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TOPICAL REVIEW — Recent advances in thermoelectric materials and devices

Strategies for optimizing the thermoelectricity of PbTe alloys*

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The thermoelectric materials have been considered as a potential candidate for the new power generation technology based on their reversible heat and electricity conversion. Lead telluride (PbTe) is regarded as an excellent mid-temperature thermoelectric material due to its suitable intrinsic thermoelectric properties. So tremendous efforts have been done to improve the thermoelectric performance of PbTe, and figures of merit, $zT > 2.0$, have been reported. Main strategies for optimizing the thermoelectric performance have been focused as the main line of this review. The band engineering and phonon scattering engineering as two main effective strategies are systemically summarized here. The band engineering, like band convergence, resonant levels, and band flatting have been addressed in improving the power factor. Additionally, phonon scattering engineerings, such as atomic-scale, nano-scale, meso-scale, and multi-scale phonon scatterings have been applied to reduce the thermal conductivity. Besides, some successful synergistic effects based on band engineerings and phonon scatterings are illustrated as a simultaneous way to optimize both the power factor and thermal conductivity. Summarizing the above three main parts, we point out that the synergistic effects should be effectively exploited, and these may further boost the thermoelectric performance of PbTe alloys and can be extended to other thermoelectric materials.

Keywords: thermoelectric PbTe alloys, band engineering, phonon scattering, synergistic effects

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1. Introduction

The world's demand for energy is becoming more and more drastic due to the increasing population and economy. Alternative clean energy sources or new energy conversion technologies play important roles in energy conservation. But several traditional green sources such as solar, wind, and geothermal are all subjected to weather or location. The thermoelectric materials have been considered as a potential candidate to relieve the energy crisis based on the reversible heat and electricity conversion.[1] The solid state TE devices which are made by TE materials have no moving parts, run quietly and are eco-friendly. Thus the thermoelectric energy conservation is expected to be an attractive way to solve the energy crisis.[2,3]

The efficiency of a thermoelectric material is characterized by the figure of merit $zT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the total thermal conductivity which includes the lattice thermal conductivity $\kappa_{\rm L}$ and electronic thermal conductivity $\kappa_{\rm e}$, and T is the absolute temperature.[4] Besides, $S^2\sigma$ is defined as the power factor. Therefore, a high power factor and a low thermal conductivity are needed to obtain a high zT. But, actually these parameters mentioned above are relevant to each other via the carrier concentration (n) as shown in Fig. 1. With n increasing, S decreases while σ increases, and thus it is a challenge to synergetically optimize the thermoelectric parameters to achieve a high zT. Therefore, many approaches were adopted to realize the independent modification of the parameters.

Based on the operating temperature of the thermoelectric materials, the traditional thermoelectric materials such as Bi_2Te_3,[5] PbTe,[6,7] and SiGe[8] can be classified to the low- (around room temperature), middle- (500 K–800 K), and high- (800 K–1200 K) temperature systems respectively. The temperatures of the waste heat which come from the industrial plant, motor vehicle, and so on are almost in the range of 500 K–800 K. In this case, as one of the best thermoelectric material, the PbTe alloy is consistent with the mid-temperature application and it is the best choice for recycling waste heat in this temperature range. In addition, many excellent figures of merit, zT over 2.0, have been obtained through band

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engineering, nanostructure, and so on in recent a few years. Therefore, it is worth to summarize these useful strategies for the good thermoelectric performance of PbTe alloys. The relative proper carrier concentration ($\sim 10^{19}$ cm^{-3}) is an important factor for the excellent thermoelectric performance of PbTe alloys.[9] Moreover, the pristine PbTe also possess intrinsic low lattice thermal conductivity ~ 2 W/m·K at room temperature.[10] And as one of the narrow band gap semiconductor, the band structure of PbTe is also beneficial for the electron transportation.[11] The experimental and theoretical results show that there is a heavy valance band (Σ band) just blow the light valance band (L band) (~ 0.1 eV). Through element doping, the Σ band can participate in the transport of electrons thus a higher Seebeck coefficient can be obtained. Due to the suitable intrinsic thermoelectric properties of PbTe, tremendous efforts have been done to improve the thermoelectricity of PbTe alloys.[12–16]

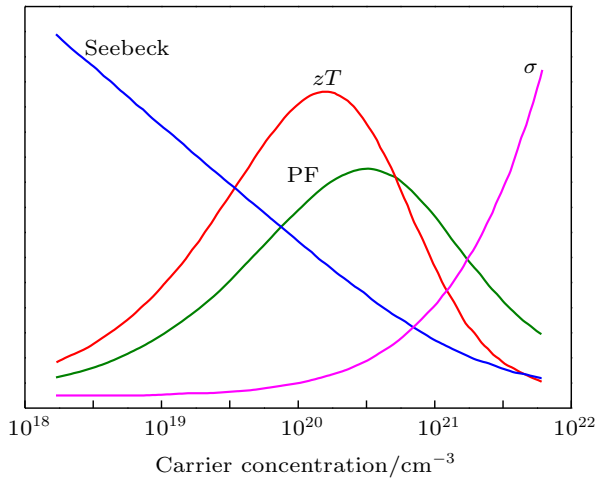


Fig. 1. (color online) The Seebeck coefficient, electric conductivity (σ), power factor (PF), and figure of merit (zT) as a function of carrier concentration.[1]

Figure 2 summarizes the figures of merit for PbTe alloys achieved in past few years. It can be seen that the zT value of the pristine PbTe has been greatly improved and the maximum zT of p-type PbTe alloys has already surpassed 2.0, which is the relatively high value among all TE materials. N-type PbTe alloys are a few inferior to p-type ones, but still own zT values of almost 1.8. Such great enhancements of thermoelectric performance for PbTe alloys are mainly resulted from the combination of many effective strategies, such as the band convergence,[17,18] resonant levels,[13,19–21] point defects, nanostructuring,[22–24] and multi-scale phonon scattering.[16,24–26]

In this review, the mentioned successful strategies for improving zT of PbTe alloys are summarized. In brief, the power factor can be enhanced through band engineering which contains band convergences, resonant levels and band flatting. The band convergences can be introduced by rising temperature or doping with selenium (Se)[17] and manganese (Mn),[14] while resonant levels can be induced by doping with group III_A elements such as indium (In)[32] or thallium (Tl).[13] The reduction of the thermal conductivity can be achieved via atomic-scale,[30] nano-scale,[24] meso-scale,[33] and multi-scale phonon scatterings.[34] Ultimately, the synergistic effects of band engineering and phonon scattering are also illustrated here.[27]

