Effect of Cu concentration on thermoelectric properties of nanostructured *p*-type $\text{MgAg}_{0.97-x}\text{Cu}_x\text{Sb}_{0.99}$

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Abstract: Recently, MgAgSb was discovered to have good thermoelectric properties. In this paper, we intend to substitute a small amount of Ag by Cu to make $\text{MgAg}_{0.97-x}\text{Cu}_x\text{Sb}_{0.99}$ ($x = 0, 0.003, 0.007$, and 0.01) thermoelectric materials aiming to decrease the lattice thermal conductivity without sacrificing the power factor. The results showed that Cu substitution not only reduced the thermal conductivity, but also improved the power factor, consequently led to improved ZT values. Among the $\text{MgAg}_{0.97-x}\text{Cu}_x\text{Sb}_{0.99}$ samples, $\text{MgAg}_{0.963}\text{Cu}_{0.007}\text{Sb}_{0.99}$ showed the highest ZT values of 0.95 at room temperature and 1.32 at 250 °C. In addition, the MgAgSb-based samples displayed much better self-compatibility factors than $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$. The effect of grain orientation on the anisotropy of thermoelectric properties of $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ has also been studied.

Keywords: MgAgSb alloys; Nanostructure; Thermoelectric; Self-compatibility factor.

1. Introduction

The thermoelectric (TE) energy conversion technology, which can be used to convert waste heat into electricity, has received much attention in the past decade. The efficiency of TE devices is governed by the dimensionless figure of merit, $ZT = (S^2 \sigma / \kappa) T$, where S , σ , κ , and T are the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively. Generally, the thermal conductivity is the sum of the lattice and electronic thermal conductivity ($\kappa_{\text{total}} = \kappa_{\text{latt}} + \kappa_{\text{ele}}$). It is well known that the electronic (S , σ)

and thermal transport properties (κ) are interdependent, changing one will negatively affect the others, which is the reason why improving ZT has been proven so challenging. In the past decades, much effort has been made to improve power factor ($S^2\sigma$) by band engineering,^[1-4] quantum confinement,^[5] and lattice thermal conductivity reduction by nanostructuring^[6-8], which has resulted in good improvement of thermoelectric performance of many materials, including Bi₂Te₃-based,^[6-7] PbX (X = Te, Se, S),^[1-2, 9-10] skutterudites,^[11-12] half-Heuslers,^[13-14] SiGe,^[15-16] SnX (X = Te, Se),^[17-18] etc. However, Bi₂Te₃ and its derivatives with Sb and Se are still the best choice in cooling applications and waste heat recovery at temperatures lower than 200 °C because of their higher ZT s in that temperature range. It is well known that Te is a rare element on earth. Therefore, it is necessary to find a comparable material containing abundant elements to replace the Bi₂Te₃-based thermoelectric materials.

In this effort, MgAgSb was recently found promising by Kirkham *et al.*^[19] even though the synthesis and crystal structure of MgAgSb was studied before.^[20, 21] However, the reported ZT values up to 300 °C were relatively low due to the unavoidable formation of impurity resulted from the phase transition during the sample preparation. Recently, we successfully synthesized pure MgAgSb samples by a two-step processing of ball milling and hot pressing to avoid going above the phase transition temperature and reported much higher thermoelectric performance on MgAg_{0.97}Sb_{0.99} alloy and MgAg_{0.965}Ni_{0.005}Sb_{0.99}.^[22] Ni substitution for Ag was intended to decrease the electrical resistivity since Ni is on the left side in the periodic table, but the experimental results showed in fact Ni was acting as an electron donor, not only decreases the carrier concentration leading to higher electrical resistivity, but also decreases the thermal conductivity, consequently leading to enhanced ZT for the MgAg_{0.965}Ni_{0.005}Sb_{0.99} alloy.^[22] Since the reported MgAg_{0.97}Sb_{0.99} and MgAg_{0.965}Ni_{0.005}Sb_{0.99} still have pretty high electrical resistivity, we decided to dope the

