Effects of Antimony content in $\text{MgAg}_{0.97}\text{Sb}_x$ on output power and energy conversion efficiency

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Abstract

We report the effect of Sb content in $\text{MgAg}_{0.97}\text{Sb}_x$ ($x = 0.99, 0.9925, 0.995$, and 1.00) on output power and leg efficiency. Due to the doubling of carrier concentration with increasing the Sb content, power factor is enhanced around 20% over the whole

temperature range. Simultaneously, the average thermoelectric figure of merit (ZT) is even enhanced a little in spite of the increased corresponding thermal conductivity. We further calculated the engineering power factor $(PF)_{eng}$, output power, engineering figure of merit $(ZT)_{eng}$ and leg efficiency by taking into account of the Thomson effect. Assuming $T_c = 300$ K and $T_h = 548$ K, leg length ~ 2 mm, an output power of ~ 1.77 W cm^{-2} and leg efficiency η of $\sim 10.1\%$ are finally obtained for the optimized composition $\text{MgAg}_{0.97}\text{Sb}_{0.995}$.

Keywords: MgAgSb ; $(PF)_{eng}$; $(ZT)_{eng}$; output power; leg efficiency

1. Introduction

Thermoelectric materials, capable to directly and reversibly convert heat energy into electrical power and provide an alternative for power generation and refrigeration, have received wide interest in the past decades. The energy conversion efficiency of thermoelectric materials is determined by the Carnot efficiency and the average dimensionless thermoelectric figure of merit $(ZT)_{ave}$ assuming all properties are constant over the whole operating temperature range [1]:

$$\eta = \frac{T_h - T_c}{T_h} \left(\frac{\sqrt{1 + (ZT)_{ave}} - 1}{\sqrt{1 + (ZT)_{ave}} + T_c / T_h} \right) \quad (1)$$

where $ZT = S^2 \sigma T / \kappa$ and S , σ , κ and T are the Seebeck coefficient, electrical conductivity, thermal conductivity, and the absolute temperature, respectively. However, for over half a century, pursuing high ZT was mainly focused on peak ZT in the thermoelectric fields. ZT above unity is regarded as a benchmark for advanced

bulk thermoelectric materials [2, 3]. Due to extensive efforts on synthesizing and measurement methods coupled with new concepts and strategies [4-6], a series of record-breaking thermoelectric performance have been reported for traditional and new materials, including BiSbTe [7, 8], PbTe [9, 10], SiGe [11, 12], CoSb₃ [13], Yb₁₄MnSb₁₁ [14], SnSe [15], *etc.*, even though some of the reports have not been confirmed yet.

For near room temperature application on waste heat recovery and regeneration, Bi₂Te₃ alloying with Se or Sb has been intensively investigated as the best n or p-type thermoelectric system since 1950s [7, 8, 16]. Recently, bulk nanostructuring has been proven to be an effective approach to lower the lattice thermal conductivity and thereby enhances the thermoelectric performance without deteriorating the electrical transport properties [17, 18]. Typically, the peak ZT for both n-type and p-type system could surpass the benchmark ~ 1 [7, 8, 16]. Nevertheless, due to the fact that Tellurium (Te) is a rare element, earth abundance around 0.001 ppm, only about one-quarter of gold (Au) ~ 0.004 ppm [19], new promising alternatives without Te should be studied and optimized for potential large-scale applications.

Recently, MgAgSb-based materials have been developed as a promising p-type candidate in low temperature applications [20-25]. Kirkham *et al.* first reported the crystal structures and thermoelectric performance from room temperature to 693 K of MgAgSb [20]. MgAgSb has complicated phase transitions from α phase to β phase and then from β phase to γ phase. A pretty high concentration of impurities

