



Cite this: DOI: 10.1039/c8ta01393d

Received 9th February 2018
Accepted 10th April 2018

DOI: 10.1039/c8ta01393d

rsc.li/materials-a

Synergetic optimization of electronic and thermal transport for high-performance thermoelectric GeSe–AgSbTe₂ alloy†Mingtao Yan,^{‡ab} Xiaojian Tan,^{‡c} Zhiwei Huang,^a Guoqiang Liu,^c Peng Jiang^{‡*a} and Xinhe Bao^{‡*a}

Rhombohedral GeSe is a promising p-type thermoelectric material with a multivalley band structure. However, its figure of merit ZT , especially average ZT is still relatively low compared with the state-of-art thermoelectric materials. Here, we show that alloying with AgSbTe₂ can synergistically optimize the electronic and thermal transport properties of GeSe. On one hand, alloying can tune the crystal field and promote the band convergence between the lower light valence band and higher heavy valence band. The rising light valence band maximum increases both the density of state effective mass and carrier mobility, leading to a significantly improved power factor. On the other hand, the phonon scattering is also enhanced by the alloying effect, resulting in a low lattice thermal conductivity of 0.7 W m^{−1}K^{−1} at 754 K. A peak ZT of ≈ 1.0 at 754 K was achieved in GeSeAg_{0.2}Sb_{0.2}Te_{0.4} and more importantly, the ZT_{avg} (0.65) between 301 K and 754 K was improved by more than 56% compared to GeSeAg_{0.2}Sb_{0.2}Se_{0.4} ($ZT_{\text{avg}} = 0.41$).

1 Introduction

Thermoelectric devices enable conversion of waste heat to electricity in an environmentally friendly manner.^{1,2} The thermoelectric performance of thermoelectric materials can be evaluated by the thermoelectric figure of merit ZT , which is defined as $ZT = \sigma S^2 T / \kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and κ is the thermal conductivity, respectively.^{3,4} The increase of ZT can be realized by boosting the power factor (σS^2) and suppressing the thermal conductivity. Traditional strategies to increase the power factor include optimizing the carrier

concentration,^{3,5} increasing carrier mobility (modulation doping^{6,7} and texturing) as well as improving the density of state effective mass (band convergence,^{8,9} resonant state doping^{10,11}), whereas the thermal conductivity can be minimized by introducing atomic scale point defects,¹² nanostructures¹³ as well as all-scale hierarchical architectures.¹⁴

Beyond improving the performance of traditional thermoelectric materials, such as BiSbTe and PbTe,¹⁵ it is of great significance to search for novel thermoelectric materials with decent performance. Recently, SnSe has drawn wide attention because of its unprecedented peak ZT of 2.6.^{16,17} GeTe has also been demonstrated to be a promising candidate with $ZT > 2.0$ through doping and alloying.^{18–20} GeSe, with a similar structure to that of SnSe and GeTe, has been predicted by density functional theory (DFT) calculations as a potential new thermoelectric material with a peak ZT of 2.5 at 800 K upon optimal hole doping.²¹ Nevertheless, it is difficult to achieve sufficient carrier concentration by doping (Cu, Ag and Na for p-type as well as Bi, Sb, La, As and I for n-type), resulting in a low ZT of 0.2 at 700 K.²² Recently, a crystal structure phase engineering strategy has been applied successfully to obtain a high peak ZT of 0.86 at 710 K by achieving high carrier concentration (1.2×10^{20} cm^{−3}) in the rhombohedral phase of GeSe *via* alloying with AgSbSe₂.²³

