The microscopic origin of low thermal conductivity for enhanced thermoelectric performance of Yb doped MgAgSb

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Abstract

An in-depth understanding of the origin of low lattice thermal conductivity κ_{lat} is considered to be the prerequisite for developing and designing high thermoelectric performance materials. However, the microscopic mechanism of low κ_{lat} for α -MgAgSb has not been fully elaborated. Here we first thoroughly unveil the underlying mechanism using density functional theory (DFT) calculations. It is demonstrated that the unique lattice dynamic properties of α -MgAgSb contribute to the low κ_{lat} , including a large number of optical branches, weak chemical bonding, the strong anharmonic coupling between longitudinal acoustic (LA) and longitudinal optical (LO) branches, high anharmonic behavior of LO branch. Nanostructuring has an effect in decreasing the lattice thermal conductivity due to the high density of boundaries and defects. Most importantly, Yb doping on the Mg site is chosen to optimize carrier concentration and simultaneously create strong point-defect phonon scattering. Collectively, a peak $ZT \sim 1.4$ at 550 K and average $ZT \sim 1.2$ from 300 K to 550 K have been achieved, which further demonstrates the realistic prospect of MgAgSb based thermoelectric materials for low-temperature waste heat harvesting.

Keywords: thermoelectric performance; DFT calculations; low lattice thermal conductivity; MgAgSb; Yb doping

1. Introduction

To effectively harness energy for the huge global requirement, thermoelectric materials, capable of realizing the direct conversion from waste heat and solar energy into electricity, have received renewed interests in the past two decades [1-6]. But nowadays, thermoelectric devices are limited in niche markets because of the relatively low conversion efficiency, which is primarily dominated by the materials'

thermoelectric figure of merit, $ZT = S^2 \sigma T / \kappa_{total}$, where S , σ , T , and κ_{total} are the Seebeck coefficient, electrical conductivity, absolute temperature, and total thermal conductivity (including lattice thermal conductivity κ_{lat} and electronic thermal conductivity κ_{ele}), respectively. Therefore, minimizing heat transport while simultaneously maintaining good electrical properties is the primary challenge for realizing high ZT [7].

Due to the structural dependence of κ_{lat} [3], alloying (or doping) and nanostructuring have been developed into effective strategies to suppress κ_{lat} [8-15], even approaching to the amorphous limit. For instance, alloying (or doping) could create stable point-defect scattering centers for phonons with short mean free path [16], due to the mass fluctuation and surrounding strain field fluctuation. A larger difference about the atom mass and ionic radius between the host atom and alloying atom leads to the stronger phonon scattering, such as Ba doping in BiCuSeO and Hf alloying in NbFeSb [17, 18]. More importantly, proper alloying (or doping) could also tune carrier concentration n near the optimized value to maximize the power factor ($PF = S^2 \sigma$) [19-21].

Alternatively, searching for compounds possessing intrinsically low κ_{lat} is critical for producing high thermoelectric performance. Those compounds usually exhibit some unique intrinsic features of crystal structure or physical properties, mainly including heavy atomic mass [22], complex unit cell [23], weak chemical bonding [24-26], liquid like ionic behavior and anharmonic bonding [27-34]. The representative example is SnSe crystals with ultralow $\kappa_{lat} \sim 0.6 \text{ W m}^{-1} \text{ K}^{-1}$ that exhibit the extremely weak Sn-Se atomic interactions and large bond anharmonicity (Grüneisen parameter ~ 3.1) [35]. Recently, the strong anharmonic coupling between transverse optical (TO) and longitudinal acoustic (LA) branches has been demonstrated to play a pronounced role in the low κ_{lat} of PbTe using a combination of inelastic neutron scattering measurements and first-principles computations [36, 37].