Ag₃Sb and Sb was shown in the work of Kirkham *et al.*, leading to the maximum ZT value only around 0.5 at 433 K [20]. In order to avoid the appearance of the impurity phase (Sb or Ag₃Sb), our group successfully adopted a two-step ball-milling process to fabricate phase pure MgAgSb materials (minor Ni substitution for Ag [21], Na doping into Mg [22], and minor substitution of Ag by Cu [23]) with ZT values ranging from 1.2 to 1.4, and a demonstration of conversion efficiency about 8.5% for $T_c = 293$ K and $T_h = 518$ K [24]. In spite of the high ZT and efficiency in the MgAgSb-based materials, the power factors in the previous reports were relatively low [21-23]. Since power factor determines the output power for given hot and cold temperatures and leg length, as shown by Eq. 2 [26], it is as important as high ZT values or even more important when the heat source is unlimited (such as solar heat), or heat source is free (such as waste heat from automobiles, steel industry, etc.) for thermoelectric devices,

$$\omega = \frac{1}{4} \frac{(T_h - T_c)^2}{L} PF \quad (2)$$

where ω , T_h , T_c , and L represent the output power density, hot side temperature, cold side temperature, and leg length of thermoelectric modules, respectively. So improving the power factor of MgAgSb-based materials is the motivation of this report.

Recently, it was found that the conventional PF and ZT could often lead to big errors in calculation of output power and leg efficiency over the whole operating temperature range using the conventional formula [27] due to the assumption of constant thermoelectric properties. Thus, Kim *et al.* proposed engineering power factor $(PF)_{eng}$ and engineering figure of merit $(ZT)_{eng}$ to reliably determine the

realistic output power and leg efficiency [27]. Therefore, the challenge is how to substantially enhance the $(PF)_{eng}$ and output power without degrading the $(ZT)_{eng}$ and leg efficiency for MgAgSb-based materials.

In our work on MgAgSb, we have achieved higher $(PF)_{eng}$ without degrading $(ZT)_{eng}$ by fine tuning the Sb content in $MgAg_{0.97}Sb_x$ ($x = 0.99, 0.9925, 0.995$, and 1.00). Due to the optimized carrier concentration with the increased Sb content, the $(PF)_{eng}$ are significantly increased without degrading the $(ZT)_{eng}$. For instance, the $(PF)_{eng}$ and output power of $MgAg_{0.97}Sb_{0.995}$ are $0.56 \text{ W m}^{-1} \text{ K}^{-1}$ and 1.77 W cm^{-2} with leg length $\sim 2 \text{ mm}$, $T_c = 300 \text{ K}$ and $T_h = 548 \text{ K}$, respectively, nearly 20% higher than those of $MgAg_{0.97}Sb_{0.99}$. Simultaneously, the leg efficiency of $\sim 10.1\%$ for $MgAg_{0.97}Sb_{0.995}$ is a little higher, in comparison with 9.9% for $MgAg_{0.97}Sb_{0.99}$.

2. Experimental section

Appropriate amount of Mg (99.98%; Alfa Aesar), Ag (99.99%; Sigma Aldrich), and Sb (99.999%; Alfa Aesar) was weighed according to the nominal composition $MgAg_{0.97}Sb_x$ ($x = 0.99, 0.9925, 0.995$, and 1.00) 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 [21-23] and finally the ball-milled powder was loaded into graphite die and hot pressed at 573 K for 5 min under a pressure of 90 MPa .

X-ray diffraction (XRD) analysis was performed using a PANalytical

multipurpose diffractometer with an X'celerator detector (PANalyticalX'Pert Pro). The microstructure was observed by a scanning electron microscope (SEM, JEOL 6330F,) and a high resolution transmission electron microscope (HRTEM, JEOL 2100F). 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) was determined by the Archimedes method, which was around 99% of the theoretical density of MgAgSb (theoretical $d = 6.31 \text{ g cm}^{-3}$). The Hall Coefficient R_H at room temperature was measured using the PPMS (Physical Properties Measurement System, Quantum Design). The carrier concentration (n_H) was obtained by $n_H = 1/eR_H$ and the carrier mobility (μ) was calculated by $\sigma = e\mu n_H$, where e is the electronic charge and σ the electrical conductivity.

Results and discussion

Figure 1a shows the X-ray diffraction (XRD) patterns of MgAg_{0.97}Sb_x samples ($x = 0.99, 0.9925, 0.995, \text{ and } 1.00$). All the MgAg_{0.97}Sb_x samples are found to be single phase within the detection limit of the XRD spectrometer, whose peaks exhibit good

match with the α -MgAgSb (space group $I\bar{4}C2$) [20, 25]. As shown in Figure 1b, the carrier concentration gradually increases from $x = 0.99$ to 0.995 and then slightly decreases from 0.995 to 1.00. This may be caused by the presence of a very minor Sb impurity phase, confirmed by the TEM and HRTEM analyses on sample MgAg_{0.97}Sb_{1.00} that is beyond the detectability of the XRD spectrometer, leading to the abnormal transport behavior that will be discussed latter.