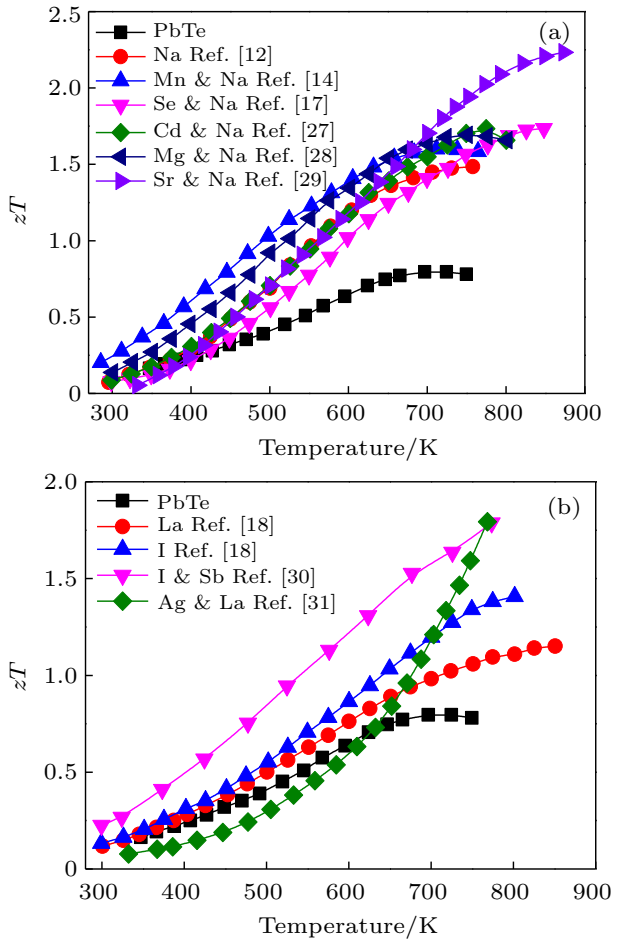


Fig. 2. (color online) Temperature-dependent figure of merit reported for typical (a) p-type, $Pb_{0.085}Na_{0.015}Te$,[12] $Pb_{0.96}Mn_{0.04}Te$: Na,[14] $PbTe_{0.85}Se_{0.15}$: 2%Na,[17] $Pb_{0.97}Cd_{0.03}Te$: Na,[27] $Pb_{0.97}Mg_{0.03}Te$: Na,[28] $Pb_{0.98}Na_{0.02}Te$-4%SrTe,[29] and (b) n-type PbTe: La,[18] PbTe: I,[18] $PbTe_{0.998}I_{0.002}$-3%Sb,[30] La doped PbTe with Ag_2Te.[31]

2. Band engineering

As above brief descriptions, band engineering is one of the best ways that have been used to optimize the electrical properties in PbTe alloys. As mentioned earlier, with the carrier concentrations increasing, the Seebeck coefficients decrease generally. However, the band engineering cannot realize the enhancement of the Seebeck coefficient and carrier concentration simultaneously. Additionally, because the zT is in positive proportional to S^2, then the enhancement of the Seebeck coefficient is more vital for the high thermoelectric performance. In general (parabolic band, energy-independent scattering approximation), the Seebeck coefficient is positive proportional to the density of state (DOS) effective mass (m_d^*),

so a high m_d^* is important for the enhancement of the Seebeck coefficient under a given carrier concentration. Band engineering can adjust the band structure of PbTe, and thereby manipulating the m_d^*. Thus the band engineering can enlarge the Seebeck coefficient, and then improve the electrical performance. In this paper, the resonance levels, band convergence, and band flatting as the specific ways of band engineering are focused, and the mechanisms of enhancing the Seebeck coefficient are discussed in detail.

2.1. Resonant levels

The resonant levels inducing via element doping can happen when the additional state lies in the conduction or valance band of the host band.[35] When the additional state has the same energy E_D with an extend state, they will resonate and create two extend states which have the same energy with other extend states. Thus the resonation among the host state and impurity state raise again and again, and so a width Γ is induced. As a result, the DOS is increased. The introduced resonant level will affect the Seebeck coefficient, in two aspects. First, resonant levels induce a narrow peak at the center of the resonant energy E_D as shown in Fig. 3(a), which is beneficial to achieve a large Seebeck coefficient. Second, resonant levels both conduct charge carriers and diffuse carriers by the resonant scattering which is correlated with Γ. So, in order to maximize the benefit of this scheme, the position and width of resonant levels are two major parameters that should be pay more attentions. The former includes the position relevant to the band edge and the positon relevant to chemical potential. Therefore, dual doping is an effective way to implement the resonant levels.[36] As for the latter, s- and p-states which possess a value of 10 meV–100 meV are more desirable to allow Fermi level inside the resonant levels.[37]

Heremans *et al.* illustrated the concept of the resonant levels experimentally in thallium (Tl)-doped PbTe alloys.[38] When the content of Tl is 2%, the effect of resonant levels significantly appears, and the large Seebeck coefficient is achieved as shown in Fig. 3(b). In the Pisarenko plot, it is easy to find that the Seebeck coefficient is obviously enhanced at the same carrier concentrations under 300 K. In this case, the large enhancement of the Seebeck coefficient leads to a doubled zT compared with the 1% doped sample as shown in Fig. 3(c). After this typical work, the resonance levels can also be formed in PbTe alloys through other dopants such as titanium (Ti)[21] and chromium (Cr),[37] which results to the high Seebeck coefficients and high figures of merit as shown in Fig. 3(b). Following the successful application of resonance levels in PbTe alloys, this strategy as a type of band engineering has been extended to other material systems, such as PbSe,[39] SnTe[40–42] and Bi_2Te_3.[43]

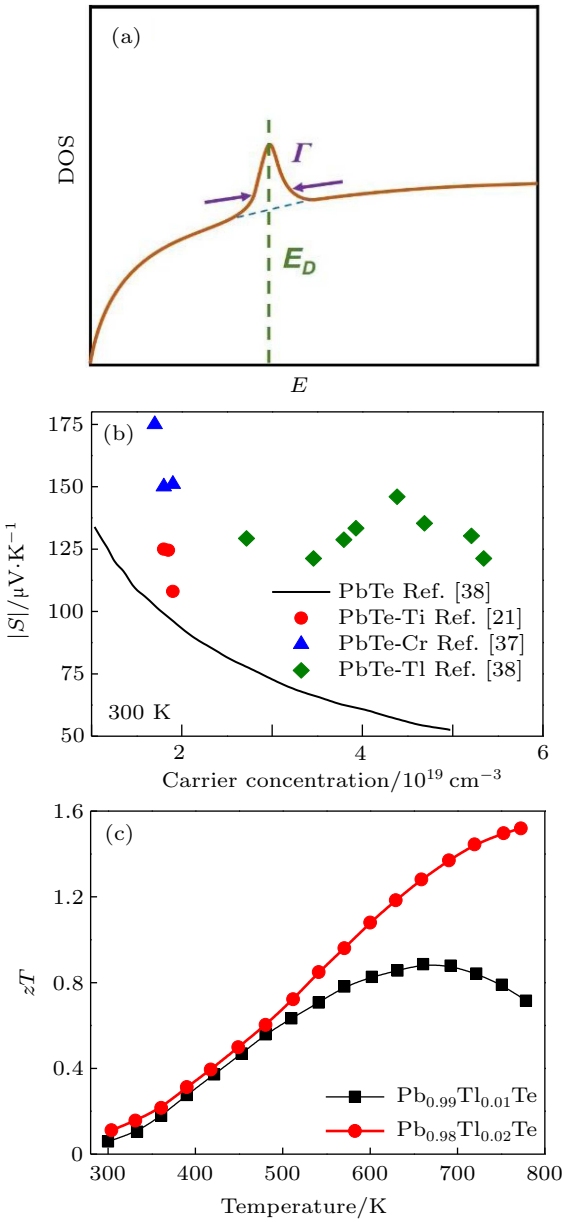


Fig. 3. (color online) (a) Schematic diagram of the density of states of the un-doped valance band in PbTe (dashed line) contrasted to that of resonant doping. E_D is the resonance level and Γ the resonance width.[19] (b) The Seebeck coefficient versus carrier concentration (dots) and the Pisarenko curve.[21,37,38] (c) The temperature dependence figure of merit for Tl-doped PbTe.[38]