materials by using selective elements to increase their electrical conductivity. It has been generally accepted that alloy scattering due to differences in the atomic mass and size is very effective on lowering the lattice thermal conductivity and changing the electrical conductivity simultaneously.^[23-25] For MgAgSb-based materials, Cu is located in the same column as Ag, but has a different atomic mass and size. Therefore, our motivation is to study the alloy effect on both the electronic and thermal properties with partial replacement of Ag by Cu. Our investigation on the thermoelectric properties of $\text{MgAg}_{0.97-x}\text{Cu}_x\text{Sb}_{0.99}$ proves that a very small amount of Cu, *e.g.*, 0.007 in $\text{MgAg}_{0.963}\text{Cu}_{0.007}\text{Sb}_{0.99}$, does result in a lower thermal conductivity and higher power factor by increasing the electrical conductivity, leading to higher ZT values of 0.95 at 25 °C and 1.32 at 250 °C, which is similar to the Ni substituted $\text{MgAg}_{0.965}\text{Ni}_{0.005}\text{Sb}_{0.99}$ but in a different mechanism.^[22]

It is reported that the crystal structure of MgAgSb at room temperature is tetragonal with different lattice coefficients of thermal expansion (CTE) in different directions ($15 \times 10^{-6} \text{ K}^{-1}$ for a-axis and $33 \times 10^{-6} \text{ K}^{-1}$ for c-axis).^[19] It implies that MgAgSb may possess anisotropic transport behavior. In this paper, the thermal and electrical transport in parallel and perpendicular to the hot press direction is also investigated to evaluate the effect of grain orientation on the thermoelectric performance of MgAgSb.

2. Experimental Section

The $\text{MgAg}_{0.97-x}\text{Cu}_x\text{Sb}_{0.99}$ ($x = 0, 0.003, 0.007, \text{ and } 0.01$) materials were synthesized by the two-step ball milling and hot pressing method reported previously.^[22] Firstly, magnesium (Mg, Sigma Aldrich, 99.8% metal basis), silver (Ag, Sigma Aldrich, 99.9% metal basis), and copper (Cu, sigma Aldrich, 99.9%) according to the designed ratio were loaded into a stainless steel jar with balls inside an argon-filled glove box, followed by ball milling for 10 hours. Following this step, antimony (Sb, Sigma Aldrich, 99.8% metal basis) chunks were

added into the jar inside the glove box, with another ball milling of 8 hours. The final powders were hot pressed at 300 °C for 5 minutes. The as-pressed disc was then annealed at 275 °C in air for 30 min prior to structure characterizations and property measurements.

X-ray diffraction spectra were collected on a PANalytical multipurpose diffractometer with an X'celerator detector (PANalyticalX'Pert Pro). The microstructures were investigated by a scanning electron microscope (SEM, JEOL 6340F) and transmission electron microscope (TEM, JEOL 2010F). The hot pressed samples were cut into bars with dimensions of 2 mm × 2 mm × 12 mm for simultaneous measurement of electrical resistivity and Seebeck coefficient using a commercial system (ULVAC ZEM-3 under a helium atmosphere from room temperature to 275 °C). The thermal and electrical transport properties were measured in the same direction. The hot pressed samples were cut and polished into coins with diameter of ~12.7 mm and thickness of ~1 mm for thermal diffusivity measurements. The thermal conductivity κ was calculated using $\kappa = \rho DC_p$, where ρ is the volumetric density determined by the Archimedes method, D the thermal diffusivity measured by laser flash apparatus (Netzsch LFA 457), and C_p the specific heat obtained on a differential scanning calorimetry thermal analyzer (Netzsch DSC 404 C). The uncertainty for the electrical conductivity is 3%, the Seebeck coefficient 5%, the thermal conductivity 7%, so the combined uncertainty for the power factor is 10% and that for ZT value is ~12%. Error bars are not shown in the figures to increase the readability of the curves.

3. Results and discussion

Figure 1 shows the XRD patterns of $\text{MgAg}_{0.97-x}\text{Cu}_x\text{Sb}_{0.99}$ as a function of Cu content. All the diffraction peaks show an excellent match to the simulation of α -phase MgAgSb . No noticeable impurity phases were observed. Based on the simple formula on energy gap $E_g =$