However, the relatively low σS^2 and high thermal conductivity at the low temperature range render rhombohedral GeSe a poor average figure of merit. As mentioned before, band engineering is an effective route to enhance the power factor by introducing band convergence.^{8,9} Furthermore, suppressed thermal conductivity by heavy element doping has been reported in some other TE materials, such as silicides.²⁴ Tellurium has been successfully used as a dopant or alloying content to regulate thermoelectric performance including increasing electrical conductivity and decreasing thermal conductivity, such as in SnSe_{1−x}Te_x.^{25,26} Based on these considerations, herein we tried to improve the thermoelectric performance of GeSe by AgSbTe₂ alloying. A peak ZT of ≈ 1.0 was achieved and more importantly, the ZT_{avg} was improved by more than 56%

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8ta01393d

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compared to $\text{GeSeAg}_{0.2}\text{Sb}_{0.2}\text{Se}_{0.4}$ ($ZT_{\text{avg}} = 0.41$). These improvements originate from the enhanced power factor at all temperatures and decreased lattice thermal conductivity caused by the alloying effect.

2 Experimental section

2.1 Synthesis

Polycrystalline samples $\text{GeSeAg}_x\text{Sb}_x\text{Te}_{2-x}$ ($x = 0, 0.05, 0.1, 0.15, 0.2, 0.3$) were prepared by the ballmilling–melting–SPS (Spark Plasma Sintering) method. The ballmilling process for 12 h at 450 rpm was used mainly to mechanically mix highly pure elemental powders of Ge (99.999%, Aladdin), Ag (99.9%, Alfa Aesar), Sb (99.999%, Alfa Aesar), Te (99.999%, Alfa Aesar), and Se (99.999%, Alfa Aesar), which were weighed according to the stoichiometric ratio $\text{GeSeAg}_x\text{Sb}_x\text{Te}_{2-x}$. The rhombohedral phase was formed during the melting process. The milled powders were sealed into a vacuum quartz tube by a Partulab device (MRVS-1002) and heated to 773 K at a heating rate of 3 K min^{−1} and held for 30 min. Then the materials were heated to 1073 K at a similar heating speed and held for 2 h. Finally, fine powders, obtained by grinding, were sintered at 773 K for 5 min under a pressure of 50 MPa by SPS. The ingots were cut for thermoelectric property measurement and characterization.

2.2 Characterization

X-ray diffraction (XRD) was performed on an Empyrean 100 with Cu K α radiation at room temperature. The structural phase transitions of $\text{GeSeAg}_x\text{Sb}_x\text{Te}_{2-x}$ were measured using an *in situ* XRD system (Rigaku D/MAX 2400) from 300 K to 550 K in a N₂ atmosphere. The high-resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) patterns were collected using a HRTEM system (JEM-2100). The morphology was determined using a scanning electron microscopy (SEM) system (QUANTA 200 FEG).

2.3 Thermoelectric transport properties

The electrical conductivities and Seebeck coefficients from 301 K to 754 K were obtained using a ZEM-3 system (ULVAC-RIKO, Japan) and the carrier concentrations and mobilities were measured on a Hall system (HL5500PC) at 300 K. The thermal transport properties were calculated by measuring the thermal diffusivity coefficient (D), heat capacity (C_p) and mass density (ρ). A laser flash analysis instrument (LFA 457, Netzsch) was used to measure D from 301 K to 754 K in a helium atmosphere. Heat capacity (C_p) measurement was performed on a Netzsch STA 449 F3 instrument at a heating rate of 10 K min^{−1} in a continuous N₂ flow.

2.4 Density functional theory calculations

The calculations were performed within the framework of DFT as implemented in the VASP code.²⁷ The exchanged–correlation energy is in the form of Perdew–Burke–Ernzerhof (PBE),²⁸ and projector-augmented wave technique^{29,30} is used for Ge and Se atoms. The cutoff energy for the wave function is set to 500 eV,

and the effect of spin–orbit coupling is included. Both atomic positions and lattice constants are fully relaxed until the magnitude of the force acting on all atoms becomes less than 0.001 eV Å^{−1}. The Fermi surface is plotted with the program Wannier90 (ref. 31) and Xcrysden.³²

