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Effects of antimony content in $MgAg_{0.97}Sb_x$ on output power and energy conversion efficiency

Zihang Liu [a, b], Jing Shuai [b], Jun Mao [c], Yumei Wang [b, d], Zhengyun Wang [b, e], Wei Cai [a], Jiehe Sui [a, **], Zhifeng Ren [b, *]

[a] National Key Laboratory for Precision Hot Processing of Metals and School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China
[b] Department of Physics and TcSUH, University of Houston, Houston, TX 77204, USA
[c] Department of Mechanical Engineering, University of Houston, Houston, TX 77204, USA
[d] Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing 100190, China
[e] School of Material Science and Engineering, Xihua University, Chengdu 610039, China

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ABSTRACT

We report the effect of Sb content in $MgAg_{0.97}Sb_x$ (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 ~10.1% are finally obtained for the optimized composition $MgAg_{0.97}Sb_{0.995}$.

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], $CoSb_3$ [13], $Yb_{14}MnSb_{11}$ [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, Bi_2Te_3 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

* Corresponding author.
** Corresponding author.
E-mail addresses: suijiehe@hit.edu.cn (J. Sui), zren@uh.edu (Z. Ren).

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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 Ag_3Sb 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 Ag_3Sb), 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 W m^{-1} K^{-1} and 1.77 W cm^{-2} with leg length ~2 mm, $T_c = 300$ K and $T_h = 548$ K, respectively, nearly 20% higher than those of $MgAg_{0.97}Sb_{0.99}$. Simultaneously, the leg efficiency of ~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 $\kappa = DC_pd$, 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 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.

3. Results and discussion

Fig. 1a shows the X-ray diffraction (XRD) patterns of $MgAg_{0.97}Sb_x$ samples (x = 0.99, 0.9925, 0.995, 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 Fig. 1b, the carrier concentration gradually increases from x = 0.99 to 0.995 and then slightly deceases 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 Fig. 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 Fig. 2b. Besides, the SEM-EDS results show that the actual compositions of four samples match well with the nominal compositions, shown in Table 1 in the Supporting Information. However, it is clearly observed from Fig. 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, Fig. 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 Fig. 2f, corresponding to the (012) plane of Sb, in agreement with the aforementioned analysis.

Fig. 3a shows the temperature dependent electrical resistivity of $MgAg_{0.97}Sb_x$ 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 3.56×10^{-5} Ω m for $MgAg_{0.97}Sb_{0.99}$ to 2.08×10^{-5} Ω m for $MgAg_{0.97}Sb_{0.995}$, which can be ascribed to the