α -MgAgSb holds great promise for low temperature waste heat harvesting [38-45], primarily due to the intrinsically low κ_{lat} . However, the underlying microscopic mechanism of such a low κ_{lat} has not been fully elaborated, especially in the lattice dynamics. Besides, because of the high optimal carrier concentration $\sim 9 \times 10^{19} \text{ cm}^{-3}$ at 300 K, previous efforts focus on tuning carrier concentration and thus enhancing PF via doping with light atoms [38-40, 43, 46], such as Li and Na doping on Mg site [39, 43], but the final ZT is almost unchanged due to the slightly decreased lattice thermal conductivity [39, 43]. Since Yb belongs to the heavy-group rare-earth elements with a rather heavy atomic mass ($\sim 173.1 \text{ g mol}^{-1}$), thus it is highly expected that Yb doping could substantially suppress the lattice thermal conductivity due to the obviously decreased phonon group velocity and mean free path. Meanwhile, Yb has a comparable ionic radius ($\sim 93 \text{ pm}$) with that of Mg ($\sim 65 \text{ pm}$), which may result in higher solid solubility on the Mg site in the distorted MgAgSb lattice. Besides, YbAgSb alloy exhibits a typical metal behavior with a low electrical resistivity ($\sim 1.5 \times 10^{-6} \Omega \text{ m}$ at room temperature) [47], so Yb doping (or alloying) could also reduce the electrical resistivity. Based on the above considerations, it is highly expected that rationally designed Yb doping not only observably suppresses κ_{lat} but also simultaneously optimizes electrical properties to achieve high ZT .

Herein, we thoroughly explore the microscopic origin of intrinsically low κ_{lat} of α -MgAgSb in the lattice dynamics using density functional theory (DFT) calculations. Microstructural observations also indicate that high density of boundaries and defects could further decrease the lattice thermal conductivity. More importantly, we achieve a peak $ZT \sim 1.4$ and average $ZT \sim 1.2$ via Yb doping, originated from tuning carrier concentration and simultaneously creating strong phonon-scattering. Assuming a leg length of 2 mm, cold side temperature of 323 K and hot side temperature of 548 K, the highest calculated conversion efficiency is around 9.4%, higher than undoped (8.4%), Li doped (8.6%) and the measured efficiency of a single leg based on Ni

doped MgAgSb (8.5% between 293 K and 518 K) [38, 43].

2. Experimental Section

Synthesis. Mg (99.98%; Alfa Aesar), Ag (99.99%; Sigma Aldrich), Sb (99.999%; Alfa Aesar) and Yb (99.95%; Alfa Aesar) were weighed according to the nominal composition $\text{Mg}_{1-x}\text{Yb}_x\text{Ag}_{0.97}\text{Sb}_{0.99}$ samples ($x = 0, 0.0025, 0.05$ and 0.01) and then loaded into the stainless steel jar in a glove-box under argon atmosphere. The two-step ball milling process was identical to our previous reports and finally the ball-milled powder was loaded into graphite die and hot pressed at 573 K for 5 min under a pressure of 80 MPa.

X-ray diffraction. X-ray diffraction (XRD) analysis was performed using a PANalytical multipurpose diffractometer with an X'celerator detector (PANalyticalX'Pert Pro). The phases were analyzed with JADE 6.0 software. The diffraction peaks of all the hot pressed samples exhibit excellent match with the α -MgAgSb (space group $I\bar{4}C2$) without any impurity phase within the detection limit of the XRD spectrometer [48], shown in the Figure S1.

Physical Characterization. Bar samples were cut from the disks and used for simultaneous measurement of the electrical resistivity (ρ) and Seebeck coefficient (S) on a commercial system (ULVAC ZEM-3). The thermal conductivity was calculated using $\kappa = DC_p d$, where D , C_p , and d are the thermal diffusivity, specific heat capacity, and density, respectively. The thermal diffusivity coefficient (D) was measured using the coin sample on a laser flash system (Netzsch LFA 457, Germany). The specific heat capacity (C_p) was measured on a differential scanning calorimetry thermal analyzer (Netzsch DSC 404 C, Germany). The density (d) around 6.2 g cm^{-3} was determined by the Archimedes method. The Hall Coefficient R_H at room temperature was measured using the PPMS (Physical Properties Measurement System, Quantum Design). The Hall carrier concentration (n_H) was obtained by $n_H = 1/eR_H$ and the Hall

carrier mobility (μ_H) was calculated by $\sigma = e\mu_H n_H$, where e is the electronic charge and σ the electrical conductivity.

