The influence of doping sites on achieving higher thermoelectric performance for nanostructured α -MgAgSb

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Abstract

P-type nanostructured α -MgAgSb holds a great promise for low temperature waste heat energy harvesting. In this work, we first investigate the effect of doping site on the carrier transport behavior of nanostructured α -MgAgSb. Ca doping on Mg site is rationally chosen to optimize carrier concentration and thus enhance power factor. It is demonstrated that Ca doping on the Mg site leads to higher mobility and power factor in comparison with doping on Sb site, originated from the less introduced perturbation to valence band upon doping. As the result of doping-site effect, a peak ZT of ~ 1.3 at ~ 550 K and average ZT of ~ 1.1 between 300 K and 550 K are achieved by Ca doping on the Mg site. Our current work only points out that doping on the site that has less influence on the charge-conducting band should be a critical doping principle in thermoelectric materials field, but also highlights the promising prospect of nanostructured α -MgAgSb for low temperature power generation.

1. Introduction

Thermoelectric materials have received extensive interests for clean energy harvesting [1-5]. However, this promising prospect is hampered by the relatively low conversion efficiency of thermoelectric devices, which is primarily determined by the materials' thermoelectric figure of merit, $ZT = S^2 \sigma T / (\kappa_{lat} + \kappa_{ele})$, where $S, \sigma, T, \kappa_{lat}$, and κ_{ele} are the Seebeck coefficient, electrical conductivity, absolute temperature, lattice thermal conductivity, and electronic thermal conductivity, respectively. Due to the inherent trade-off between σ and S via carrier concentration [1], tuning carrier concentration via effective doping has long been regarded as the most straightforward approach to enhance power factor ($PF = \sigma S^2$) for achieving high output power density [6-9], especially for heavy band system that needs a high carrier concentration to reach [10, 11]. Generally different dopants at different lattice sites are considered equivalent if a comparable carrier concentration is finally achieved in the rigid band approximation [1, 6, 8], because the corresponding ionized impurity scattering for

carriers merely depends on dielectric constant, doping concentration and carrier concentration for a specific compound [12, 13]. In fact, valence band is normally dominated by anion atomic orbitals while conduction band by cation orbitals regarding an ionic lattice, first predicted by Ioffe [14]. Therefore, doping on anion or cation sites would introduce the perturbation to valence or conduction band that may affect the corresponding carrier mobility of hole or electron [14], respectively. However, the doping effect on which site has long been disregarded even though it may have a significant influence on the carrier transport behavior in heavily doped semiconductors. For instance, n-type $\text{PbTe}_{1-x}\text{Se}_x$ compounds have a higher mobility than the p-type counterparts owing to the corresponding perturbation to valence band with Se alloying on Te site [14].

For low temperature power generation applications, p-type BiSbTe alloy has always been the only promising material since 1950s [16-19]. Recently, mechanically robust nanostructured α -MgAgSb based alloys with superior thermoelectric performance was successfully synthesized by a simple two-steps ball milling and quick hot press method [20-27]. α -MgAgSb has only one heavy valence band located at the X-point in the Brillouin zone [28-30], which requires high carrier concentration to achieve good thermoelectric properties [25]. Thus, previous work mainly focused on tuning carrier concentration by doping on the Mg or Ag site [20-22, 25]. So far there is no relevant report about the doping on the Sb site in the nanostructured α -MgAgSb, which offers a chance to compare the role of doping at cation and anion sites on the carrier transport behavior.

Herein, Ca doping on the Mg site was first chosen to optimize the carrier concentration and thus enhance the power factor. Then, we studied the electrical transport properties of doping on the Sb site, including As, Bi, Sn and Pb. Compared with Ca and Li doping on the Mg site, it can be clearly observed that doping on Sb site gave rise to much lower mobility and power factor due to the influence on the valence band. Finally, we have achieved a peak ZT of ~ 1.3 at ~ 550 K and an average ZT of ~ 1.1 between 300 K and 550 K upon Ca doping on the Mg site. Our work sheds

new light on the carrier transport behavior of nanostructured α -MgAgSb, which could help and contribute to realizing the rational doping in other thermoelectric systems.