As shown in the Figure 2a, the average grain size of the MgAg_{0.97}Sb_{0.995} sample is around 150 nm, further confirmed by the low magnification TEM image shown in Figure 2b. Besides, the SEM-EDS results show that the actual compositions of four samples match well with the nominal compositions, shown in the Table 1 in the Supporting Information. However, it is clearly observed from Figure 2c that some small nanograins ranging from 10 nm to 20 nm, similar to the microstructure of p-type nanostructured bulk BiSbTe [7], could be found along the [001] direction for MgAg_{0.97}Sb_{0.995} sample, caused by the combination of the long-time high energy ball milling and quick hot press process [28]. The large numbers of multiscale grain boundaries will contribute to the effective scattering of the medium and long wavelength phonons [29]. Moreover, Figure 2d shows that the grain boundary is very clear between (111) and (022) crystal planes, demonstrating the highly crystallized nature for MgAgSb based samples. For MgAg_{0.97}Sb_{1.00} sample, some small black nanodots could be observed from the low magnification TEM image and the size of those nanodots range from 5 nm to 10 nm under the high magnification TEM observations along the $[32\bar{1}]$ direction. Furthermore, the interplanar space of the

nanodots is 0.2186 nm, shown in Figure 2f, corresponding to the (012) plane of Sb, in agreement with the aforementioned analysis.

Figure 3a shows the temperature dependent electrical resistivity of $\text{MgAg}_{0.97}\text{Sb}_x$ samples ($x = 0.99, 0.9925, 0.995$, and 1.00). It is clear that the electrical resistivity monotonously decreases over the whole measured temperature range with increasing Sb content up to $x = 0.995$. Typically, the electrical resistivity at room temperature decreased from $3.56 \times 10^{-5} \Omega \text{ m}$ for $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ to $2.08 \times 10^{-5} \Omega \text{ m}$ for $\text{MgAg}_{0.97}\text{Sb}_{0.995}$, which can be ascribed to the gradually increased carrier concentration shown in Figure 1b. Briefly, MgAgSb can be expressed as $(\text{Mg}^{+2}\text{Ag}^{+1}\text{Sb}^{-3})$ according to the normal valence state in the solid state chemistry. Thus, increasing Sb content would lead to generation of Ag and Mg vacancies, which will definitely increase the carrier concentration in the p-type semiconductor. It is well known that vacancies play a critical role in the transport properties of thermoelectric materials [30], including BiCuSeO [31, 32], and YbZn_2Sb_2 [33], *etc.* Therefore, even fine tuning of the Sb content could undoubtedly influence the thermoelectric properties of the MgAgSb system. More importantly, the lower electrical resistivity is beneficial for choosing and producing reliable contacts for the subsequent module fabrication. However, because of the reduction of carrier concentration, the electrical resistivity of $\text{MgAg}_{0.97}\text{Sb}_{1.00}$ at room temperature has even increased compared with that of $\text{MgAg}_{0.97}\text{Sb}_{0.995}$, probably due to the undetectable amount of Sb impurity phase.

As shown in Figure 3b, the positive Seebeck coefficients indicate p-type

semiconducting nature for MgAgSb. Similarly, the Seebeck coefficients at room temperature first dramatically decrease and then slightly increase with increasing the Sb content, consistent with the tendency of electrical resistivity. More importantly, all the samples exhibit peak values of Seebeck coefficient, the typical characteristic of bipolar diffusion effect because of the small band gap ~ 0.1 eV for MgAgSb [25]. In addition, although the carrier concentration has exceeded 10^{19} cm^{-3} for all the samples, the Seebeck coefficients are still relatively high $\sim 200 \mu\text{V K}^{-1}$ over the entire measured temperature range. For instance, the Seebeck coefficients for sample $\text{MgAg}_{0.97}\text{Sb}_{0.995}$ range from $195 \mu\text{V K}^{-1}$ at 548 K to $236 \mu\text{V K}^{-1}$ at 373 K. The large Seebeck coefficient for MgAgSb system may be related to the high effective mass at the Fermi level (m^*) [2]. Generally, a rough estimation of the effective mass can be obtained by the following Eqs. 3-5 based on the single parabolic band model [34].