Theoretical calculation. DFT calculations are performed using the Vienna Ab initio Simulation Package (VASP) with the projector augmented wave (PAW) scheme [49], and the generalized gradient approximation of Perdew, Burke and Ernzerhof (GGA-PBE) for the electronic exchange-correlation functional [50]. The energy cut-off for the plane wave expansion is 500 eV. The Brillouin zones are sampled by Monkhorst-Pack k-point meshes for all compounds [51], with meshes chosen to give a roughly constant density of k points ($30 \text{ \AA}^{-3}$). Atomic positions and unit cell vectors are relaxed until all the forces and components of the stress tensor are below 0.01 eV/ $\text{\AA}$ and 0.2 kbar, respectively. Vibrational properties are calculated using the supercell (192 atoms in the $2 \times 2 \times 2$ supercell) force constant method by the Phonopy [52]. In the quasiharmonic DFT phonon calculations, the system volume is isotropically expanded by 4% from the DFT relaxed volume. The Grüneisen parameter (γ_i) is defined as [30, 53]

$$\gamma_i = -\frac{V}{\omega_i} \frac{\partial \omega_i}{\partial V} \quad (1)$$

It characterizes the relationship between phonon frequency and volume change. The Debye temperature (θ_D) is calculated using $\theta_D = \omega_D/k_B$, where ω_D is the largest acoustic frequency in each direction; the phonon velocity v is the slope of the acoustic phonon dispersion around the point. The Grüneisen parameters, Debye temperatures, and phonon velocities are averaged by the weight of the high-symmetry points.

3. Results and discussion

Synergistic optimization of thermoelectric performance

Figure 1 shows the synergistic strategies of enhancing thermoelectric performance via Yb doping and the corresponding ZT as well as calculated efficiency.

First, Yb doping tunes the Fermi level closer to the valence band and thus enhances PF (Figure 1a). Second, the intrinsically low κ_{lat} of MgAgSb contributes to the high ZT , which can be attributed to the unique lattice dynamic properties, including large number of optical phonon branches, weak chemical bonding, longitudinal optical (LO)-longitudinal acoustic (LA) branches scattering and high anharmonic behavior of LO branch (Figure 1b). Third, Yb doping could further suppress κ_{lat} because of the strong point-defect scattering to phonons due to the large difference in atom mass and size between Mg and Yb (Figure 1c). Due to the enhanced PF and significantly suppressed κ_{lat} , Figure 1d shows that ZT has been improved over the whole measured temperature range upon Yb doping. Specifically, $\text{Mg}_{0.995}\text{Yb}_{0.005}\text{Ag}_{0.97}\text{Sb}_{0.99}$ exhibits the highest average $ZT \sim 1.2$, higher than that of $\text{MgAg}_{0.97}\text{Sb}_{0.99} \sim 1.0$ and $\text{Mg}_{0.99}\text{Li}_{0.01}\text{Ag}_{0.97}\text{Sb}_{0.99} \sim 1.1$ (Figure 1e) [42, 43]. According to the method proposed by Kim *et al.* and assuming a leg length of 2 mm, cold side temperature of 323 K and hot side temperature of 548 K (see the supporting information) [54], Figure 1e shows that the corresponding calculated single leg conversion efficiency is around 9.4%, higher than undoped (8.4%), Li doped (8.6%) as well as the measured efficiency of a single leg based on Ni doped MgAgSb (8.5% between 293 K and 518 K) [38, 43].

Enhancing power factor by tuning carrier concentration

Figure 2 presents the electrical transport properties of $\text{Mg}_{1-x}\text{Yb}_x\text{Ag}_{0.97}\text{Sb}_{0.99}$. Hall carrier concentration n first increases and then saturates, which may be related with low solid solubility of Yb on the Mg sublattice, while mobility μ monotonically decreases with increasing Yb doping concentration. Electrical resistivity ρ first decreases and then arises with the increased doping concentration (Figure 2b). Since YbAgSb exhibits a typical metal behavior (room-temperature $\rho \sim 1.5 \times 10^{-6} \Omega \text{ m}$) [47], Yb doping on the Mg site leads to reduced ρ compared with pristine $\text{MgAg}_{0.97}\text{Sb}_{0.99}$. In addition, ρ of undoped and doped samples fit the temperature dependence of $T^{3/2}$

