factor in the entire temperature range, as shown in Fig. 2(b). Obviously, the maximum power factor $\sim 36.7 \, \mu W \, cm^{-1} \, K^{-2}$ can be obtained in the sub-nanostructured PbTe-Cu system at 373 K, but the maximum power factor in the nanostructured LIST-Ag system can only achieve $\sim 17 \, \mu W \, cm^{-1} \, K^{-2}$ at 300 K. Similar carrier transport properties can also be observed in $n$-type sub-nanostructured PbSe systems. As shown in Fig. 2(c), the carrier mobility in $n$-type PbSe-Zn and PbSe-Cu can be favorably preserved even close to the theoretical value, while the AgPb₁₈SbSe₂₀-Cl and PbSe-CdSe systems with nanostructures present much low carrier mobility because of intensified carrier scattering by large nanostructures. Correspondingly, the calculated power factor of PbSe with sub-nanostructures is much larger than that of PbSe with nanostructures in the whole measured temperature range shown in Fig. 2(d).

**FIG. 3.** TEM observations of sub-nanostructures: (a) Cu interstitial cluster and (b) Cu interstitial arrays in PbTe-Cu₂Te; (c) the grain boundary and (d) line defects in PbTe-MnTe; (e) and (f) ABF-STEM images taken from PbSe and PbZn₄Se along their [1 0 0] zone axis, respectively; (g) intensity-scan profiles obtained from the ABF images as indicated by blue and red hollow arrows shown in (e) and (f), respectively; (h) and (i) represent dislocations in the PbSe-Cu system. The TEM examples of (a) and (b) are cited from PbTe-Cu₂Te, (c) and (d) are cited from PbTe-MnTe, (e)–(g) are cited from PbSe-Zn, and (h) and (i) are cited from PbSe-Cu.

Different structures (such as nanostructures and sub-nanostructures) have different effects on the carrier mobility and the lattice thermal conductivity. As shown in Fig. 4(a), the ratio of carrier mobility to lattice thermal conductivity ($\mu/\kappa_{lat}$) at room-temperature and the minimum $\kappa_{lat}$ is compared between in $n$-type PbTe with nanostructures and sub-nanostructures. The value of $\mu/\kappa_{lat}$ in PbTe-Cu₂Te and PbTe-Cu with sub-nanostructures are much larger than that in LIST-Ag and PBT-Ag₂Te with nanostructures, and the minimum $\kappa_{lat}$ in PbTe with sub-nanostructures

including nanoscale line defects and atomic-scale interstitial clusters. These sub-nanostructures could form a strain network for effectively scattering phonons from long to medium wavelengths while having little influence on carrier mobility. Both of Cu and Mn interstitials play important roles in scattering phonons from short to medium wavelengths in $n$-type PbTe. In $n$-type PbSe system, the small extra Zn atoms form interstitials in Fig. 3(f) compared with the Zn-free PbSe in Fig. 3(e). The additional Zn pear can be clearly found in Fig. 3(g), which well proves the existence of Zn interstitials. The Zn interstitials can enormously decrease the lattice thermal conductivity but slightly scatter carriers, thus maintaining a high carrier mobility. The dislocation in Fig. 3(i) caused by Cu atoms occupying the interstitial sites of PbSe in Fig. 3(h) has only little influence on the carrier transport, and the interstitial site might serve as the ideal doping site to regulate the electrical transport properties in the $n$-type PbSe system. The high-resolution TEM observations reveal that the sub-nanostructures in PbTe and PbSe can be controllably achieved through introducing small atoms (Cu and Zn) to form interstitials and clusters and obtaining high solid solution to form massive point defects and dislocations. Noticeably, these approaches to form sub-nanostructures can be extended to other thermoelectric systems.
and nanostructures all show comparably low lattice thermal conductivity about \( \sim 0.4 \text{ W m}^{-1}\text{K}^{-1} \). Thus, the \( ZT \) value in Fig. 4(b) is obviously enhanced in the entire temperature range. The average \( ZT (ZT_{\text{ave}}) \) values of sub-nanostructured PbTe systems can achieve \( \sim 1.0 \) in PbTe-Cu, \( \sim 1.02 \) in PbTe-Cu\(_2\)Te, and \( \sim 1.05 \) in PbTe-MnTe at 300–873 K, which are much higher than the \( ZT_{\text{ave}} \) values in nanostructured PbTe, such as \( \sim 0.32 \) in PbTe-Ag\(_2\)Te and \( \sim 0.82 \) in LIST-Ag at 300–873 K. In the \( n \)-type PbSe system, compared with the value of \( \mu/k_{\text{lat}} \) with \( n \)-type nanostructured AgPb\(_{18}\)SbSe\(_{20}\)-Cl and PbSe-CdSe, the value of \( \mu/k_{\text{lat}} \) in sub-nanostructured PbSe-Zn and PbSe-Cu systems presents an obvious increasing tendency and the minimum \( k_{\text{lat}} \) is obtained from PbSe-Cu with sub-nanostructures which achieve \( \sim 0.44 \text{ W m}^{-1}\text{K}^{-1} \) [Fig. 4(c)]. The existence of sub-nanostructures in \( n \)-type PbSe could obviously enhance the \( ZT \) value over the 300–873 K temperature range, as shown in Fig. 4(d). In \( n \)-type PbTe/PbSe-based systems, sub-nanostructures can well maintain carrier mobility and simultaneously scatter phonon, finally obviously enhance thermoelectric performance. Besides, in PbTe/Se systems, the Cu or Ag atoms also can reduce lattice thermal conductivity and maintain high carrier mobility simultaneously in Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\)\(^{37} \) and SnSe\(_2\)\(^{38} \).

**SUMMARY AND PERSPECTIVE**

Recent progress in maintaining carrier mobility to achieve high thermoelectric performance in \( n \)-type PbTe and PbSe is summarized in this perspective. The origin of maintained high carrier mobility comes from the sub-nanostructures (interstitials, clusters, and dislocations) that slightly impede the carrier transport properties but strongly intensify phonon transport because of largely different carrier and phonon mean free paths. The size of sub-nanostructures is close to the length of the phonon mean free path (10\(^2\)–10\(^3\) nm). Finally, the power factor and \( ZT \) values in \( n \)-type sub-nanostructured PbTe and PbSe systems have an obvious improvement compared to the \( n \)-type PbTe and PbSe systems with nanostructures. This perspective highlights the importance of maintaining high carrier mobility to achieve high thermoelectric performance. Notably, besides sub-nanostructures, band sharpening and approaching a topological state to a lower carrier effective mass can also be expected to maintain high carrier transport properties. These strategies to optimize carrier transport properties are worth being systematically investigated and extended to other thermoelectric systems.

**ACKNOWLEDGMENTS**

This work was supported by the National Key Research and Development Program of China (Grant Nos. 2018YFA0702100 and 2018YFB0703600), the National Natural Science Foundation of China (Grant Nos. 51632005 and 51772012), the Beijing Natural Science Foundation (Grant No. JQ18004), the Shenzhen Peacock Plan team (Grant No. KQTD2016022619565991), 111 Project (Grant No. B17002), National Postdoctoral Program for Innovative Talents (Grant No. BX20190028), and Postdoctoral Science Foundation of China (Grant No. 2019M660399). L.D.Z. acknowledges support from the National Science Fund for Distinguished Young Scholars (Grant No. 51925101).

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