2.2. Band convergence

Band convergence as another band engineering method can also improve the Seebeck coefficient. The aim of this kind of band engineering is to increase the band convergence due to $m_d^* = N_v^{2/3} m_d^*$, where N_v is the number of degenerate conducting bands and m_d^* is the energy band effective mass. Band convergence can be formed when multiple bands have the same energy or little energy difference at the band extrema (orbital degeneracy), or with degeneration of multiple carrier pockets in the Brillouin zone (valley degeneracy) induced by crystal symmetry. As for p-type PbTe alloys, they have two-band structure in the valence band. Numbers of experiments[11,44]

and theories[45] have proved that a heavy valence band (Σ band) is slightly below the light valence band (L band). The L valence band has N_v of 4 while the valence band maxima at Σ point has a large N_v of 12. As shown in Fig. 4(a), along with the temperature rising, the light bands shift down but the heavy bands almost stay constant.[46] This results to high band convergence of $N_v = 4 + 12 = 16$ and finally the Seebeck coefficient gets improved significantly.[12] Moreover, Pei *et al.* showed that the band convergence can also be manipulated to desired temperatures. The energy offset between the L band and Σ band will be increased monotonously with increasing Se contents in Na-doped PbTe alloys. In this case, the desired temperature where effective band convergence occurs will rise.[17] Thus the optimized band convergence will further improve the figure of merit of PbTe at high temperature range.

Besides the influence of temperature on band convergence, dopants-induced band convergence which is resulted from the enlarged band gap via manganese (Mn),[14] magnesium (Mg)[28] or cadmium (Cd)[27] doping will press the light band, and further decrease the energy difference between L band and Σ band ($\Delta E_{L-\Sigma}$) as shown in Fig. 4(b). As a result, the heavy Σ band can participate in electrical transport more efficiently and thus the higher Seebeck coefficient and carrier concentration are achieved. For instant, in Mn-, Mg-, Cd-doped PbTe alloys, the direct optical band gap (E_g) which detected through Fourier transform infrared spectrometer is enlarged monotonously with increasing doping amounts. The increased bang gap can effectively decrease $\Delta E_{L-\Sigma}$, thus the numbers of convergence bands (N_v) are raised and eventually higher Seebeck coefficients are achieved. Cd-doped PbTe is set as an example to further illustrate the band convergence as shown in Fig. 4(c).[27] The red and black dot lines are theoretical Pisarenko curves for two-band model (TBM) and single band model (SBM) respectively. And the Seebeck coefficient for TBM is higher than that of SBM. The experimental results of Cd-doped PbTe (blue dots) are obviously more coincident with TBM simulation. With Cd doping, the light bands become lower in energy but the heavy bands are roughly constant and the band convergence occurs. Thus Cd doping could enhance the Seebeck coefficient of PbTe via band convergence. The Seebeck coefficients of elements-doped ones are much higher than those of the pristine PbTe in the mid-temperature range as summarized in Fig. 4(d). Thus band convergence is one of the best way for the PbTe application in industrial applications. Based on the outstanding of electrical performance caused by band convergence, many excellent figures of merit are obtained. All in all, the band convergence derived by temperature or composition can be a type of band engineering to optimize the thermoelectric performance of PbTe alloys effectively, especially for p-type PbTe. After the concept of band convergence is presented, successful works of PbTe alloys have been reported. And other thermoelectric alloys such as Mg_2Si,[47] SnTe[48] also utilize band convergence for getting better thermoelectric performance. Therefore, the band convergence has been considered as an effective way to enhance figures of merit for thermoelectric alloys.

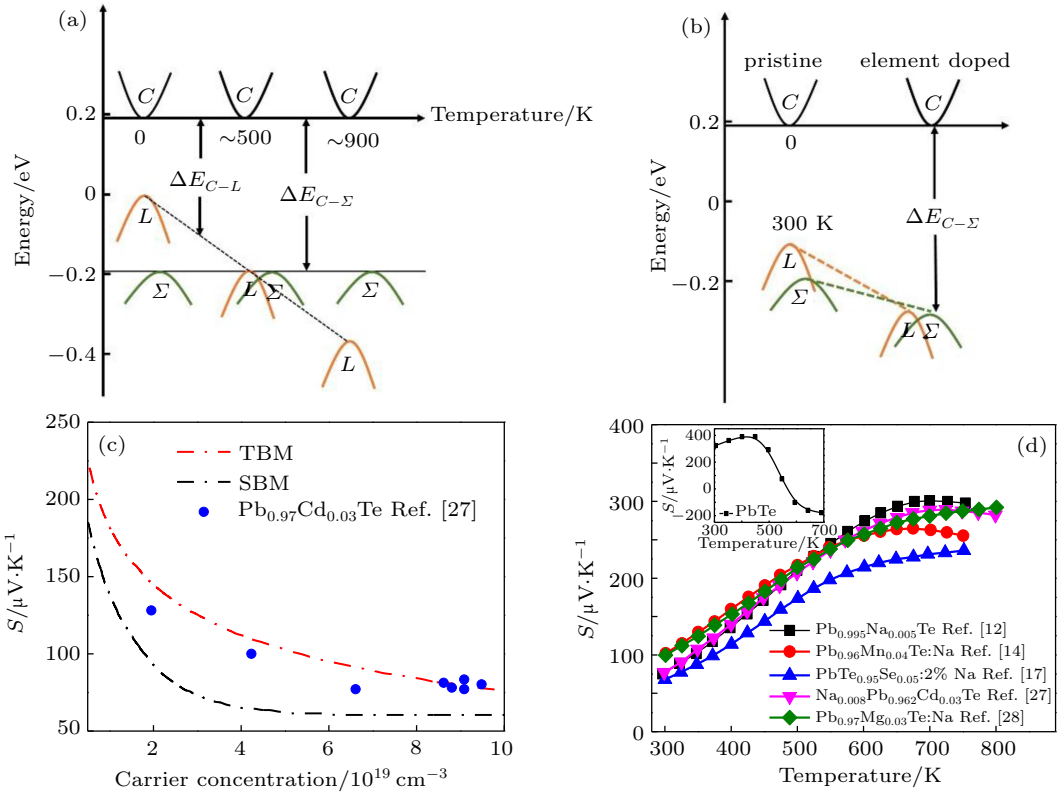


Fig. 4. (color online) Scheme of temperature-induced band convergence in Na- and Se-doped PbTe.[17] (b) Scheme of dopants-induced band convergence in doped PbTe.[28] (c) Pisarenko plot of two-band model (red dot line), single-band model (black dot line) and Cd-doped PbTe (blue dots).[27] (d) Enhanced Seebeck coefficient via band convergence by elements doping.[12,14,17,27,28] The inset presents the Seebeck coefficient of undoped PbTe for comparison.