$2eS_{max}T$ developed by Goldsmid,^[26] where S_{max} and T refer to the peak Seebeck coefficient (**Figure 3b**) and corresponding temperature, respectively, the band gap E_g of $MgAg_{0.97-x}Cu_xSb_{0.99}$ samples was estimated and listed in **Table 1**. The band gap is first decreased and then increased with increasing of the Cu content. The carrier concentration listed in **Table 1** is obviously increased when the Cu content is increased up to 0.7%, and then saturated when the Cu content is 1%. Meanwhile, the mobility of $MgAg_{0.96}Cu_{0.1}Sb_{0.99}$ sample is also markedly decreased. From the change of carrier concentration and band gap as a function of Cu content, it can be concluded that the Cu is successfully incorporated into the lattice in $MgAg_{0.97-x}Cu_xSb_{0.99}$, and a very minor second phase beyond the detectability of the XRD spectrometer could exist in the $MgAg_{0.96}Cu_{0.01}Sb$ sample. Therefore, we inferred the Cu solubility limit in the $MgAg_{0.97}Sb_{0.99}$ is around 0.7%.

The scanning electron microscope images (SEM) (**Figure 2a and b**) indicate that the sample is densely packed and the grain size varies from 40 nm to 200 nm. It is shown in **Figure 2c** that individual grains are highly crystallized and the grain boundaries are clean. The elemental distributions determined by energy dispersive X-ray spectroscopy (EDX) indicate that all the elements are homogeneously distributed throughout the sample, as shown in **Figure 2d**.

Figure 3 shows the temperature dependence of thermoelectric properties of $MgAg_{0.97-x}Cu_xSb_{0.99}$ samples. The electrical resistivity of all samples first increases and then decreases with temperature. For Cu substituted samples, the electrical resistivity is lower than that of $MgAg_{0.97}Sb_{0.99}$ sample over the entire temperature range as shown in **Figure 3a**. Meanwhile, the electrical resistivity is first decreased and then increased with the increase of the Cu content at any temperature. It is worthy noting that Cu substitution to Ag in $MgAg_{0.97-x}Cu_xSb_{0.99}$ materials decreases the electrical resistivity, especially for

MgAg_{0.063}Cu_{0.007}Sb_{0.99} sample. It is about ~25 $\mu\Omega$ m at room temperature, increases to ~33 $\mu\Omega$ m at 100 °C before it decreases to ~18 $\mu\Omega$ m at 275 °C. Table 1 lists the carrier concentration (n_H) and Hall mobility (μ_H) dependence of Cu content in MgAg_{0.97-x}Cu_xSb_{0.99} samples. The carrier concentration and Hall mobility affect the electrical resistivity (ρ) of MgAg_{0.97-x}Cu_xSb_{0.99} samples by the relationship $1/\rho = n_H e\mu_H$. Compared with the MgAg_{0.97}Sb_{0.99} sample, the MgAg_{0.97-x}Cu_xSb_{0.99} (x= 0.003 and 0.007) samples possess lower electrical resistivity, which could be attributed to the enhanced carrier concentration and almost unchanged Hall mobility listed in Table 1. Oppositely, when the Cu substitution is 0.01, the electrical resistivity of MgAg_{0.96}Cu_{0.01}Sb_{0.99} is increased compared to the MgAg_{0.963}Cu_{0.007}Sb_{0.99} sample, which could be ascribed to the decreased Hall mobility caused by the appearance of a minor secondary phase beyond the detectability of the XRD spectrometer.

For MgAg_{0.97-x}Cu_xSb_{0.99} samples, the Seebeck coefficient displays similar trend with the electrical resistivity as shown in **Figure 3b**. The positive Seebeck coefficient indicates a *p*-type electrical transport behavior. It is shown that the Seebeck coefficient reaches a maximum at around 75 °C and 100 °C for the MgAg_{0.97}Sb_{0.99} and Cu substituted samples, respectively. The appearance of Seebeck coefficient peak of the Cu substituted samples is a sign of onset of bipolar effect as intrinsic carriers are excited. This onset is also reflected in the upturn thermal conductivity (discussed later in **Figure 3d**). The bipolar effect affects the Seebeck coefficient due to the contribution of minority carriers. For MgAg_{0.963}Cu_{0.007}Sb_{0.99}, the Seebeck coefficient starts at ~234 $\mu\text{V K}^{-1}$ at room temperature, then increases to ~256 $\mu\text{V K}^{-1}$ before decreasing to ~207 $\mu\text{V K}^{-1}$ at 275 °C, which is lower than that of MgAg_{0.97}Sb_{0.99} in the entire temperature range.