3 Results and discussion

The powder XRD patterns for the $\text{GeSeAg}_x\text{Sb}_x\text{Te}_{2-x}$ ($x = 0, 0.05, 0.1, 0.15, 0.2, 0.3$) samples at room temperature are displayed in Fig. 1(a), which distinctly indicate a phase transition from the orthorhombic structure ($Pnma$) ($a = 10.830$ Å, $b = 3.832$ Å, $c = 4.396$ Å) of pure GeSe to the rhombohedral structure ($R3m$) of $\text{GeSeAg}_x\text{Sb}_x\text{Te}_{2-x}$ ($x = 0.05, 0.1, 0.15, 0.2$). HRTEM image and SAED pattern (Fig. S1†) further confirm the rhombohedral structure ($R3m$) for $\text{GeSeAg}_{0.2}\text{Sb}_{0.2}\text{Te}_{0.4}$, which is consistent with the peak identification from XRD results. This structural phase transition also leads to the different morphology, which is evidenced in the SEM images (Fig. S2†). Orthorhombic GeSe exhibits evident layered structures, which disappear for rhombohedral $\text{GeSeAg}_x\text{Sb}_x\text{Te}_{2-x}$.

When $x = 5\%$, the rhombohedral structure is formed completely with a hexagonal unit cell as $a = b = 3.960$ Å, and $c = 10.148$ Å, as shown in Fig. 1(b). Compared to AgSbSe_2 alloying,²³ where $x = 0.1$ is required to form the rhombohedral phase, AgSbTe_2 alloying exhibits a higher promoting efficiency towards the formation of the rhombohedral phase. When $x > 20\%$, the two peaks in the range of $2\theta = 42\text{--}47^\circ$ approach closer with increasing AgSbTe_2 amount, suggesting that the rhombohedral phase gradually evolves into a cubic structure. This alloying-induced structural phase transition is also confirmed by the change of the lattice parameter c derived from XRD peaks, shown in Fig. 1(b), which is less than the values of linear changes with increasing x (black line). The lattice parameter a or b linearly increases with increasing x , which satisfies Vegar's law, implying that Ge^{2+} is substituted by Ag^+ and Sb^{3+} .

Previous report has shown that rhombohedral GeSe possesses two valence band maxima (VBMs),²³ one near the L -point and the other near the Z -point. As shown in Fig. 1(b), the changing tendency of lattice constants a/b and c is quite

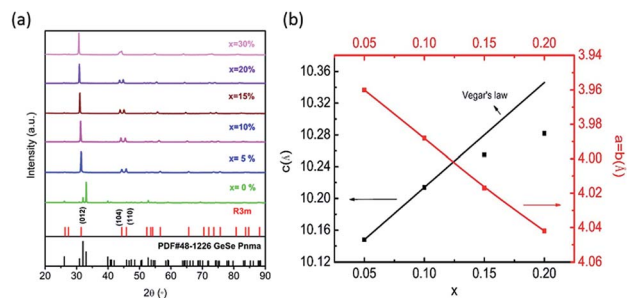


Fig. 1 (a) Room temperature powder XRD of $\text{GeSe}-x\text{AgSbTe}_2$ ($x = 0\%, 5\%, 10\%, 15\%, 20\%, 30\%$) samples. (b) Refined crystal cell parameters ($a = b$ and c) from the XRD patterns versus alloying contents of $\text{GeSeAg}_x\text{Sb}_x\text{Te}_{2-x}$ ($x = 0.05, 0.1, 0.15, 0.2$) (black line represents Vegar's law).