2.3. Band flattening

Band flattening can enhance the Seebeck coefficient through optimizing band effect mass, m_b^*. By element doping or alloying, the m_b^* can be modified, and then the Seebeck coefficients get enhanced. Although, the increased m_b^* can improve the Seebeck coefficient, higher m_b^* also results in a lower carrier mobility which leads to a lower electrical conductivity. This is because the mobility is inversely proportional to the inertial effect mass ($\mu = \tau e/m_I^*$) which is equal to m_b^* for the isotropy PbTe. Meanwhile, the decreased scattering time τ reduces the carrier mobility either. Therefore, the appropriate m_b^* is needed. As for iodine (I)- and lanthanum (La)-doped n-type PbTe alloys,[18] the La doping induces 20% higher effective mass than that of I doped ones and thus it leads to a higher Seebeck coefficient. The Seebeck coefficients of La-doped samples are higher than those of I-doped ones at each fixed concentration as shown in Fig. 5(a). Thus a higher effective mass is beneficial for enhancing the Seebeck coefficient. But the carrier mobility is declined inversely which is presented in Fig. 5(b) and the electrical conductivity is influenced consequently. So band flattening can improve the Seebeck coefficient positively, but the simultaneously optimized band effective mass and carrier mobility are needed.

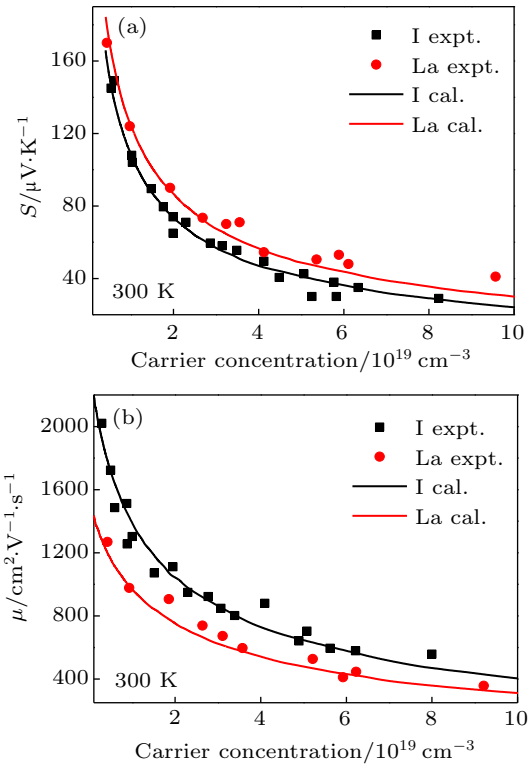


Fig. 5. (color online) (a) Seebeck coefficient and (b) carrier mobility as functions of carrier concentration for I- and La-doped PbTe.[18]

3. Phonon scattering

Besides the improvement of the electrical property by band engineering, reducing the thermal conductivity is another effective approach to increase zT. The lattice thermal conductivity as the main part of the total thermal conductivity can be reduced by many kinds of phonon scatterings. In general, the phonon can be separated into three types according to the propagation wavelength, i.e., short, medium, and long wavelength phonons. In addition, Bo *et al.* calculated the percentage contribution to the lattice thermal conductivity for PbTe from various frequency phonons. The calculation results show that short wavelength phonons of about 5 nm or less contribute 25% of the lattice thermal conductivity, while more than 50% of the lattice thermal conductivity is offered via phonons with medium wavelength of 5 nm–100 nm, and the rest of the lattice thermal conductivity is donated from long wavelength phonons of 0.1 μm–1 μm.[49] For effectively scattering these different wavelength phonons and reducing the lattice thermal conductivity, the phonon scatterings at atomic-scale, nano-scale, and meso-scale have been correspondingly utilized in PbTe alloys. The schematic diagram of the phonon scattering is shown in Fig. 6. The details of the phonon scattering effects and their mechanisms are discussed below.

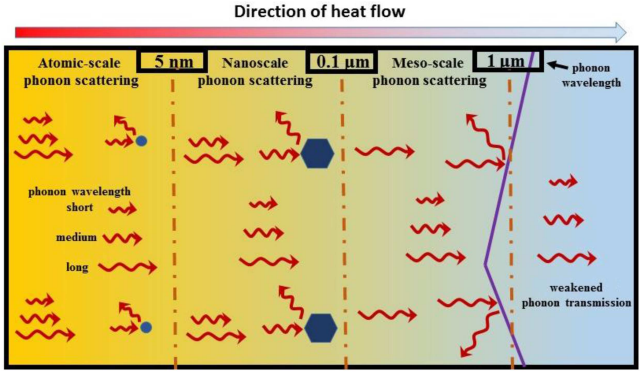


Fig. 6. (color online) The schematic diagram of phonon scatter progress.

3.1. Atomic-scale phonon scattering

For disturbing the transportation of short wavelength phonons, the atomic-scale phonon scattering is an effective way which can be achieved by defect engineering. Defect engineering can shorten the mean free phonon path (wavelength) obviously through manipulating different types of point defects, and further lead to the lower lattice thermal conductivity. In general, the point defects can be formed by introducing dopant atoms into the main matrix. As long as the alloying elements are introduced into the matrix, inevitable structural variation at atomic scale occurs. The dopant atoms can induce mass contrast and local bond strain which can restrict the short wavelength phonon transmission significantly. As we all know, most reported high figures of merit are achieved by elements doping. The atomic-scale phonon scattering obtained by point defects is ubiquitous in most excellent thermoelectric material systems. For example, the lattice thermal conductivity can be reduced from 2.25 $W\cdot m^{-1}\cdot K^{-1}$ to 1.25 $W\cdot m^{-1}\cdot K^{-1}$ at 300 K with 2.5% Se adopted in PbTe.[17] This reduction of κ_L is resulted from the atomic-scale phonon

scattering which is caused by the impurity atoms-induced mass difference and local strain, and can be well characterized by the Debye–Callaway model. In addition, with the increased density of point defects, the lattice thermal conductivity will further decline with the increase of Se content as shown in Fig. 7. In the recent report, Liangwei Fu *et al.* have discovered an Sb_{Pb}-Sb_{Te} dual-site substitutional point defects in the n-type $PbTe_{0.998}I_{0.002}$-x%Sb ($x = 1$–4) composites.[50] Due to the phonon scattering of point defects by dual-site doping, a lowest κ_L of about 0.62 $W{\cdot}m^{-1}{\cdot}K^{-1}$ at 773 K has been obtained for the $PbTe_{0.998}I_{0.002}$–3%Sb sample. Therefore, many researches are focused on the contribution of the defect scattering, and many low lattice thermal conductivities κ_L have been obtained as shown in Fig. 8.[27,28,51–53] Based on the reports and discussions, the point defect as an effective method can be used to scatter the short wavelength phonons at atom scale, and then reduce the lattice thermal conductivity. In addition, point defects do not affect electrical properties, and the corresponding electrical properties can be optimized occasionally by inducing other physical effects. Thus, the optimized phonon scattering at atomic-scale together with the modified electrical performance can synergistically enhance the thermoelectric performance of PbTe alloys.