Figure 3c shows the power factor ($PF = S^2 \sigma$) calculated from the measured electrical conductivity and Seebeck coefficient for the $\text{MgAg}_{0.97-x}\text{Cu}_x\text{Sb}_{0.99}$ samples. The power factors of all the samples first decrease and then increase, finally saturate (a little decrease in case of $x = 0.003$ and 0.01) with temperature up to 275°C . The increased power factor after Seebeck coefficient peak should be ascribed to the enhanced electronic conductivity. The Cu substituted samples have higher power factors than $\text{MgAg}_{0.97}\text{Sb}_{0.99}$. Especially, for $\text{MgAg}_{0.963}\text{Cu}_{0.007}\text{Sb}_{0.99}$, the power factor is $\sim 22 \mu\text{W cm}^{-1} \text{K}^{-2}$ at room temperature, then decreases to $\sim 20 \mu\text{W cm}^{-1} \text{K}^{-2}$ before increasing to $\sim 23 \mu\text{W cm}^{-1} \text{K}^{-2}$ at 275°C , which is higher than that of $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ in the entire temperature range.

Figure 3d shows the total thermal conductivity as a function of temperature for the $\text{MgAg}_{0.97-x}\text{Cu}_x\text{Sb}_{0.99}$ samples. The densities of the samples measured by the Archimedes method are in the range of 6.18 to 6.20 g cm^{-3} , which is 98% of the theoretical density 6.31 g cm^{-3} . In a conservative way, the specific heat (C_p) of $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ (shown in the inset of Figure 3d) is used for the calculation of the total thermal conductivity of all the Cu substituted samples. The total thermal conductivity of all samples first decreases and then increases with temperature. The increase of thermal conductivity is due to the bipolar effect, which is consistent with the temperature dependence of electrical resistivity and Seebeck coefficient shown in **Figure 3a** and **b**.

For the $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ sample, the κ_{total} values are much lower than that of the high performance thermoelectric materials such as PbTe ,^[10] skutterudites,^[11] even lower than that of the nanostructured $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$.^[6] This can be ascribed to the distorted structure and large unit cell, which is the prerequisite of low thermal conductivity, such as Zn_4Sb_3 ,^[27] SnSe ,^[17] rocksalt I-V-VI₂ semiconductors (AgSbTe_2 and AgBiSe_2),^[28-29] etc. Apart from this, the strong

phonon scattering, due to the deficiencies at both Ag and Sb sites and nanostructure, is also beneficial to the reduced thermal conductivity. For the Cu substituted samples, the thermal conductivity is lower than that of $\text{MgAg}_{0.97}\text{Sb}_{0.99}$, and decreases with the increase of Cu content. Even though the electrical conductivity of the Cu substituted samples is higher than that of the $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ sample (**Figure 3a**), meaning the electronic thermal conductivity of the Cu substituted samples is higher than that of $\text{MgAg}_{0.97}\text{Sb}_{0.99}$, the total thermal conductivity of the Cu substituted samples is rather lower, indicating the fact that Cu is very effective on reducing the lattice thermal conductivity since the electronic thermal conductivity is $\kappa_{ele} = L\sigma T$, where L is Lorenz number. It is well known that the total thermal conductivity comprises three parts, including lattice thermal conductivity, electronic thermal conductivity, and bipolar thermal conductivity ($\kappa_{total} = \kappa_{latt} + \kappa_{ele} + \kappa_{bipol}$). For MgAgSb-based sample, the intrinsic excitation occurs after 100 °C. In order to clarify the effect of Cu substitution on the κ_{latt} , the κ_{latt} is calculated from $\kappa_{latt} = \kappa_{total} - \kappa_{ele}$ before the occurrence of intrinsic excitation. Here the κ_{ele} is calculated by the Wiedemann-Franz relation, $\kappa_{ele} = L\sigma T$. For free electrons, $L = 2.45 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}$. However, for most thermoelectric materials, the real Lorenz number is lower than that value, which can be obtained from fitting the respective Seebeck coefficient values with an estimate of the reduced chemical potential.^[30] The Lorenz number and κ_{ele} of the $\text{MgAg}_{0.97-x}\text{Cu}_x\text{Sb}_{0.99}$ samples are shown in **Figure 1S** (Lorenz number calculation details can be found in the SI). A clear trend can be seen that the κ_{latt} decreases due to the Cu substitution as shown in **Figure 3e**. Namely, the κ_{latt} decreases from 0.62 for $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ to 0.51 for $\text{MgAg}_{0.963}\text{Cu}_{0.007}\text{Sb}_{0.99}$ at room temperature. The reduction in the lattice thermal conductivity of Cu substituted $\text{MgAg}_{0.97-x}\text{Cu}_x\text{Sb}_{0.99}$ sample can be explained by the point defects on the basis of the Callaway model,^[31] in which the point defect scattering in a solid solution system originates from both the mass difference (Cu 63.55, Ag 107.87) and the interatomic coupling force differences derived from the size difference of $\text{Ag}^{+1}(1.26\text{\AA})$ and