opposite with AgSbTe₂ alloying, and the value of c/a becomes smaller and smaller as listed in Table 1. To elucidate the influence of crystal field variation on the relative energy level of the VBMs, DFT calculations were performed. Fig. 2(a) presents the calculated band structure of pristine and AgSbTe₂ alloyed GeSe. It is interesting that the second VBM (LVBM) near the Z-point moves up to be close to the first VBM (HVBM) near the L-point. Since the locations of VBMs for rhombohedral GeSe deviate from the high symmetry k -points, the valence band convergence in Fig. 2(a) is not obvious. To better understand the band modification by AgSbTe₂ alloying, we plotted the Fermi surface at the carrier concentration of $2 \times 10^{20} \text{ cm}^{-3}$ for pristine and alloyed GeSe in Fig. 2(b) and (c), respectively. It is evident that there are only threefold symmetric pockets (HVBM) near the L-point for GeSe, whereas for AgSbTe₂-alloyed GeSe, additional sixfold symmetric pockets (LVBM) appear near the Z-point. Fig. 2(c) exhibits complete band convergence in rhombohedral GeSe and the valley number N_v increases from 3 to 9. The increased N_v is highly beneficial to improve the density of state (DOS) effective mass and Seebeck coefficient.⁸ In addition, the curvature of the LVBM pocket is larger than that of the HVBM one, which could lead to higher carrier mobility. Overall, it is reasonable to expect enhanced power factor in AgSbTe₂-alloyed GeSe.

Table 1 Hall carrier concentration and carrier mobility, the value of c/a as well as density of GeSe- x AgSbTe₂ ($x = 0, 0.05, 0.1, 0.15, 0.2, 0.3$) samples

Samples	Carrier concentration (cm^{-3})	Carrier mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	Values of c/a	Density (g cm^{-3})
$x = 0\%$	4.29×10^{14}	0.78	—	5.20
$x = 5\%$	2.67×10^{20}	12.23	2.563	5.28
$x = 10\%$	1.84×10^{20}	17.42	2.561	5.56
$x = 15\%$	9.00×10^{19}	22.85	2.553	5.68
$x = 20\%$	8.90×10^{19}	10.50	2.544	5.70
$x = 30\%$	4.20×10^{19}	10.40	—	5.86

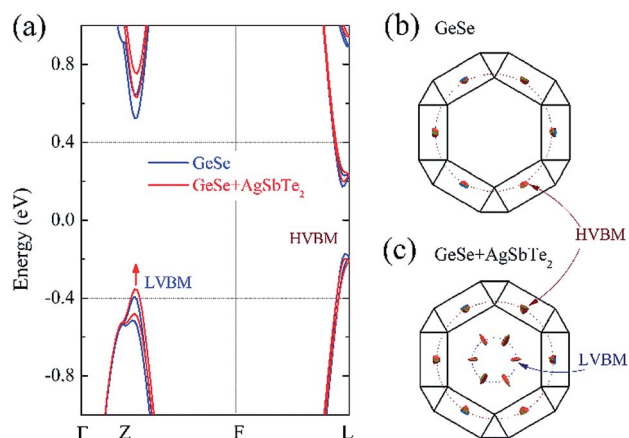


Fig. 2 (a) The band structure of GeSe and GeSe + AgSbTe₂ calculated by DFT. (b) and (c) The Fermi surface of GeSe and GeSe + AgSbTe₂ when the carrier concentration is $2 \times 10^{20} \text{ cm}^{-3}$.