2. Experimental section

Synthesis. All the chemicals were purchased from Alfa Aesar and then weighed according to the nominal composition $\text{Mg}_{1-x}\text{Ca}_x\text{Ag}_{0.97}\text{Sb}_{0.99}$ samples ($x = 0, 0.0025, 0.005, \text{ and } 0.01$). The synthesis process was totally identical with our previous reports [20-25].

X-ray diffraction. X-ray diffraction (XRD) analysis was performed using a PANalytical multipurpose diffractometer with an X'celerator detector (PANalytical X'Pert Pro). The phases were analyzed with JADE 6.0 software. The microstructure was observed by a scanning electron microscope (SEM, JEOL 6330F) and a high resolution transmission electron microscope (HRTEM, JEOL 2100F). Thin TEM specimens were prepared by conventional methods, including cutting, grinding, dimpling, and Ar-ion milling from the bottom and top surfaces of the discs with a liquid nitrogen cooling stage operated at 2.5 keV and an incidence angle of 3° using a Gatan PIPS 695. Finally, Ar-ion milling with lower-voltage and incidence angle was continually performed for 1 hour to clean out the amorphous layer on the surface.

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), shown in the Figure S1. 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. The electronic structure of α -MgAgSb was calculated by the density-functional theory (DFT) as implemented in the open-source Quantum Espresso program package[31]. We used the projected augment wave (PAW) potentials, provided by the standard solid-state pseudo potential library. The exchange-correlation function was taken within the generalized gradient approximation (GGA) in the parameterization of Perdew–Burke–Ernzerhof (PBE)[32]. A plane-wave basis was adopted for the expansion of the valence electron wavefunctions with kinetic-energy cutoffs of 50 Ry. For ground state calculations we used an $8 \times 8 \times 8$ Monkhorst–Pack k-point mesh. In addition, the spin–orbit couplings were not included in the current calculations.

3. Results

Figure 1a shows the X-ray diffraction (XRD) patterns of $\text{Mg}_{1-x}\text{Ca}_x\text{Ag}_{0.97}\text{Sb}_{0.99}$ samples ($x = 0, 0.0025, 0.005, \text{ and } 0.01$). The diffraction peaks of all the samples exhibit good match with the α -MgAgSb (space group $I\bar{4}C2$) and no impurity phases could be observed within the detection limit of the XRD spectrometer[33]. Besides, the XRD peaks shift to low angle with increasing Ca alloying content (Figure 1b), which implies that Ca may totally enter into Mg site in the MgAgSb lattice.

Figure 2a reveals that the typical grain size, ranging from 100 to 200 nm, is significantly smaller, compared with that of the report by Ying *et al*[28]. The ubiquitous *in-situ* nanoinclusions around 10 nm can be observed in Figure 2b, similar to the nanostructured BiSbTe[17]. Those plentiful grain boundaries and interfaces with different orientation and atomic spacing increase the phonons scattering with medium-to-long mean free path[34, 35].