$\text{Cu}^{+1}(0.73\text{\AA})$. With the increase of Cu substitution, the intensity of point defect scattering should be increased, correspondingly the lattice thermal conductivity is also decreased. It should be noted that the total thermal conductivity of the $\text{MgAg}_{0.96}\text{Cu}_{0.01}\text{Sb}_{0.99}$ sample is further decreased, but the lattice thermal conductivity is little increased. The reduced total thermal conductivity should be ascribed to the decreased electronic thermal conductivity. The increased lattice thermal conductivity may be related to the appearance of a minor secondary phase beyond the detectability of the XRD spectrometer. This part should be further investigated.

Figure 3f shows the ZT values of the $\text{MgAg}_{0.97-x}\text{Cu}_x\text{Sb}_{0.99}$ samples. Compared with the $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ sample, the decreased thermal conductivity and the improved power factor lead to higher peak and average ZT values in the Cu substituted samples. We achieved ZT s of 0.95 at room temperature and 1.32 at 250 °C in sample $\text{MgAg}_{0.963}\text{Cu}_{0.007}\text{Ag}_{0.99}$, comparable to the ZT s of $\text{MgAg}_{0.965}\text{Ni}_{0.005}\text{Sb}_{0.99}$.^[22]

Self-compatibility factor ($c = (\sqrt{1 + ZT} - 1)/(ST)$) is very important for thermoelectric generators because the thermoelectric material properties may change dramatically from the hot side to the cold side.^[32] If the self-compatibility factors differ by a factor of two or more, the thermoelectric materials will not be efficient. Therefore, self-compatibility factor acting as an important material property should also be considered when selecting high ZT thermoelectric materials for applications. The self-compatibility factors of $\text{MgAg}_{0.97-x}\text{Cu}_x\text{Sb}_{0.99}$ materials are shown in **Figure 4**. For comparison, the self-compatibility factor of nanostructured $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ is also plotted. The ZT value and Seebeck coefficient of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ from the previous publication are used to calculate the self-compatibility factor of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$.^[6] For the $\text{MgAg}_{0.97-x}\text{Cu}_x\text{Sb}_{0.99}$ samples, the self-compatibility factor varies by less than 20%, while that of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ is almost 3 in the

whole temperature range, which means higher conversion efficiency of $\text{MgAg}_{0.97-x}\text{Cu}_x\text{Sb}_{0.99}$ than $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ is possible.

In order to investigate the anisotropy of the thermoelectric properties, thick $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ samples were prepared. **Figure 5** shows the X-ray diffraction patterns of both the planes perpendicular and parallel to the press direction, respectively. These two XRD spectra look like very similar except some differences in the intensity of a few typical peaks marked by arrows in **Figure 5**, indicating that there is a little bit grain orientation anisotropy. This is reflected on the physical properties (discussed below).

Figure 6 shows the temperature dependence of thermoelectric properties for the as-pressed samples in both the directions perpendicular ($\perp$) and parallel ($\parallel$) to the press direction. The electrical resistivity ($\rho_{\parallel}$) of the parallel direction is higher than that ($\rho_{\perp}$) of the perpendicular direction below 150 °C (**Figure 6a**), which indicates that there is grain orientation, consistent with the results shown by XRD (**Figure 5**). After 150 °C, the electrical resistivity of both directions is almost same, which can be ascribed to the intrinsic excitation. The Seebeck coefficients of the as-pressed sample display similar trend with the electrical resistivity as shown in **Figure 6b**, which is inconsistent with the fact that Seebeck coefficients of single crystals or polycrystal is nearly isotropic in different crystal orientations.^[33-35] The related reason is not clear. Based on the electrical resistivity and Seebeck coefficient, the corresponding power factors of the as-pressed samples in both directions are very similar and shown in **Figure 6c**.