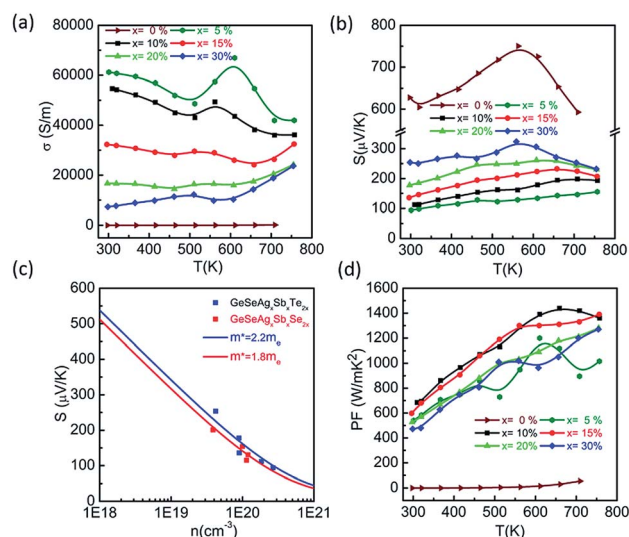


Fig. 3 Temperature dependent electrical conductivities (a), Seebeck coefficients (b), power factor (d) of GeSe- x AgSbTe₂ ($x = 0\%, 5\%, 10\%, 15\%, 20\%, 30\%$). (c) DOS effective mass calculated using the relationship of Seebeck coefficient with carrier concentration (Pisarenko plot).

Table 1 shows the carrier concentration and mobility of GeSeAg _{x} Sb _{x} Te _{$2x$} at room temperature as well as the value of lattice c/a . The carrier concentration decreases with increasing AgSbTe₂ alloying amount for rhombohedral GeSeAg _{x} Sb _{x} Te _{$2x$} samples. For GeSeAg_{0.2}Sb_{0.2}Te_{0.4}, the carrier concentration decreases to $8.9 \times 10^{19} \text{ cm}^{-3}$, which is the optimal carrier concentration as discussed in the following parts. The carrier mobility of GeSeAg _{x} Sb _{x} Te _{$2x$} samples increases first and then decreases, with a peak value ($22.85 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) for GeSeAg_{0.15}Sb_{0.15}Te_{0.3}, which is higher than that of GeSeAg _{x} Sb _{x} Te _{$2x$} .²³ This is because the holes possessing higher carrier mobility participate in conductivity due to the upshift of LVBM as suggested by DFT.

The temperature dependent electronic transport properties of GeSeAg _{x} Sb _{x} Te _{$2x$} ($x = 0\%, 5\%, 10\%, 15\%, 20\%, 30\%$) are presented in Fig. 3. Considering the minor anisotropic effect for rhombohedral GeSeAg _{x} Sb _{x} Te _{$2x$} (Fig. S3†), the following discussions only focus on the properties along the direction perpendicular to the pressing direction. In Fig. 3(a), the electrical conductivity (σ) of pure GeSe and GeSeAg_{0.3}Sb_{0.3}Te_{0.6} increases with temperature, indicating semiconducting behavior, while the σ of rhombohedral GeSeAg _{x} Sb _{x} Te _{$2x$} ($x = 0.05, 0.1, 0.15, 0.2$) decreases with temperature, which is a typically highly degenerate semiconductor behavior.^{33,34} The humps (540 K, 550 K, 520 K and 500 K for $x = 0.05, 0.1, 0.15, 0.2$) are related to the temperature-induced structural phase transition to the cubic phase, which is supported by the temperature dependent XRD patterns (Fig. S4†). The increase of electrical conductivity and decrease of Seebeck coefficients at high temperature for samples GeSeAg _{x} Sb _{x} Te _{$2x$} ($x = 0.1, 0.15, 0.2$) is attributed to the thermal excitation of minority carriers. The σ value of orthorhombic GeSe is only 0.0045 S m^{-1} at room temperature, which reaches 158 S m^{-1} at 710 K. Upon forming GeSeAg _{x} Sb _{x} Te _{$2x$} solid solution with the rhombohedral structure, the σ at room temperature all increases dramatically due to the high carrier