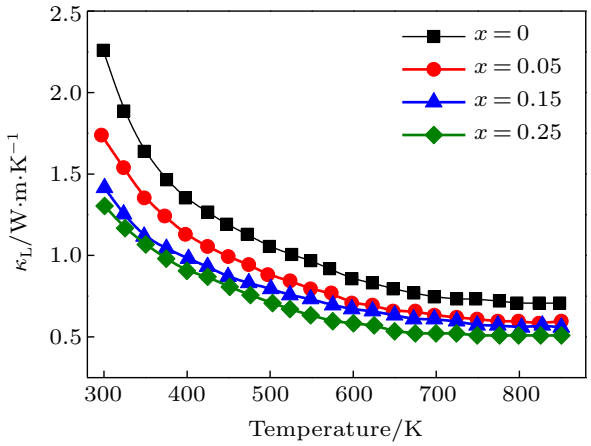


Fig. 7. (color online) The lattice thermal conductivity of $PbTe_{1-x}Se_x$ alloys.[17]

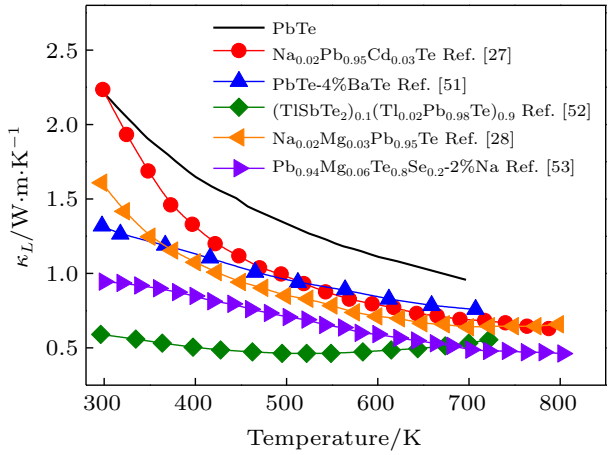


Fig. 8. (color online) The lattice thermal conductivities for the reported PbTe systems including contributions of point defects.[27,28,51–53]

3.2. Nano-scale phonon scattering

Nanostructuring is the most popular and effective way to weaken the medium wavelength phonon heat transmission by increasing the phonon scattering, which results in low lattice thermal conductivity. In recent decades, nanostructure as a powerful method has pushed the thermoelectric performance to a high level, especially in optimizing the lattice thermal conductivity. In these previous researches, it can be found that the reported nanostructures are mainly focused on the nano-grain, nano-precipitation, and heterogeneous nanocomposite as shown in Fig. 9. These three factors are discussed as models of PbTe alloys in the following.

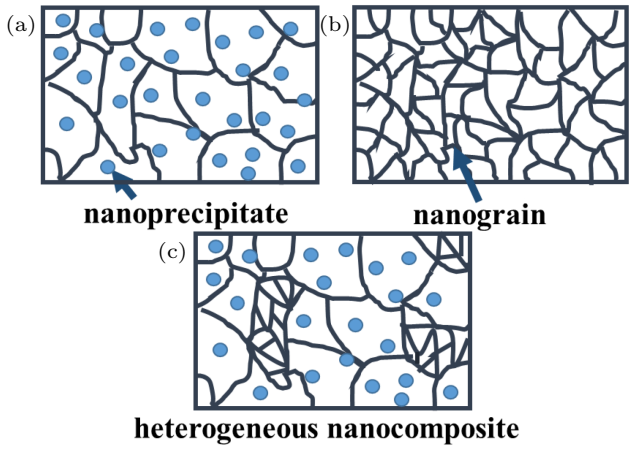


Fig. 9. (color online) The schematic diagram of (a) nano-precipitate, (b) nano-grain, and (c) heterogeneous nanocomposite in PbTe.

3.2.1. Nano-grain

The grains with size around 100 nm or lower can be the scattering sources of the medium wavelength phonons. P-type PbTe thermoelectric bulk materials with nano-grains have been fabricated by attrition milling and Spark Plasma Sintering.[54] The nano-grained sample with grain sizes as small as 80 nm–1000 nm has got a κ of 1.15 $W{\cdot}m^{-1}{\cdot}K^{-1}$ which is much lower than those of samples with grain sizes over 1 μm. This is because the increased interfaces which formed by large amount of nano-scale grains increase the intensity of the phonon scattering. Yang Li *et al.* have reported the nanostructured $Na_{0.02}Pb_{0.98}Te$ samples. The nano-grains with sizes of 20 nm–100 nm have been obtained, which are resulted from the high energy ball milling and semisolid powder processing. The minimum lattice thermal conductivity, $\kappa_L = 0.74$ $W{\cdot}m^{-1}{\cdot}K^{-1}$ has been addressed at 623 K. This value of the lattice thermal conductivity is lower than that of samples with grain size over 100 nm. Besides these examples, many other relevant studies have reported the reduction of the lattice thermal conductivity by the nano-grains.[32,55,56] In a word, with the scattering of nano-scale phonons, the corresponding lattice thermal conductivity will be obviously optimized when the sizes of nano-grains reach to a suitable value.

3.2.2. Nano-precipitation

Nano-precipitations as the embedded second phase within the host material produce many interfaces. It can also combine the mass contrast between the two phases.[57] So the medium wavelength phonons can be significantly scattered, and the lower lattice thermal conductivity will be achieved. As reported before, a plenty of researches have been focused on the nano-precipitation and demonstrated the successful reduction in the lattice thermal conductivity, while the power factor is not strongly affected.[22,58,59] In general, to form the nano-precipitation in bulk alloys, the introduced nano-precipitate phase is strongly depended on its solubility and compatibility in the matrix phase. In addition, the nano-precipitations are always selectively precipitated in the matrix phase by some separation processes such as the thermal treatment. As a typical example, in the process of the so-called "matrix encapsulation", to achieve a minority phase A inside a majority phase B, the former must has very low or no solubility in the solid state but complete solubility in the liquid state. The major phase B should have an equal or higher melting point than the minor phase, so that during rapid cooling it will be first to solidify thereby precipitating and simultaneously encapsulating nanocrystals of phase A.[60] Besides, the nano-precipitation is also relevant to the formation of nucleation, synthesis conditions, and so on.[61] Therefore, the composition, size, size distribution, and morphology can be chosen as modified factors. By regulating these factors, it is feasible to control the scattering intensity of medium wavelength phonons, and then reduce the lattice thermal conductivity.

As for the PbTe example, PbTe-x%M systems with small nanoparticles precipitating in the PbTe matrix (where M = Sb, Bi, and InSb and $2 \leq x \leq 16$) have been successfully prepared.[60] The Sb and InSb nano-inclusions act as effective scattering sources over a wide spectral range of phonons within the matrix. The 2% Sb-doped PbTe alloy exists the minimum average size of nano-precipitations, and has presented a low room-temperature lattice thermal conductivity of ~ 0.8 W·m^{-1}·K^{-1} as shown in Fig. 10. However, the lattice thermal conductivity of PbTe–Bi system has not been reduced,

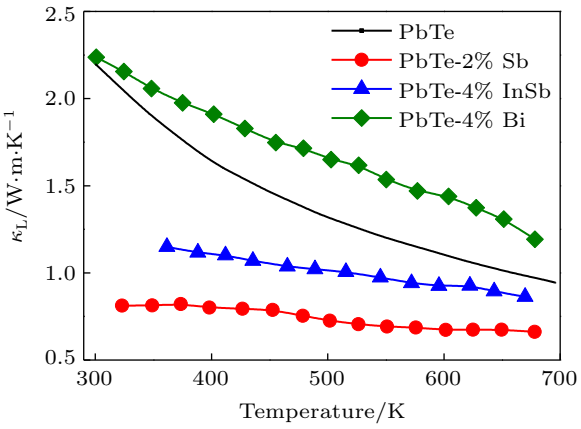


Fig. 10. (color online) Comparison of lattice thermal conductivities for PbTe, as well as PbTe with Sb, Bi, and InSb nano-inclusions.[60]

which value is almost the same with intrinsic PbTe alloy. This is attributed to the very little acoustic mismatch between the Bi nanophase and the PbTe matrix, which have nearly the same mass. These results indicate that the composition of nano-precipitation should be delicately designed previously. So only the optimized nano-precipitation or designed doping element can effectively scatter the corresponding wavelength phonons and reduce the thermal conductivity. Until now, many confirmed compositions of nano-precipitations in PbTe alloys have been reported, such as SrTe,[62] Ag_2Te,[31] HgTe,[63] MgTe.[64] In these PbTe alloys with nano-precipitations, the lattice thermal conductivities are reduced and then the figures of merit are improved, as shown in Fig. 11.