before the intrinsic excitation, indicating carrier transport mechanism is mainly dominated by acoustic phonon scattering at the low temperature range. Figure 2c shows that Seebeck coefficient S decreases somewhat upon Yb doping, due to the increased n . Figure 2d shows the Pisarenko plots, S dependence on n , with $m^* = 2.4 m_0$ at room temperature assuming single parabolic band model and the acoustic phonon scattering mechanism [43, 55], where m_0 is the electron mass. Apparently, all the experimental data, including Yb and Li doping and tuning of Sb content [42, 43], fall nearly on the calculated line, indicating that the valence band structure remains almost unchanged. Compared with pristine $\text{MgAg}_{0.97}\text{Sb}_{0.99}$, PF could be finally enhanced by around 20% at the entire temperature range for $\text{Mg}_{0.995}\text{Yb}_{0.005}\text{Ag}_{0.97}\text{Sb}_{0.99}$ (Figure 2e). Since the band structure is almost unchanged upon Yb doping, tuning carrier concentration should be the only approach to enhance PF . As aforementioned, Yb doping increases the carrier concentration from $2.9 \times 10^{19} \text{ cm}^{-3}$ ($\text{MgAg}_{0.97}\text{Sb}_{0.99}$) to $4.6 \times 10^{19} \text{ cm}^{-3}$ ($\text{Mg}_{0.995}\text{Yb}_{0.005}\text{Ag}_{0.97}\text{Sb}_{0.99}$), meanwhile shifting the Fermi level from -0.75 to -0.13 (Table 1). Normally, the optimal reduced Fermi energy η should be close to zero for most thermoelectric materials with an acoustic phonon scattering mechanism for charge carrier [56]. This statement can well explain the enhancement of PF upon Yb doping. Nevertheless, the optimized carrier concentration n_{opt} is around $9 \times 10^{19} \text{ cm}^{-3}$ (Figure 2f) [43], still higher than that of Yb doping. Further enhancement of PF could be possible by dual doping.

Suppressing lattice thermal conductivity via strong point-defect scattering

Figure 3a shows that total thermal conductivity κ_{total} first decreases because of Umklapp scattering and then increases significantly due to bipolar effect. Electrical thermal conductivity κ_{ele} can be calculated from the Wiedemann-Franz relationship ($\kappa_{ele} = L\sigma T$), where L is the Lorenz number calculated based on the single parabolic band model with the acoustic phonon scattering mechanism [43, 55]. Thus, κ_{lat} is obtained by subtracting κ_{ele} from κ_{total} before intrinsic excitation, shown in the Figure

3b. It is obvious that the pristine $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ has a low κ_{lat} , room-temperature value only around $0.66 \text{ W m}^{-1} \text{ K}^{-1}$, which is mainly due to the intrinsic lattice dynamics properties that will be thoroughly discussed latter. Upon Yb doping, room-temperature κ_{lat} decreases to $0.6 \text{ W m}^{-1} \text{ K}^{-1}$ for $\text{Mg}_{0.995}\text{Yb}_{0.005}\text{Ag}_{0.97}\text{Sb}_{0.99}$. Generally, materials with low κ_{lat} possess short phonon mean free path (MFP) l that can be evaluated by the following equation:

$$k_{lat} = \frac{1}{3} C_v v_a l \quad (2)$$

where C_v is the heat capacity, v_a is the average sound velocity $\sim 1276 \text{ m s}^{-1}$. The obtained phonon mean free path l of nanostructured $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ is around 0.53 nm , even less than that of SnSe (0.84 nm) [35]. This points out that phonon scattering by point defect is an effective strategy to further reduce the κ_{lat} . Yb doping will generate strong phonon scattering due to the large mass and size difference (Mg: 24.3 g mol^{-1} and 66 pm vs. Yb: 173.1 g mol^{-1} and 93 pm) causing surrounding strain field fluctuation based on the Rayleigh-type scattering mechanism [57]. Since $\text{Mg}_{0.995}\text{Yb}_{0.005}\text{Ag}_{0.97}\text{Sb}_{0.99}$ has the comparable lattice thermal conductivity with that of $\text{Mg}_{0.99}\text{Li}_{0.01}\text{Ag}_{0.97}\text{Sb}_{0.99}$ [43], it is reasonable to say that Yb doping is more effective in suppressing lattice thermal conductivity. Due to that Li (6.94 g mol^{-1} , 60 pm) has a smaller difference between atomic mass and ionic radius with Mg, Li has a larger solid solubility than Yb on the Mg site, which could result in the higher carrier concentration and power factor in comparison with Yb doping. However, Yb doping has more obvious effect in suppressing lattice thermal conductivity. The modified Debye-Callaway model is employed to semi-qualitatively compare the contribution of site disorder in the lattice [43, 58, 59], presented in the supporting information. The calculated results, given as dash lines in Figure 3b, show good agreement with experimental values before the onset of bipolar effect. Table 2 shows the calculation parameters, where parameter A corresponds to the strength of phonon scattering of point defects. The gradually increased parameter A indicates stronger and stronger

point-defect scattering upon Yb doping, consistent with previous analysis.

Exploring the origin of low lattice thermal conductivity

Since low κ_{lat} in solid has close relation with the lattice dynamics properties, phonon and Grüneisen dispersions along the high symmetry directions within the Brillouin zone are calculated using DFT phonon calculations within the quasi-harmonic approximation (Figure 4) [49-52]. Because of the large number of atoms (24 atoms) in the primitive cell of MgAgSb, there will be 3 acoustic branches and 69 optical branches. It is generally assumed that optical branches have small or negligible contributions to κ_{lat} in bulk materials mainly due to their low phonon velocities [60], which is beneficial to achieve low κ_{lat} [61]. Figure 4a shows one extremely anomalous longitudinal optical (LO) branch (orange). The boundary frequency of LO branch at the Γ point is extremely low ($\sim 17 \text{ cm}^{-1}$), even smaller than that of SnSe ($\sim 20 \text{ cm}^{-1}$) and PbTe ($\sim 32 \text{ cm}^{-1}$) [33, 37], indicating the soft nature of this LO branch. It has a large slope of the phonon dispersion around the Γ point that means a high phonon velocity and thus may partially participate in heat transporting, similar with that of PbTe [37, 62]. In addition, there is a strong volume dependence of the LO phonon frequency around the zone center that implies the strong anharmonic behavior of this LO branch. More importantly, the observed “avoided crossing” interaction between LO and longitudinal acoustic (LA) branches leads to the abruptly changed slope away from the center of Brillouin zone [36, 63], especially for LA branch along the Γ -Y direction where the acoustic character is maintained only within a small region of wave vectors with $|q| < 0.2 \text{ \AA}^{-1}$. However, it is rather difficult to qualitatively calculate the contribution of this LO branch, due to this extremely time-consuming feature, for example using ShengBTE to solve the Boltzmann Transport Theory [64]. For those significant heat transport acoustic phonon branches, the saturated frequencies merely reach around $20\text{-}35 \text{ cm}^{-1}$, which are even lower than

those of SnSe and PbTe [33, 37]. Hence, those anomalously low acoustic-mode frequencies means the intrinsically weak chemical bonding in MgAgSb compound, which could be directly manifested by the low Young's modulus of MgAgSb (55.0 GPa) [65]. The weak chemical bonding results in the phonon modes softening that finally mitigates phonon propagation. The weak chemical bonding is possibly related with Ag-Sb bonding, where Ag has an abnormal occupied site, which leads to the low defect formation energy of Ag vacancy in α -MgAgSb revealed by first-principles calculation [44].