concentration and relatively higher mobility as listed in Table 1. The σ value for samples of $x = 0.05$ increases to $61\,213\text{ S m}^{-1}$ because of increased carrier concentration ($2.67 \times 10^{20}\text{ cm}^{-3}$). With further increase of the alloying fraction x , the electrical conductivity decreases due to the reduction of carrier concentration and mobility. In the case of $\text{GeSeAg}_{0.2}\text{Sb}_{0.2}\text{Te}_{0.4}$, the σ is $16\,702\text{ S m}^{-1}$ at 301 K and reaches $24\,169\text{ S m}^{-1}$ at 754 K, which is higher than that of $\text{GeAg}_{0.2}\text{Sb}_{0.2}\text{Se}_{1.4}$, mainly due to the upshift of LVBM contributing to higher carrier mobility. In Fig. 3(b), the positive Seebeck coefficients (S) confirm that $\text{GeSeAg}_x\text{Sb}_x\text{Te}_{2x}$ samples are p-type semiconductors, which is consistent with the Hall measurement. The S of pristine GeSe is $628\text{ }\mu\text{V K}^{-1}$ at room temperature, which increases with temperature up to 563 K, then decreases to $592\text{ }\mu\text{V K}^{-1}$ at 710 K. For $\text{GeSeAg}_x\text{Sb}_x\text{Te}_{2x}$ solid solution with the rhombohedral structure, the room temperature S decreases compared to pristine GeSe. For $x = 0.05$, S decreases to $94\text{ }\mu\text{V K}^{-1}$. Then with increasing x values, S increases. For example, the Seebeck coefficient of $\text{GeSeAg}_{0.2}\text{Sb}_{0.2}\text{Te}_{0.4}$ reaches $177\text{ }\mu\text{V K}^{-1}$ at room temperature, which increases to $261\text{ }\mu\text{V K}^{-1}$ at 608 K, then decreases to $231\text{ }\mu\text{V K}^{-1}$ at 754 K. The decent S values obtained compared to $\text{GeSeAg}_x\text{Sb}_x\text{Se}_{2x}$ can be attributed to the increased band convergence between LVBM and HVBM.

In order to confirm the scenario that alloying with AgSbTe_2 increases the DOS effective mass, a single parabolic band model was used to estimate the value. We consider the scattering factor as acoustic scattering ($r = -1/2$).^{35–38}

$$F_i(\eta) = \int_0^\infty \frac{x^i}{1 + e^{x-\eta}} dx \quad (1)$$

$$S = \frac{k_B}{e} \left[\frac{(r+5/2)F_{(r+3/2)}(\eta)}{(r+3/2)F_{(r+1/2)}(\eta)} - \eta \right] \quad (2)$$

$$n = \frac{1}{eR_H} = \frac{8\pi(2m_d^*k_B T)^{3/2}}{3h^3} \frac{(r+3/2)^2 F_{(r+1/2)}^2(\eta)}{(2r+3/2)F_{(2r+1/2)}(\eta)} \quad (3)$$

where k_B is the Boltzmann constant, e is the electron charge, m_d^* is the DOS effective mass, η is the reduced Fermi energy, T is the absolute temperature, h is the Planck constant, and $F_i(\eta)$ is the Fermi integral, respectively. As shown in Fig. 3(c), the DOS effective mass indeed increases to $2.2m_e^*$ in $\text{GeSeAg}_x\text{Sb}_x\text{Te}_{2x}$ compared to $1.8m_e^*$ in $\text{GeSeAg}_x\text{Sb}_x\text{Se}_{2x}$.²³

As a result, high power factors (σS^2) are obtained for samples of $\text{GeSeAg}_x\text{Sb}_x\text{Te}_{2x}$, which are presented in Fig. 3(d). The power factor of pristine GeSe is $0.0018\text{ }\mu\text{W m}^{-1}\text{K}^{-2}$ at room temperature and increases to $56\text{ }\mu\text{W m}^{-1}\text{K}^{-2}$ at 710 K. The power factor of GeSe was improved significantly through the phase transition of the orthorhombic phase to the rhombohedral phase by forming solid solution with AgSbTe_2 , due to the enhanced electrical conductivity and Seebeck coefficients as discussed above. The power factor is increased to $684\text{ }\mu\text{W m}^{-1}\text{K}^{-2}$ at room temperature for $\text{GeSeAg}_{0.1}\text{Sb}_{0.1}\text{Te}_{0.2}$ and reaches $1440\text{ }\mu\text{W m}^{-1}\text{K}^{-2}$ at 659 K, which is the highest power factor in GeSe-based materials. Notably, due to the modified electronic structures, for $\text{GeSeAg}_{0.2}\text{Sb}_{0.2}\text{Te}_{0.4}$, the power factor is higher than that of $\text{GeSeAg}_{0.2}\text{Sb}_{0.2}\text{Se}_{0.4}$ at all temperature ranges, as shown in Fig. S5(a).[†] Furthermore, the power factor of