$$m^* = \frac{h^2}{2k_B T} \left[\frac{n}{4\pi F_{1/2}(\eta)} \right]^{2/3} \quad (3)$$

$$S = \pm \frac{k_B}{e} \left(\frac{(r+3/2) F_{r+3/2}(\eta)}{(r+3/2) F_{r+1/2}(\eta)} - \eta \right) \quad (4)$$

$$F_n(\eta) = \int_0^\infty \frac{\chi^n}{1 + e^{\chi - \eta}} d\chi \quad (5)$$

where $F_n(\eta)$ is the n^{th} order Fermi integral, η the reduced Fermi energy, r the scattering factor, h the Plank constant, k_B the Boltzmann constant, and e the electron charge. As acoustic phonon scattering is commonly the main scattering mechanism for most thermoelectric materials, the scattering factor r of $-1/2$ could be considered in calculation [3]. The obtained effective mass (m^*) for $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ is $2.1 m_e$, much higher than some complex Zintl compound, such as $0.9 m_e$ for Sr_3GaSb_3 [35] and 1.2

m_e for $\text{Yb}_9\text{Mn}_{4.2}\text{Sb}_9$ [36]. The large effective mass could be ascribed to the high density of states (DOS) of valence band at the X-point [25]. The calculated effective mass m^* for $\text{MgAg}_{0.97}\text{Sb}_x$ samples ($x = 0.9925, 0.995$, and 1.00) are $2.4 m_e, 2.7 m_e$, and $2.5 m_e$, respectively. The weighted mobility $\beta \sim \mu (m^*)^{3/2}$, the important criteria for high power factor [2, 3], shown in Figure 3c, gradually increases with increasing Sb content at room temperature, indicating that increasing Sb content is beneficial to optimize the electrical transport properties of MgAgSb-based materials.

For practical applications, high output power is as important as high leg efficiency or even more important when the heat source is unlimited (such as solar heat), or heat source is free (such as waste heat from automobiles, steel industry, etc.) for thermoelectric devices [26]. As indicated in Eq. 2, increasing the power factor or reducing the leg length can achieve high output power density. However, reducing the leg length could lead to a much larger thermo-mechanical reliability issue and accelerate the device failure due to increased temperature gradient across the leg. Therefore, increase the power factor is a more sensible approach to achieve output power for practical applications. Power factor ($PF = S^2\sigma$) calculated from the measured electrical resistivity and Seebeck coefficient is plotted in Figure 3d. Due to the decreased electrical resistivity, power factor of $\text{MgAg}_{0.97}\text{Sb}_x$ samples ($x = 0.9925, 0.995$, and 1.00) are enhanced over the whole measured temperature range, consistent with the increased weighted mobility (Figure 3c). For example, the power factor for $\text{MgAg}_{0.97}\text{Sb}_{0.995}$ sample are 22.2 and $24.2 \mu\text{W cm}^{-1} \text{K}^{-2}$ at 300 K and 548 K , respectively, about 20% higher than those of $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ sample.

Figure 4a presents the total thermal conductivity κ_{total} of $\text{MgAg}_{0.97}\text{Sb}_x$ samples ($x = 0.99, 0.9925, 0.995, \text{ and } 1.00$). It is clear that increasing Sb content from 0.99 to 1.00 gradually increases the κ_{total} over the whole measured temperature range. Normally, the κ_{total} consists of three parts, including lattice thermal conductivity (κ_{lat}), electronic thermal conductivity (κ_{ele}), and bipolar thermal conductivity (κ_{bip}). κ_{ele} can be easily estimated from the Wiedemann-Franz relationship ($\kappa_{ele} = L\sigma T$), where L is the Lorenz number and is obtained by fitting the respective Seebeck coefficient with an estimate of the reduced chemical potential using a single parabolic band (SPB) model with acoustic phonon scattering by Eqs. 3-5 and 6 [34], rather than using a constant value $2.45 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$ for degenerate semiconductor.

$$L = \left(\frac{k_B}{e}\right)^2 \left[\frac{3F_2(\eta)}{F_0(\eta)} - \left(\frac{2F_1(\eta)}{F_0(\eta)}\right)^2 \right] \quad (6)$$