Besides nanograins and nanoinclusions, two types of nanotwins, lamellar and

spearhead shaped, can be clearly observed in Figure 3a and 3b, respectively. The typical width of nanotwins is on the order of several nanometers, much smaller than that in nanotwinned copper fabricated by pulsed electrodeposition[36]. The inset in Figure 3a presents the corresponding fast Fourier transformation (FFT) pattern along the [011] zone axis direction, which indicates a typical type-I twin relationship $(4\bar{1}\bar{1})_M$ and $(4\bar{1}\bar{1})_T$ among the lamellae that are symmetrical to each other with respect to the $(2\bar{3}3)$ plane. The presence of the tapering twins is generally as a consequence of decreasing boundary area and thus lowering the boundary energy[37]. Those clean and coherent nanotwin boundaries act as additional phonon scattering centers without degrading the electrical transport properties[34]. Furthermore, the nanotwin boundaries could be able to selectively scatter low-energy carriers by potential barrier scattering, therefore enhancing the Seebeck coefficient or suppressing the bipolar effect[2, 38]. That is why nanostructured MgAgSb has a comparable electrical resistivity but a higher Seebeck coefficient in comparison with coarse MgAgSb[28]. The mechanism of nanotwin formation in nanostructured MgAgSb may be related to the high energy ball milling process that normally generates substantially higher angle micro and nano-sized grain boundaries as well as deformation and stress[39]. Since the required formation energy for twin boundary is much lower than the conventional high angle grain boundary, the presence of twin will thus reduce the total interfacial energy under a thermodynamic situation[37]. In addition, compounds with phase transformation behavior prefer to form the twin structure, as observed in a variety of alloys[40, 41].

Figure 4 presents the temperature dependent thermoelectric properties of $\text{Mg}_{1-x}\text{Ca}_x\text{Ag}_{0.97}\text{Sb}_{0.99}$ samples. Electrical resistivity ρ monotonically decreases with increasing Ca doping concentration at the whole measured temperature range (Figure 4a). Specifically, room-temperature ρ of $\text{Mg}_{0.99}\text{Ca}_{0.01}\text{Ag}_{0.97}\text{Sb}_{0.99}$ ($\sim 1.8 \times 10^{-5} \Omega \text{ m}$) is about half of that of the undoped $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ ($\sim 3.6 \times 10^{-5} \Omega \text{ m}$). Since CaAgSb compound exhibits a typical semi-metal behavior and its room-temperature ρ is around

$2.5 \times 10^{-6} \Omega \cdot \text{m}$ [42], ρ of Ca doped MgAgSb samples will be lower than pristine MgAgSb when Ca alloying on the Mg site. Due to the increased carrier concentrations shown in Table 1, S decreases somewhat upon doping (Figure 4b), in accordance with the tendency of ρ . In addition, MgAgSb based materials exhibit peak values of S below 400 K owing to the very small band gap or semi-metal characteristic [26, 28-30, 43]. This is related with the onset of bipolar effect, because minority carriers, namely electron in p-type MgAgSb, are thermally excited across the band gap and lead to the reduced S . Power factor ($PF = S^2 \sigma$) calculated from the measured electrical resistivity and Seebeck coefficient is plotted in Figure 4c. Compared with the pristine $\text{MgAg}_{0.97}\text{Sb}_{0.99}$, PF is enhanced around 20% upon Ca doping due to the optimized carrier concentration. Figure 4d shows the total thermal conductivity κ_{total} first decreases slightly because of Umklapp scattering and then increases significantly due to the bipolar effect at higher temperature. Since electronic thermal conductivity κ_{ele} can be calculated from the Wiedemann-Franz relationship, $\kappa_{\text{ele}} = L \sigma T$, where L , Lorenz number, is calculated assuming the single parabolic band model based on Equation (1-4) [44, 45]:

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

$$F_n(\eta) = \int_0^\infty \frac{\chi^n}{1 + e^{\chi-\eta}} d\chi \quad (2)$$

$$\eta = \frac{E_f}{k_B T} \quad (3)$$

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

where k_B is the Boltzmann constant, e is the electron charge, η is the reduced Fermi energy, $F_n(\eta)$ is the n^{th} order Fermi integral, r is the scattering factor. As acoustic phonon scattering is the main scattering mechanism for most thermoelectric materials above room temperature [1, 6], the scattering factor r could be considered as -1/2 in