The temperature dependent thermal conductivity of the as-pressed $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ sample in both directions is very similar and is shown in **Figure 6d**. Combining with the

power factor and thermal conductivity, ZT dependence of temperature for $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ sample in both directions is shown in **Figure 6e**. The ZTs in both the parallel and perpendicular directions are basically the same within the experimental errors of ZTs of about 10-12%.

4. Conclusions

Cu substituted $\text{MgAg}_{0.97-x}\text{Cu}_x\text{Sb}_{0.99}$ materials were made through a two-step ball milling and hot pressing method by avoiding the phase transition. We found that Cu substitution played an important role in tuning both the thermal and electrical transport of $\text{MgAg}_{0.97-x}\text{Cu}_x\text{Sb}_{0.99}$ samples. The Cu substitution of Ag in $\text{MgAg}_{0.97-x}\text{Cu}_x\text{Sb}_{0.99}$ samples improved the power factor and also decreased thermal conductivity. The ZT value at room temperature is close to 1 and increases with temperature to a maximum of ~ 1.32 at $250\text{ }^{\circ}\text{C}$ for $\text{MgAg}_{0.963}\text{Cu}_{0.007}\text{Sb}_{0.99}$. Meanwhile, the self-compatibility factors of the $\text{MgAg}_{0.97-x}\text{Cu}_x\text{Sb}_{0.99}$ samples are much less temperature dependent than $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$, displaying potential for higher thermal energy to electricity conversion efficiency. Study on the thermoelectric properties along the parallel and perpendicular to hot press direction shows that $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ has little anisotropy. This tellurium-free thermoelectric material is a potential candidate to replace Bi_2Te_3 -based materials now used for cooling and waste heat recovery applications at lower than $300\text{ }^{\circ}\text{C}$.

Supporting Information

Supporting Information is available from the Acta Materialia or from the author.

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References

1. K. Biswas, J. Q. He, I. D. Blum, C. I. Wu, T. P. Hogan, D. N. Seidman, V. P. Dravid, M. G. Kanatzidis, *Nature* 2012, **489**, 414-418.
2. Y. Z. Pei, X. Y. Shi, A. LaLonde, H. Wang, L. D. Chen, G. J. Snyder, *Nature* 2011, **473**, 66-69.
3. Y. Pei, H. Wang, G. J. Snyder, *Adv. Mater.* 2012, **24**, 6125-6135.
4. W. Liu, X. J. Tan, K. Yin, H. J. Liu, X. F. Tang, J. Shi, Q. J. Zhang, C. Uher, *Phys. Rev. Lett.* 2012, **108**, 166601.
5. L. D. Hicks, M. S. Dresselhaus, *Phys. Rev. B* 1993, **47**, 12727-12731.
6. B. Poudel, Q. Hao, Y. Ma, Y. C. Lan, A. Minnich, B. Yu, X. Yan, D. Z. Wang, A. Muto, D. Vashaee, X. Y. Chen, J. M. Liu, M. S. Dresselhaus, G. Chen, Z. F. Ren, *Science* 2008, **320**, 634-638.
7. K. F. Hsu, S. Loo, F. Guo, W. Chen, J. S. Dyck, C. Uher, T. Hogan, E. K. Polychroniadis, M. G. Kanatzidis, *Science* 2004, **303**, 818-821.
8. Y. C. Lan, A. J. Minnich, G. Chen, Z. F. Ren, *Adv. Funct. Mater.* 2010, **20**, 357-376.
9. G. Mahan, B. C. Sales, J. Sharp, *Physics Today* 1997, **50**, 42-47.
10. G. J. Snyder, E. S. Toberer, *Nat. Mater.* 2008, **7**, 105-114.
11. X. Shi, J. Yang, J. R. Salvador, M. F. Chi, J. Y. Cho, H. Wang, S. Q. Bai, J. H. Yang, W. Q. Zhang, L. D. Chen, *J. Am. Chem. Soc.* 2011, **133**, 7837-7846.
12. G. S. Nolas, D. T. Morelli, T. M. Tritt, *Annu. Rev. Mater. Sci.* 1999, **29**, 89-116.
13. X. Yan, G. Joshi, W. S. Liu, Y. C. Lan, H. Wang, S. Lee, J. M. Simonson, S. J. Poon, T. M. Tritt, G. Chen, Z. F. Ren, *Nano Lett.* 2011, **11**, 556-560.