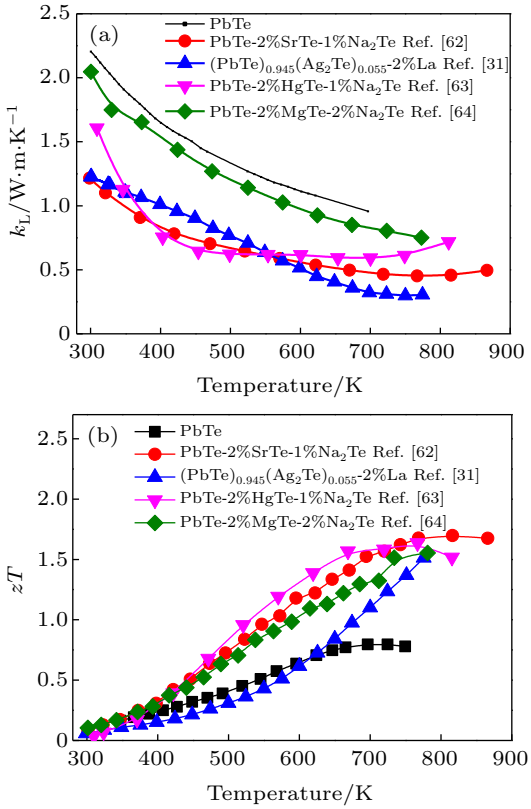


Fig. 11. (color online) (a) Lattice thermal conductivities and (b) zT values for the reported PbTe bulks with different nano-precipitates.[31,62–64]

Besides the composition of nano-precipitations, the size and size distribution of nano-precipitations should also be optimized to reduce the lattice thermal conductivity. Wang *et al.* reported an enhanced zT value of ~ 2.0 at 773 K by optimizing the size and size distribution of the nano-precipitations in the 2%Na-doped PbTe bulks.[16] The analysis reveals that this zT enhancement is greatly attributed to the reduction of the lattice thermal conductivity as shown in Fig. 12. The QH sample (quenching followed by hot-pressing) achieved the lowest lattice thermal conductivity of ~ 0.5 W·m^{-1}·K^{-1}. It is due to the smallest sizes (2 nm $\sim$ 6 nm) of nano-precipitations of Na_2Te and the suitable space between them in this sample which can effectively scatter the phonons in a wide range

of wavelength. What is more, it has been found that nano-precipitations of Na_2Te also exist in other samples, but the lattice thermal conductivity is not reduced clearly in comparison with the QH sample as shown in Fig. 12(a). This indicates that the nano-precipitations may not always effectively reduce the lattice thermal conductivity, while the right grain size and suitable space between them are needed as shown in Fig. 12(c). All in all, the nano-precipitation is a good phonon scattering source which can effectively reduce the lattice thermal conductivity. However, the doping element, grain size together with many other influencing factors for nano-precipitations should be optimized. In this case, the scattering of medium wavelength phonons can become more effective.

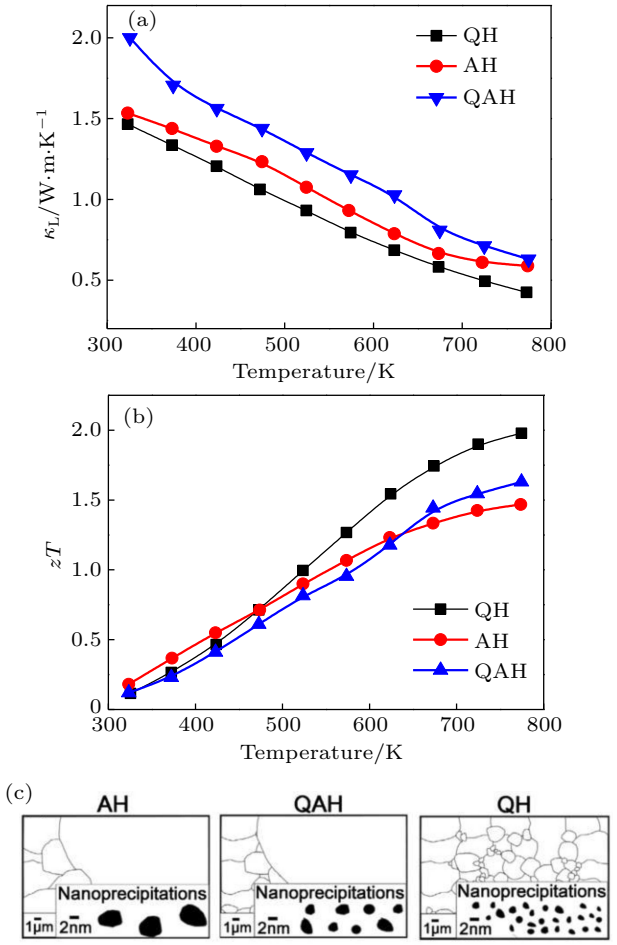


Fig. 12. (color online) (a) Lattice thermal conductivities and (b) zT values for (c) samples with different sizes nano-precipitates which are handled with different processes (QH: hot-pressing; AH: annealing followed by hot-pressing; QAH: quenching and annealing followed by hot-pressing).[16]

3.2.3. Heterogeneous nanostructure

The heterogeneous nanostructure which combines the advantages of nano-grains and nano-precipitations in PbTe bulks can further increase the phonon scattering and then reduce the lattice thermal conductivity. One case of the heterogeneous nanostructured PbTe bulk has been reported.[15] This research shows that the heterogeneous PbTe nanocomposite exhibits a zT around 2.0 at 773 K which is 25% increased in comparison with to the homogeneous nanocomposites. This high figure of merit is mainly due to the lower lattice thermal conductivity. According to the theoretical analysis as shown in Fig. 13(a), the experimental data of the ISW sample (quenching in iced salt water) showed the trend of the heterogeneous nanocomposite which lays between the nanodot nanocomposite and nanograined nanocomposite. At last, the phonon mean free path has been found more effectively reduced in the heterogeneous nanostructured PbTe alloy compared to the homogeneous PbTe nanocomposites. This shortening of phonon mean free path is attributed to the significantly decreased interparticle distance in the heterogeneous nanocomposite which nanodots are resided in a more confined region as shown in Fig. 13(b). In addition, the inhomogeneous phase of PbTe–PbS (8, 30%) solid solutions has been found.[65] The incipient phase separation has been effective controlled by the rapidly quench process, and then the inhomogeneous nanostructure has been formed. Finally, the phonon scattering increased and the lattice thermal conductivity is reduced due to the formed heterogeneous nanostructure.[66] Based on the discussions above, it can be seen that the heterogeneous nanostructure is obviously an optimizing approach to significantly increase the phonon scattering at nano-scale, and then reduce the lattice thermal conductivity.