To quantitatively elucidate the strength of anharmonicity of MgAgSb, the dispersion of the Grüneisen parameters for all acoustic branches and special LO branch are calculated. According to the formula proposed by Leibfried and Schlömann [66], the lattice thermal conductivity κ_{lat} is given by:

$$\kappa_{lat} = B \frac{MV^{1/3}\theta_D^3}{\gamma^2 T} \quad (3)$$

where B a numerical coefficient, M the average atomic mass, V the average atomic volume and θ_D the Debye temperature. As known, anharmonic bonding could strengthen phonon-phonon interaction and thus significantly suppress the lattice thermal conductivity [30]. As shown in Figure 4b, the majority of Grüneisen parameters along the high symmetry directions are positive throughout the Brillouin zone. Both LA and LO branches possess higher Grüneisen parameters, compared with those of two TA branches. Typically, the maximum Grüneisen parameters of LO branch around Γ point is extraordinarily high ~ 5.8 . The average corresponding Grüneisen parameters ($\bar{\gamma}$) of three acoustic branches are calculated based on $\bar{\gamma} = \sqrt{(\gamma_i)^2}$, shown in Table 2. The $\bar{\gamma}$ of LA branch is about 1.9, surpassing that of TA and TA' branches by a factor of at least 2. The anharmonic behavior may be related with the distorted Mg-Sb rocksalt lattice [48]. Besides, we can clearly observe the sudden change of Grüneisen parameters around Γ point for LA and LO branches,

originated from the “avoided-crossing” interaction [36, 63].

Based on the phonon dispersion, the Debye temperatures and phonon velocities of three acoustic phonon branches can be also obtained, shown in Table 3. Those three acoustic branches (TA, TA', and LA) have an extremely low Debye temperature (39 K, 44 K, 49 K), even lower than that of SnSe (62 K, 72 K, 62 K) [33]. Since there is a close relationship between the stiffness and Debye temperature, the low Debye temperatures of those three acoustic branches means the weak chemical bonding. Similarly, the low phonon velocities could demonstrate this conclusion as well. Due to that our DFT phonon calculation is based on the crystal structure of undoped MgAgSb, it could not give any information about the effect of Yb doping on phonon transport. In addition, it is impossible to perform the phonon calculation about Yb doping, because the supercell would become extremely large because of the very low Yb doping content in our work. Except for this unique lattice dynamic properties of pristine MgAgSb, nanostructuring has been demonstrated as an effective strategy to further suppress κ_{lat} . As reported by Ying *et al.* [45], pristine MgAgSb with coarse grains has a room-temperature κ_{lat} around $0.82 \text{ W m}^{-1} \text{ K}^{-1}$, 24% higher than that of nanostructured MgAgSb ($0.66 \text{ W m}^{-1} \text{ K}^{-1}$). This suppression could be ascribed to the strong phonon scattering through high density of boundaries and defects mainly resulted from long-time high energy ball milling process [43]. Here, we perform an investigation on the microstructure of $\text{Mg}_{0.995}\text{Yb}_{0.005}\text{Ag}_{0.97}\text{Sb}_{0.99}$ by means of scanning electron microscope (SEM) and transmission electron microscope (TEM), given in the Figure 5. The results clearly show that nanostructured MgAgSb has an average grain size around 150 nm as well as high density of stacking faults and dislocations, which could scatter medium and long-wavelength phonons.

4. Conclusion

In summary, DFT calculations demonstrate that the unique lattice dynamic properties

contribute to the low κ_{lat} of MgAgSb, including a large number of optical branches, weak chemical bonding, strong anharmonic coupling between LO and LA branches, and high anharmonic behavior of LO branch. In addition, nanostructuring has an effect in decreasing the lattice thermal conductivity due to the high density of boundaries and defects. Furthermore, Yb doping continues to obviously decrease the κ_{lat} because of the strong point-defect phonon scattering. Simultaneously, tuning the carrier concentration via Yb doping also leads to enhanced PF around 20%. As a result, a peak $ZT \sim 1.4$ and average $ZT \sim 1.2$ have been achieved, which highlights the promising prospect of Yb doped MgAgSb materials for low temperature power generation.

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Figure Caption

Figure 1. Synergistic strategies to enhance the thermoelectric performance via Yb doping. (a) A schematic diagram about the effect of tuning Fermi level, (b) schematic illustration of the microscopic origin of low lattice thermal conductivity for MgAgSb, (c) a schematic diagram about point-defect phonon scattering, (d) ZT dependence of temperature, (e) comparison of average ZT and calculated efficiency for undoped, Li doped [43], and Yb doped MgAgSb.