14. G. Joshi, X. Yan, H. Z. Wang, W. S. Liu, G. Chen, Z. F. Ren, *Adv. Energy Mater.* 2011, **1**, 643-647.
15. G. H. Zhu, H. Lee, Y. C. Lan, X. W. Wang, G. Joshi, D. Z. Wang, J. Yang, D. Vashaee, H. Guilbert, A. Pilliteri, M. S. Dresselhaus, G. Chen, Z. F. Ren, *Phys. Rev. Lett.* 2009, **102**, 196803.
16. B. Yu, M. Zebarjadi, H. Wang, K. Lukas, H. Z. Wang, D. Z. Wang, C. Opeil, M. Dresselhaus, G. Chen, Z. F. Ren, *Nano Lett.* 2012, **12**, 2077-2082.
17. L. D. Zhao, S. H. Lo, Y. S. Yang, H. Sun, G. J. Tan, C. Uher, C. Wolverton, V. P. Dravid, M. G. Kanatzidis, *Nature* 2014, **508**, 373-377.
18. Q. Zhang, B. L. Liao, Y. C. Lan, K. Lukas, W. S. Liu, K. Esfarjani, C. Opeil, D. Broido, G. Chen, Z. F. Ren, *P. Natl. Acad. Sci. USA*, 2013, **110**, 13261-13266.
19. M. J. Kirkham, A. M. dos Santos, C. J. Rawn, E. Lara-Curzio, J. W. Sharp, A. J. Thompson, *Phys. Rev. B* 2012, **85**, 144120.
20. H. Nowotny, W. Sibert, *Z. Metallkd.* 1941, **33**, 391-394.
21. B. R. T. Frost, G. V. Raynor, *Proc. R. Soc. London A*, 1950, **203**, 132-147.
22. H. Z. Zhao, J. H. Sui, Z. J. Tang, Y. C. Lan, Q. Jie, D. Kraemer, K. McEnaney, G. Chen, Z. F. Ren, *Nano Energy*. 2014, **7**, 97-103.
23. G. A. Slack, *Phys. Rev.* 1957, 105, 829.
24. X. Yan, W. S. Liu, H. Wang, S. Chen, J. Shiomi, K. Esfarjani, H. Z. Wang, D. Z. Wang, G. Chen, Z. F. Ren, *Energy Environ. Sci.* 2012, **5**, 7543-7548.
25. J. Li, J. H. Sui, Y. L. Pei, C. Barreteau, D. Berardan, N. Dragoe, W. Cai, J. Q. He, L. D. Zhao, *Energy Environ. Sci.* 2012, **5**, 8543-8547.
26. H.J. Goldsmid, *Introduction to Thermoelectricity*, Springer-Verlag, Berlin Heidelberg, 2010.
27. G. J. Snyder, M. Christensen, E. Nishibori, T. Caillat, B. B. Iveren, *Nat. Mater.* 2004, **3**, 458.

28. D. T. Morelli, V. Jovovic, J. P. Heremans, *Phys. Rev. Lett.* 2008, **101**, 035901.
29. M. D. Nielsen, V. Ozolins, J. P. Heremans, *Energy Environ. Sci.* 2013, **6**, 570-578.
30. D. M. Rowe, C. M. Bhandari, Modern thermoelectric, Reston Publishing Company, Inc.:
Reston, Virginia, 1983.
31. J. Callaway, H. C. Von Baeyer, *Phys. Rev.* 1960, **120**, 1149-1154.
32. G. J. Snyder, T. Ursell, *Phys. Rev. Lett.* 2003, **91**, 148301.
33. X. Yan, B. Poudel, Y. Ma, W. S. Liu, G. Joshi, H. Wang, Y. C. Lan, D. Z. Wang, G. Chen,
Z. F. Ren, *Nano Lett.* 2010, **10**, 3373.
34. M. Carle, P. Pierrat, C. Lahalle-Gravier, S. Scherrer, H. Scherrer, *J. Phys. Chem. Solids*,
1995, **56**, 201.
35. J. H. Sui, J. Li, J. Q. He, Y. L. Pei, D. Berardan, H. J. Wu, N. Dragoe, W. Cai, L. D. Zhao,
Energy Environ Sci, 2013, **6**, 2916.