calculation. Lattice thermal conductivity κ_{lat} is obtained by subtracting κ_{ele} from κ_{total} before intrinsic excitation, shown in Figure 4e. Apparently, Ca doping leads to the gradual suppression of low-temperature κ_{lat} , which is related with the corresponding point defect scattering between host atom (Mg) and alloying atom (Ca) because of mass fluctuation and surrounding strain field fluctuation. Due to the larger increase in PF than the smaller increase in total thermal conductivity, ZT has been improved at the whole measured temperature range upon Ca doping (Figure 4f). The highest peak ZT and average ZT , obtained in $Mg_{0.995}Ca_{0.005}Ag_{0.97}Sb_{0.99}$, reaches ~ 1.3 and ~ 1.1 , respectively, even higher than those of $Mg_{0.99}Li_{0.01}Ag_{0.97}Sb_{0.99}$ (~ 1.2 , ~ 1.0) [25].

Figure 5 shows the temperature dependent electrical transport properties for $MgAg_{0.97}Sb_{0.99-x}M_x$ ($M=As, Bi, Sn$ and Pb) ($x = 0, 0.005$ and 0.01). Table 2 shows their corresponding carrier concentration and mobility. As shown in the Figure 5a, with increasing doping concentration, As doping obviously decreases the ρ while Bi doping slightly increases the ρ . This distinct behavior may be related with the change of band gap or the difference of electronegativity upon isovalent doping [46-49], which need further experiments and theoretical calculations to support this speculation that is beyond our scope of present work. As expected, As doping leads to the substantial reduction of S because of the increased carrier concentration (Figure 5b). In contrast, Bi doping does not change S too much (Figure 5b). Finally, PF increases moderately upon As doping, but Bi doping lowers the PF (Figure 5c).

Due to the acceptor characteristic of Sn or Pb, ρ decreases somewhat shown in the Figure 5d. It should be mentioned that Sn doping leads to a much lower ρ compared with that of Pb doping. The relatively high doping effectiveness of Sn doping is possibly ascribed to the very small difference of atom mass and radius between Sn and Sb. The increased carrier concentration leads to the decreased S upon Sn or Pb doping (Figure 5e). As a result, Figure 5f shows that PF of doped samples are almost same with pristine sample although the highest carrier concentration of Sn doping could reach $5.0 \times 10^{19} \text{ cm}^{-3}$. Given the above results, it is quite clear that doping on Sb site gives rise to the lower PF despite the increased carrier

concentration, compared with that of Ca doping on Mg site.

4. Discussion

Figure 6 shows the calculated partial density of state (DOS) of α -MgAgSb. The calculated band structure and total DOS have been given somewhere else [27]. It is obvious that p orbital of Sb exhibits a significantly higher DOS than other atom orbital near the Fermi level, consistent with the recent reports [28, 43, 50]. This indicates that the high total DOS of heavy valence band is predominantly decided by the p orbital of Sb. In general, valence band is dominated by anion atomic orbitals while conduction band by cation orbitals regarding an ionic lattice [14], in perfect accordance with the present calculation results.

Historically, different dopants at different sites are considered equivalent when reaching the same carrier concentration in the rigid band approximation. However, it may have a significant influence on the carrier transport behavior due to the perturbation to the corresponding band [14]. For example, anion dopants normally lead to higher mobility than cation dopants at high carrier concentration in n-type PbSe system [15]. In order to investigate this often-overlooked effect, taking MgAgSb as a sample, we compare the electrical transport properties of Ca doping and Li doping at Mg site with dopants on the Sb site, including As, Bi, Sn and Pb (Figure 7).