$\text{GeSeAg}_{0.2}\text{Sb}_{0.2}\text{Te}_{0.4}$ is rather stable after two-cycle heating and cooling processes (Fig. S6[†]).

The thermal transport properties of $\text{GeSeAg}_x\text{Sb}_x\text{Te}_{2x}$ as a function of temperature are shown in Fig. 4. The total thermal conductivity (κ_{tot}) was calculated using the equation $\kappa_{\text{tot}} = D \cdot C_p \cdot \rho$. Thermal diffusivity coefficient (D) and heat capacity (C_p) are presented in Fig. S7[†] and mass density (ρ) is shown in Table 1. The lattice thermal conductivity (κ_{lat}) of $\text{GeSeAg}_x\text{Sb}_x\text{Te}_{2x}$ was calculated from $\kappa_{\text{lat}} = \kappa_{\text{tot}} - \kappa_{\text{ele}}$. Electrical thermal conductivity (Fig. S8[†]) was calculated from $\kappa_{\text{ele}} = L\sigma T$, and L (Lorenz number) was obtained from the SPB model using the following formula:^{35–38}

$$L = \left(\frac{k_B}{e} \right)^2 \left[\frac{(r+7/2)F_{(r+5/2)}(\eta)}{(r+3/2)F_{(r+1/2)}(\eta)} - \left(\frac{(r+5/2)F_{(r+3/2)}(\eta)}{(r+3/2)F_{(r+1/2)}(\eta)} \right)^2 \right] \quad (4)$$

The κ_{tot} of pristine GeSe is $2.9\text{ W m}^{-1}\text{K}^{-1}$ at room temperature and decreases rapidly to $0.85\text{ W m}^{-1}\text{K}^{-1}$ at 710 K. In contrast, the thermal conductivities, especially the lattice thermal conductivities, of $\text{GeSeAg}_x\text{Sb}_x\text{Te}_{2x}$ are greatly suppressed and barely depend on the temperature (Fig. 4). For $\text{GeSeAg}_{0.05}\text{Sb}_{0.05}\text{Te}_{0.1}$, the κ_{tot} at room temperature decreases to $1.39\text{ W m}^{-1}\text{K}^{-1}$. When $x > 0.05$, the κ_{tot} of $\text{GeSeAg}_x\text{Sb}_x\text{Te}_{2x}$ further decreases with increasing AgSbTe_2 content due to the decreased electrical thermal conductivity (Fig. S8[†]). The suppressed and temperature-insensitive lattice thermal conductivities of GeSe by AgSbTe_2 alloying, similar to $\text{GeSeAg}_x\text{Sb}_x\text{Se}_{2x}$, can be attributed to the impurity or point defect.^{23,39} It is worth pointing out that the thermal conductivity of $\text{GeSeAg}_{0.2}\text{Sb}_{0.2}\text{Te}_{0.4}$ is lower than that of $\text{GeSeAg}_{0.2}\text{Sb}_{0.2}\text{Se}_{0.4}$, as shown in Fig. S5(b),[†] which can be attributed to two reasons: (i) Te has larger mass and atomic radius than Se, exhibiting slower phonon speed,^{40,41} leading to a lower lattice thermal conductivity; (ii) AgSbTe_2 alloying can promote the formation of point defects due to the different electronegativities of Te and Se, further enhancing the phonon scattering.^{42–44}