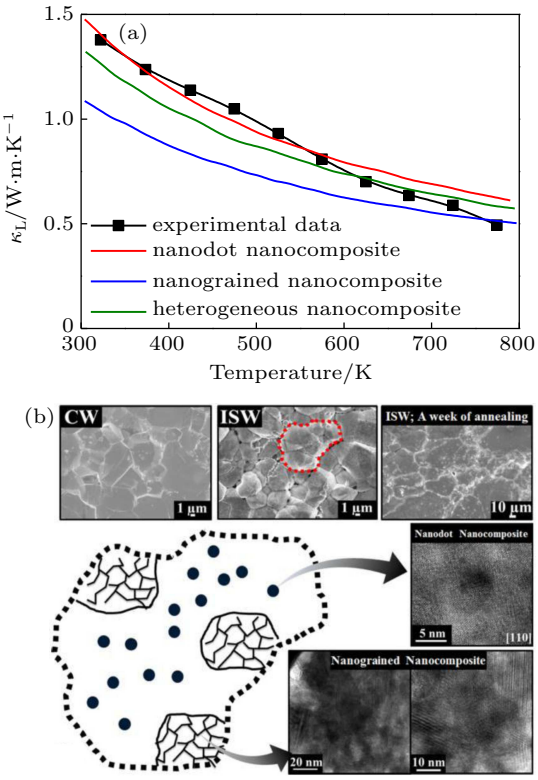


Fig. 13. (color online) (a) The lattice thermal conductivity and (b) heterogeneous nanostructure which nanodots are resided in a more confined region for the ISW sample (quenching in iced salt water).[15]

From the discussions above, as effective nano-scale scattering sources, the nano-grain, nano-precipitation, and heterogeneous nanostructure can obviously reduce the lattice thermal

conductivity by increasing the medium wavelength phonon scattering, and then enhance the thermoelectric figure of merit. Meanwhile, the effect of nano-scale phonon scattering is also affected by the doping element, grain size, and specific microstructure of heterogeneous nanostructure. Actually, many other factors can influence the nano-scale phonon scattering expect for the above descriptions, such as the shape and morphology of the nano-precipitation in PbTe alloys.[67,68] Anyway, the nano-scale phonon scattering as one of the most popular approaches will further enhance the thermoelectric performance by optimizing the mentioned factors.

3.3. Meso-scale phonon scattering

The long wavelength phonon is almost unaffected by point defects and nanostructure. Indeed, the meso-scale boundary scattering is a universal way to scatter the long wavelength phonons in bulk materials. The increased interfaces within microstructure formed by grain boundaries can scatter the long wavelength phonon. However, the microstructure grain size in bulk materials should be also modified. Corresponding to the phonon with mean free paths of 100 nm to 1 μm,[49] the grains around 1 μm are easy to form the effective meso-scale phonon scattering which can limit the transport of the long wavelength phonon and then reduce the lattice thermal conductivity. However, more factors should be considered to achieve the most specific or right grain size such as the grain shape, composition of specimen, and so on. As for PbTe alloys, rather low lattice thermal conductivities have been obtained due to the phonon scattering of grain boundaries at mesoscale.[63,69–71] For SnTe which is homostructural with PbTe, the meso-scale scattering via grain boundaries has been also found as an important contribution for the low κ_L with Hg alloying.[72] The experimental lattice thermal conductivity is much lower than the calculated κ_L which is based on the Klemens–Drabble (KD) model for the point defect effect when the content of Hg is over 3%. So this subtractive part of the lattice thermal conductivity is not from the point defects but via the meso-scale phonon scattering by the grains with sizes from 0.4 μm to 2 μm. Anyway, the optimization of the grain boundary at meso-scale is a common way to effectively reduce the lattice thermal conductivity by scattering the long wavelength phonons.

3.4. Multi-scale phonon scattering

The three scattering sources mentioned above can effectively scatter specific wavelength phonons. However, in a bulk material, there always exist two or more kinds of phonon scatterings. If the multi-scale phonon scattering is reasonably modified, the effect on the lattice thermal conductivity should be more significant. Therefore, many researches are focused on modulating the multi-scale phonon scattering in bulk materials, and some outstanding results have been reported.[6,73–75] Multi-scale hierarchical architecture nanostructured Na-doped PbTe–SrTe alloys have been synthesized. In this multi-scale hierarchical architecture, the atomic-scale, nano-scale, and meso-scale scattering sources are achieved corresponding to all wavelength phonon scatterings.[6] Sodium (Na)-induced point defect can reduce the thermal conductivity by almost 25%. Followed by the grain boundary scattering and the strontium (Sr) doping which play the role in the nanostructuring scattering, the lowest lattice thermal conductivity of $Pb_{0.98}Na_{0.02}Te$–4%SrTe is 0.5 $W\cdot m^{-1}\cdot K^{-1}$ at 915 K as shown in Fig. 14(a). Based on the low lattice thermal conductivity by integrated phonon scattering, a high figure of merit that $zT \sim 2.2$ at 915 K in p-type Na-doped PbTe–SrTe alloy has been achieved as shown in Fig. 14(b). This value is higher than that of the single atomic scale or nanoscale phonon scattering as shown in Fig. 14(c).

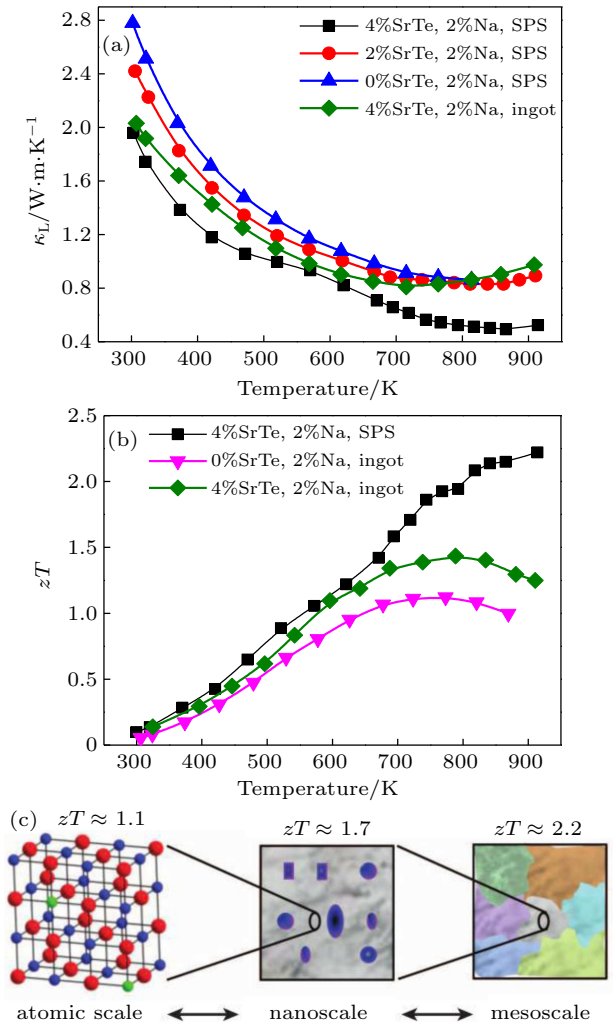


Fig. 14. (color online) (a) Reduced lattice thermal conductivities and (b) zT values for SPS samples with the multi-scale hierarchical architecture compared with ingot samples. (c) The schematic view of $zT \sim 1.1$ for atomic scale phonon scattering, $zT \sim 1.7$ for atomic and nanoscale phonon scattering and $zT \sim 2.2$ for all-scale phonon scattering.[6]