Figure 2. Electrical transport properties of $\text{Mg}_{1-x}\text{Yb}_x\text{Ag}_{0.97}\text{Sb}_{0.99}$ ($x = 0, 0.25\%, 0.5\%$ and 1%). (a) Doping concentration dependent carrier concentration and mobility, (b) temperature dependent electrical resistivity, (c) temperature dependent Seebeck coefficient (d) carrier concentration dependent Seebeck coefficient at room temperature, (e) temperature dependent power factor, (f) carrier concentration dependent power factor. The solid line in (d) and (f) are calculated based on single parabolic band model and acoustic phonon scattering mechanism. The filled diamond, unfilled square, and unfilled circle represent the measurement data for Yb doping, Li doping [43], and tuning of the Sb content [42], respectively.

Figure 3. (a) Total thermal conductivity κ_{total} and (b) lattice thermal conductivity κ_{lat} dependence of temperature for $\text{Mg}_{1-x}\text{Yb}_x\text{Ag}_{0.97}\text{Sb}_{0.99}$ ($x = 0, 0.25\%, 0.5\%$ and 1%).

Figure 4. (a) Phonon dispersions and (b) the corresponding Grüneisen dispersions of MgAgSb. The thick lines and thin lines in the top panel represent the phonon dispersions at the DFT equilibrium volume and the expansion cell (+4%), respectively. The red, green, blue and orange lines highlight TA, TA', LA, and LO phonon branches, respectively. The inset is the first Brillouin zones of MgAgSb with high-symmetry points (red points) that are considered in our current calculations.

Figure 4. Typical microstructures for $\text{Mg}_{0.995}\text{Yb}_{0.005}\text{Ag}_{0.97}\text{Sb}_{0.99}$ sample. (a) SEM

image, (b) high magnification TEM image showing high density of stacking faults. The inset corresponds to the fast Fourier transformation (FFT) image along the [001] direction, (c) corresponding inverse FFT (IFFT) image of stacking fault, (d) corresponding IFFT image of high density of dislocations along (040) plane. The inset means the geometric phase analysis (GPA) image of dislocation core.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Table 1. Electric transport properties of $\text{Mg}_{1-x}\text{Yb}_x\text{Ag}_{0.97}\text{Sb}_{0.99}$ ($x = 0, 0.25\%, 0.5\%$ and 1%)

Composition	n_H	μ_H	m^*	η
	(10^{19} cm^{-3})	($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	(m_e)	
$\text{MgAg}_{0.97}\text{Sb}_{0.99}$	2.7	64.9	2.35	-0.75
$\text{Mg}_{0.9975}\text{Yb}_{0.0025}\text{Ag}_{0.97}\text{Sb}_{0.99}$	3.9	64.0	2.33	-0.31
$\text{Mg}_{0.995}\text{Yb}_{0.005}\text{Ag}_{0.97}\text{Sb}_{0.99}$	4.6	63.1	2.39	-0.18
$\text{Mg}_{0.99}\text{Yb}_{0.01}\text{Ag}_{0.97}\text{Sb}_{0.99}$	4.7	60.1	2.37	-0.13

Table 2. Fitting parameters for lattice thermal conductivity κ_{lat} in the Debye-Callaway model

Composition	C (10^{-18} s K $^{-1}$)	A (10^{-40} s 3)	L_{eff} (nm)
MgAg _{0.97} Sb _{0.99}	8.98	1.99	100
Mg _{0.9975} Yb _{0.0025} Ag _{0.97} Sb _{0.99}	8.98	2.38	100
Mg _{0.995} Yb _{0.005} Ag _{0.97} Sb _{0.99}	8.98	2.43	100

Table 3. Average Debye temperature, phonon velocity, and Grüneisen parameter of longitudinal (LA) and transverse (TA/TA') phonons in MgAgSb calculated from the phonon dispersion

Phonon type	Debye Temperature (K)	Phonon velocity (m s ⁻¹)	Grüneisen parameter
TA	39	1488	0.8
TA'	44	1815	0.6
LA	49	3005	1.9

Graphical abstract

The microscopic origin of intrinsically low κ_{lat} of α -MgAgSb in the lattice dynamics was thoroughly revealed using density functional theory (DFT) calculations. More importantly, we achieve a peak $ZT \sim 1.4$ and average $ZT \sim 1.2$ via Yb doping.