Finally, the temperature dependent ZT was calculated using the equation $ZT = \sigma S^2 T / \kappa$ and is presented in Fig. 5(a). The ZT of pristine GeSe is only 0.046 at 710 K due to its low electrical conductivity. Alloying with AgSbTe_2 enhances the ZT greatly on account of the optimized carrier concentration and lowered lattice thermal conductivity as discussed above. The maximum

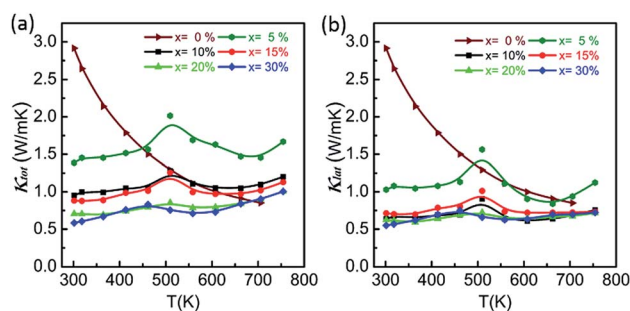


Fig. 4 (a) Temperature dependent total thermal conductivity and (b) lattice thermal conductivity of $\text{GeSe}-x\text{AgSbTe}_2$ ($x = 0, 0.05, 0.1, 0.15, 0.2, 0.3$) samples.

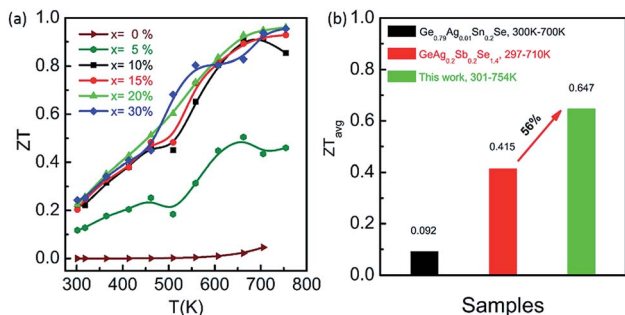


Fig. 5 (a) Temperature dependent ZT of GeSe-xAgSbTe₂ (x = 0%, 5%, 10%, 15%, 20%, 30%). (b) The average ZT of Ge_{0.79}Ag_{0.01}Sn_{0.2}Se, GeAg_{0.2}Sb_{0.2}Se_{1.4}, and GeSe-20% AgSbTe₂.

value of $ZT = 0.96$ was achieved for GeSeAg_{0.2}Sb_{0.2}Te_{0.4}, which is 21 times larger than that of the pristine GeSe. As shown in Fig. 5(b) the ZT_{avg} of GeSeAg_{0.2}Sb_{0.2}Te_{0.4} reaches 0.64, 56% improvement beyond GeSeAg_{0.2}Sb_{0.2}Se_{0.4}.

4 Conclusions

In this work, rhombohedral GeSe has been synthesized successfully by alloying with AgSbTe₂. By regulating the electronic structures with band convergence, the carrier mobility and DOS effective mass were increased, leading to higher electrical conductivity and Seebeck coefficient. Meanwhile, enhanced phonon scattering by the alloying effect further decreased the thermal conductivity. Finally, we achieved remarkably improved ZT (0.96) and ZT_{avg} (0.64) for GeSeAg_{0.2}Sb_{0.2}Te_{0.4}. These results indicate that higher performance thermoelectric properties can be realized in rhombohedral GeSe by carrier concentration optimization and thermal conductivity suppression simultaneously.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank Prof. Can Li for the Hall measurement. P. J. is grateful for the financial support from the National Natural Science Foundation of China (NSFC) (Grant: 51290272) and Dalian Institute of Chemical Physics (Grant: DICP ZZBS201608).

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