In another example, the lowest lattice thermal conductivities of 0.64 $W{\cdot}m^{-1}{\cdot}K^{-1}$ at 300 K and 0.37 $W{\cdot}m^{-1}{\cdot}K^{-1}$ at 923 K have been obtained in K-doped $PbTe_{0.7}S_{0.3}$ alloy.[75] This is also resulted from the fabrication of multi-scale phonon scattering which has large number of nano-precipitates together with atomic-scale defects and meso-scale grains. The low lattice thermal conductivity leads to the figure of merit, $zT > 2$, at a very wide temperature range from 673 K to 923 K. Therefore, if the optimized multi-scale phonon scattering is utilized, the low lattice thermal conductivity and the high figure of merit would be more possibly achieved in PbTe alloys.

4. Synergistic effect on electrical–thermal transport

As we all know, the thermoelectric parameters, S, ρ, and κ, are coupled with each other. When one of these parameters is changed, the others will be affected in concurrently although we always try to separate them for independent controlling such as the band engineering and phonon scattering. Because of this coupled relationship, these three parameters may exist "one point" in a material. In this "one point", the corresponding synergistic effect should be simultaneously improved in electrical and thermal performance. This synergistic effect on electrical–thermal transport will lead to excellent thermoelectric performance. In the previous reports, the synergistic effects have been found to bring about excellent thermoelectric figures of merit. For PbTe alloys with embedded nano-precipitations, as previously discussed, the nano-precipitations will reduce the lattice thermal conductivity while the Seebeck coefficient can also be optimized. The optimized Seebeck coefficient is resulted from the scattering of low-energy electrons by barriers. This is called the energy filtering effect, as charge carriers with kinetic energies smaller than chemical potential will contribute negatively to the Seebeck coefficient.[76] So when the introduced barriers by the embedded nano-precipitations have the suitable chemical potential, the low-energy carriers can be effectively scattered and then the Seebeck coefficient will be enhanced.[77–80] Finally, a rather high Seebeck coefficient caused by the energy filtering effect and a reduced lattice thermal conductivity from the nano-scale phonon scattering synergistically lead to the high thermoelectric figures of merit. What is more, Kanatzidis *et al.* also found that the carrier mobility and the lattice thermal conductivity are synergistically optimized in PbTe alloys with both Pb and Sb nano-precipitates.[81] Recently, energetic hierarchical architectures by introducing InSb into n-type PbTe matrix have been built to achieve effective scattering of low-energy charge carriers at the entire temperature range.[69] The multiphase energy barriers between the nano-phase and matrix can boost the power factor in the entire temperature range via the significant enhancement of the Seebeck coefficient. On the other hand, the strengthened interface scattering by the intensive phase boundaries yields an extremely low lattice thermal conductivity. As a result, a record high zT value of ~ 1.83 has been achieved at 773 K for the n-type PbTe–4%InSb composite. All in all, when the low lattice thermal conductivity is achieved via the phonon scattering at nano-scale, the other mechanisms may also be induced such as the energy filtering effect. By rational optimization of the nanostructure, the synergistic effect on electrical and thermal transports will play a useful role in enhancing the thermoelectric figure of merit.

Besides the nanostructuring effect, the band engineering and phonon scattering are often combined for simultaneously optimizing electrical properties and the thermal conductivity to obtain the effective synergistic effect. Some successful examples have been reported. In the 2.5% K-doped $PbTe_{0.7}S_{0.3}$ sample, except for the multi-scale phonon scattering by hierarchical architecturing which have been mentioned before, the carrier concentration tuning and band engineering also make a great contribution to the high average zT.[75] What is more, SrTe embedded into the PbTe matrix can widen the band gap and further increase the band convergence of the two valence bands of PbTe, and then the power factor with maximal value over 30 $\mu W{\cdot}cm^{-1}K^{-2}$ has been achieved. Meanwhile, the endotaxial SrTe nano-precipitations lead to an extremely low lattice thermal conductivity of 0.5 $W{\cdot}m^{-1}{\cdot}K^{-1}$. As the synergistically optimized result, a record figure of merit that $zT = 2.5$ has been gotten at 923 K.[82] Besides these described examples, a large number of studies have also demonstrated the success in synergistic optimizing the thermoelectric properties for PbTe.[31,50,83–87] Parts of high zT values over 2.0 for p-type PbTe and record zT values about 1.8 for n-type PbTe have been presented in Fig. 15. Therefore, all above-mentioned mechanisms can be combined, and searching for effective synergistic effects will further improve the figure of merit of PbTe alloys.

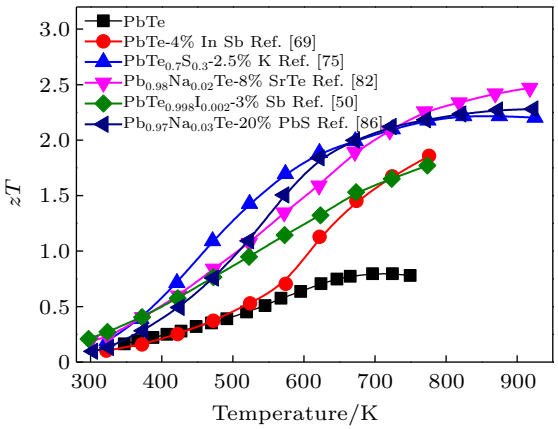


Fig. 15. (color online) Parts of the high zT values for p-type PbTe and record zT values for n-type PbTe.[50,69,75,82,86]

5. Summary and outlook

With the relatively proper carrier concentration (about $\sim 10^{19}$ cm^{-3}) and low lattice thermal conductivity (~ 2 W·m^{-1}·K^{-1}) at room temperature, telluride (PbTe) has been known as one of the excellent TE materials. Herein, the current research progress on PbTe alloys has been reviewed and the successful strategies for optimizing thermoelectric performance have been focused. Band engineering, phonon scattering engineering, and synergistic effects are summarized in detail. The band engineering, such as the resonance level, band convergence, and band flattening can lead to good electrical properties of PbTe alloys. Additionally, atomic-scale, nano-scale, meso-scale, and multi-scale phonon scatterings can effectively scatter various wavelength phonon transports. Finally, the synergistic effects based on the band engineering and phonon scattering engineering have been discussed, which lead to some high figures of merit over 2.0. In this review, it is also found that the achieved figures of merit for p-type PbTe alloys are generally higher than those of n-type samples. One non-negligible reason is that the band engineering is not effectively worked in n-type PbTe alloys. For matching the p-type PbTe as well as further improving the thermoelectric performance of n-type PbTe, the delicate modified band structure, the optimized carrier concentration, the modulated phonon scatterings, and the effective synergistic effects should be further studied.

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