The dashed lines in the Figure 7 are calculated based on Equations (1-3, 5, 6) assuming the single parabolic band model [44].

$$n_H = \frac{(2m^*k_B T)^{3/2}}{3\pi^2\hbar^3} \frac{(r+3/2)^2 F_{(r+1/2)}^2(\eta)}{(2r+3/2)F_{(2r+1/2)}(\eta)} \quad (5)$$

$$\mu_H = \left[\frac{e\pi\hbar^4}{\sqrt{2}(k_B T)^{3/2}} \frac{dv_L^2}{E_{def}^2(m^*)^{5/2}} \frac{(2r+3/2)F_{(2r+1/2)}(\eta)}{(r+3/2)^2 F_{(r+1/2)}(\eta)} \right] \quad (6)$$

where m^* is the total density of state (DOS) effective mass, d is density $\sim 6.2 \text{ g cm}^{-3}$, v_L is the longitudinal velocity of sound $\sim 3708 \text{ m s}^{-1}$ [28], E_{def} is deformation potential coefficient $\sim 6.3 \text{ eV}$ [24]. As shown in Figure 7a, the mobility reduction of doping on

Mg site matches well with the theoretical model. However, dopants on Sb site lead to a lower carrier mobility at the same carrier concentration. As known, acoustic phonon scattering is generally assumed to be the dominating origin for carrier transport in semiconductor, whose strength is decided by the intrinsic material parameters such as material density, longitudinal velocity of sound, effective mass, and deformation potential coefficient [6, 51]. Given that the present doping concentration would not result in a substantial influence on those parameters, additional carrier scattering center must be considered for the mobility difference. Ionized impurity scattering merely depends on dielectric constant, doping concentration and carrier concentration for a specific compound, which is typically independent of doping-site. Because doping on the Sb site leads to a reasonable change of carrier concentration, dopants may totally enter into the Sb site considering the present ultralow doping concentration. Therefore, the only remaining factor is the introduced perturbation to the valence or conduction band upon doping, as previously discussed. Since high total DOS of heavy valence band is predominantly decided by the p orbital of Sb, doping on the Sb site would introduce the perturbation to the valence band while doping on the Mg site have less extra influence on the valence band. Thus, doping on Sb site may deteriorate the corresponding carrier mobility, eventually much lower than doping on the Mg site.

Due to the different mobility upon doping, Figure 7b shows that lower ρ can be obtained by rational doping of Ca on the Mg site. Figure 7c shows that all the experimental data fall nearly on the calculated Pisarenko plot with $m^* = 2.4 m_e$, which clearly illustrates that band structure is almost unchanged and irrelevant with doping-site. Finally, carrier concentration dependent PF of doping on the Mg site is basically consistent with the theoretical model, which is obviously higher than that of doping on the Sb site, especially in the heavily doped range (Figure 7d). Therefore, in order to achieve optimum mobility and PF , doping on the right site that has less influence on the charge-conducting bands should be a critical doping principle.

5. Conclusion

In summary, we compare the electrical transport properties of dopants on different sites in nanostructured α -MgAgSb. Thenoticeably lower carrier mobility and power factor of doping on Sb site is due to the introduced perturbation to valence band. In contrast, power factor could be enhanced around 20% via Ca doping on Mg site that is basically consistent with the theoretical model. As a result, a peak ZT of ~ 1.3 at 550 K and average ZT of ~ 1.1 between 300 K and 550 K are realized byrationally choosing Ca doping. Our work not only elucidates the critical role of doping site on the electrical transport behavior of nanostructured α -MgAgSb, but also may be applicable to other thermoelectric systems and help optimize the corresponding properties.