Since it is difficult to accurately estimate the κ_{bip} simply using the direct theoretical calculation or the linear extensional method, Figure 4b show the κ_{lat} from 300 K to only 373 K before the onset of bipolar effect. The κ_{lat} for $\text{MgAg}_{0.97}\text{Sb}_x$ samples at 300 K ranges from $0.64 \text{ W m}^{-1} \text{ K}^{-1}$ to $0.68 \text{ W m}^{-1} \text{ K}^{-1}$, much lower than that of the nanostructured BiSbTe [7] and BiTeSe [16] alloy compounds. The intrinsic low κ_{lat} may be related to significant phonon scattering across multiple length scales. The atomic scale scattering is caused by the distorted Mg-Sb rocksalt-type sublattice and large cell unit [20], while the nanoscale and mesoscale scattering results from the substantial multiscale grain boundaries.

Combing the electrical and thermal properties, the corresponding ZT values are shown in Figure 5a. Although the peak ZT value is slightly reduced when Sb content

is over 0.995, the average ZT value for $\text{MgAg}_{0.97}\text{Sb}_{0.995}$ close to 1.1, the simple integral average ZT from 300 K to 548 K, are even increased a little due to the improved ZT at near room temperature, shown in Figure 5b.

To evaluate the output power and leg efficiency of $\text{MgAg}_{0.97}\text{Sb}_x$ samples, engineering power factor $(PF)_{eng}$, engineering figure of merit $(ZT)_{eng}$, output power, and leg efficiency were calculated assuming the leg length of 2 mm, $T_c = 300$ K and $T_h = 548$ K, which was thoroughly presented in the Supporting Information. Figure 6a and 5b shows the hot side temperature dependence of $(PF)_{eng}$ and output power, respectively. Obviously, both $(PF)_{eng}$ and output power increase monotonously with increasing the hot side temperature. Moreover, increasing Sb content from 0.99 to 1.00 gradually increases the $(PF)_{eng}$ and output power under the same hot side temperature. For instance, $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ exhibits a $(PF)_{eng} \sim 0.48 \text{ W m}^{-1} \text{ K}^{-1}$ and output power $\sim 1.50 \text{ W cm}^{-2}$ with $T_c = 300$ K and $T_h = 548$ K. In comparison, $\text{MgAg}_{0.97}\text{Sb}_{0.995}$ exhibits a higher $(PF)_{eng} \sim 0.56 \text{ W m}^{-1} \text{ K}^{-1}$ and output power $\sim 1.77 \text{ W cm}^{-2}$ under the temperature gradient, about 16.7% and 18.0%, respectively. Meanwhile, both $(ZT)_{eng}$ and leg efficiency of $\text{MgAg}_{0.97}\text{Sb}_x$ samples ($x = 0.9925$, 0.995, and 1.00) are increased a little, shown in Figure 6c and 6d. Therefore, our results indicate that $\text{MgAg}_{0.97}\text{Sb}_{0.995}$ compound is a better alternative for near room temperature commercial application for waste heat recovery, as compared with the reported $\text{MgAg}_{0.97}\text{Sb}_{0.99}$.

Conclusion

In summary, fine tuning the Sb content in $\text{MgAg}_{0.97}\text{Sb}_x$ samples ($x = 0.99, 0.9925, 0.995, \text{ and } 1.00$) was demonstrated as an effective way to achieve some enhancement of output power coupled with maintaining high leg efficiency. $(PF)_{eng}$ and output power under the same hot side temperature were increased by nearly 20% although the $(ZT)_{eng}$ and leg efficiency are similar. As a result, a high output power $\omega_{max} \sim 1.77$ W cm^{-2} and leg efficiency $\eta \sim 10.1\%$ are theoretically achieved for $\text{MgAg}_{0.97}\text{Sb}_{0.995}$ with leg length ~ 2 mm, $T_c = 300$ K and $T_h = 548$ K, in comparison with the $\omega_{max} \sim 1.50$ W cm^{-2} and $\eta \sim 9.9\%$ for $\text{MgAg}_{0.97}\text{Sb}_{0.99}$.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Graphical Abstract

Large enhancement of output power coupled with high leg efficiency could be successfully achieved via finely tuning the Sb content for MgAg_{0.97}Sb_x ($x = 0.99, 0.9925, 0.995, \text{ and } 1.00$).