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Figure Caption

- Figure 1.** (a) XRD patterns and (b) enlarged XRD patterns from 36° to 44° for $\text{Mg}_{1-x}\text{Ca}_x\text{Ag}_{0.97}\text{Sb}_{0.99}$ samples ($x = 0, 0.0025, 0.005, \text{ and } 0.01$).
- Figure 2.** (a) Typical SEM image and (b) medium magnification TEM image for $\text{Mg}_{0.995}\text{Ca}_{0.005}\text{Ag}_{0.97}\text{Sb}_{0.99}$ sample.
- Figure 3.** High magnification TEM image for $\text{Mg}_{0.995}\text{Ca}_{0.005}\text{Ag}_{0.97}\text{Sb}_{0.99}$ sample. (a) Lamellar type-I $(41\bar{1})$ nanotwins and (b) spearhead shaped type-I $(2\bar{3}3)$ nanotwins; The inset corresponds the fast Fourier transformation (FFT) image along the C zone $[011]$ axis direction.
- Figure 4.** Temperature dependent thermoelectric properties of $\text{Mg}_{1-x}\text{Ca}_x\text{Ag}_{0.97}\text{Sb}_{0.99}$ samples ($x = 0, 0.0025, 0.005 \text{ and } 0.01$). (a) electrical resistivity, (b) Seebeck coefficient, (c) power factor, (d) total thermal conductivity (e) lattice thermal conductivity, and (f) ZT .
- Figure 5.** Temperature dependent electrical transport properties for $\text{MgAg}_{0.97}\text{Sb}_{0.99-x}\text{M}_x$ samples ($\text{M}=\text{As, Bi, Sn and Pb}$) ($x = 0, 0.005 \text{ and } 0.01$). (a) Electrical resistivity, (b) Seebeck coefficient and (c) power factor for As and Bi doping. (d) Electrical resistivity, (e) Seebeck coefficient and (f) power factor for Sn and Pb doping.
- Figure 6.** The calculated partial DOS of $\alpha\text{-MgAgSb}$ using DFT and GGA-PBE [31]. The vertical line denotes the Fermi energy.
- Figure 7.** Carrier concentration dependent electrical transport properties of MgAgSb based materials, including dopants Li [24], Ca, As, Bi, Sn and Pb. (a) Mobility, (b) electrical resistivity, (c) Seebeck coefficient, and (d) power factor. The dashed lines are calculated based on single parabolic band model with acoustic phonon scattering mechanism [44].

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Table 1 Electrical transport properties for $\text{Mg}_{1-x}\text{Ca}_x\text{Ag}_{0.97}\text{Sb}_{0.99}$ samples ($x=0, 0.0025, 0.005$ and 0.01)

Composition	n_H (10^{19} cm^{-3})	μ_H ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	m^* (m_e)	η
$\text{MgAg}_{0.97}\text{Sb}_{0.99}$	2.7	64.9	2.35	-0.75
$\text{Mg}_{0.9975}\text{Ca}_{0.0025}\text{Ag}_{0.97}\text{Sb}_{0.99}$	3.1	64.3	2.38	-0.61
$\text{Mg}_{0.995}\text{Ca}_{0.005}\text{Ag}_{0.97}\text{Sb}_{0.99}$	4.1	63.2	2.39	-0.18
$\text{Mg}_{0.99}\text{Ca}_{0.01}\text{Ag}_{0.97}\text{Sb}_{0.99}$	5.7	60.8	2.38	0.09

Table 2 Carrier concentration and mobility for $\text{MgAg}_{0.97}\text{Sb}_{0.99-x}\text{M}_x$ samples (M=As, Bi, Sn and Pb) ($x=0.005$ and 0.01)

Composition	n_H (10^{19} cm^{-3})	μ_H ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)
$\text{MgAg}_{0.97}\text{Sb}_{0.985}\text{As}_{0.005}$	6.0	50.3
$\text{MgAg}_{0.97}\text{Sb}_{0.98}\text{As}_{0.01}$	8.1	45.1
$\text{MgAg}_{0.97}\text{Sb}_{0.985}\text{Bi}_{0.005}$	2.9	56.6
$\text{MgAg}_{0.97}\text{Sb}_{0.98}\text{Bi}_{0.01}$	3.1	49.6
$\text{MgAg}_{0.97}\text{Sb}_{0.985}\text{Sn}_{0.005}$	3.7	56.4
$\text{MgAg}_{0.97}\text{Sb}_{0.985}\text{Sn}_{0.01}$	5.0	48.4
$\text{MgAg}_{0.97}\text{Sb}_{0.985}\text{Pb}_{0.005}$	3.2	55.6
$\text{MgAg}_{0.97}\text{Sb}_{0.985}\text{Pb}_{0.01}$	3.5	52.9