Figure Captions

Figure 1. XRD patterns of $\text{MgAg}_{0.97-x}\text{Cu}_x\text{Sb}_{0.99}$ samples, the simulated XRD pattern was shown at the bottom for comparison.

Figure 2. SEM and TEM images of hot pressed sample $\text{MgAg}_{0.963}\text{Cu}_{0.007}\text{Sb}_{0.99}$. (a) low magnification and (b) medium magnification SEM image of a freshly broken surface of disc sample $\text{MgAg}_{0.963}\text{Cu}_{0.007}\text{Sb}_{0.99}$; (c) high resolution TEM image of $\text{MgAg}_{0.963}\text{Cu}_{0.007}\text{Sb}_{0.99}$; and (d) elemental distribution determined by EDX.

Figure 3. Temperature dependent thermoelectric properties of $\text{MgAg}_{0.97-x}\text{Cu}_x\text{Sb}_{0.99}$ samples. (a) Electrical resistivity; (b) Seebeck coefficient; c) power factor (PF); (d) total thermal conductivity; inset showing the heat capacity of $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ from 30 °C to 280 °C; (e) lattice thermal conductivity; and (f) figure of merit ZT .

Figure 4. Thermoelectric self-compatibility factor of $\text{MgAg}_{0.97-x}\text{Cu}_x\text{Sb}_{0.99}$ samples as a function of temperature for $x = 0, 0.003, 0.007$, and 0.01 . The self-compatibility factor of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ is also plotted for comparison.

Figure 5. XRD patterns of planes perpendicular and parallel to the hot press direction of the as-pressed $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ samples.

Figure 6. Thermoelectric properties of the as-pressed $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ sample in directions parallel and perpendicular to the hot press direction. (a) Electrical resistivity, (b) Seebeck coefficient, (c) Power factor, (d) Thermal conductivity, and (e) ZT .

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Table 1. Carrier concentration, Hall mobility, band gap at room temperature of $\text{MgAg}_{0.97-x}\text{Cu}_x\text{Sb}_{0.99}$ ($x = 0, 0.003, 0.007$, and 0.01) samples.

$\text{MgAg}_{0.97-x}\text{Cu}_x\text{Sb}_{0.99}$	$x = 0$	$x = 0.003$	$x = 0.007$	$x = 0.01$
Carrier concentration (10^{19} cm^{-3})	2.3	2.8	3.4	3.6
Hall mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	73.6	72.7	73.8	54.1
Band gap (eV)	0.21	0.19	0.18	0.19

Supporting Information

Effect of Cu concentration on thermoelectric properties of nanostructured *p*-type $\text{MgAg}_{0.97-x}\text{Cu}_x\text{Sb}_{0.99}$

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Figure 1S. Lorenz number a), and electronic thermal conductivity b) as a function of temperature for $\text{MgAg}_{0.97-x}\text{Cu}_x\text{Sb}_{0.99}$.

S1 Lorenz number calculation:

It is well known that the total thermal conductivity comprises three parts: lattice thermal conductivity, electronic thermal conductivity, and bipolar thermal conductivity ($\kappa_{total} = \kappa_{latt} + \kappa_{ele} + \kappa_{bipol}$). For MgAgSb-based sample, the intrinsic excitation occurs after 100 °C. In order to clarify the effect of Cu substitution on the κ_{latt} , the κ_{latt} is calculated from $\kappa_{latt} = \kappa_{total} - \kappa_{ele}$ before the occurrence of intrinsic excitation. Here the κ_{ele} is calculated by the Wiedemann-Franz relation, $\kappa_{ele} = L\sigma T$. For free electrons, $L = 2.45 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}$. However, for most thermoelectric materials, the real Lorenz number is lower than that value. In fact, the Lorenz number depends on the scattering parameter r and will decrease as the reduced Fermi energy η decreases with increasing temperature. The Lorenz number can be given as:

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

For the Lorenz number calculation, we should get reduced Fermi energy η firstly; the calculation of η can be derived from the measured Seebeck coefficients by using the following relationship:

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

where $F_n(\eta)$ is the n^{th} order Fermi integral,

$$F_n(\eta) = \int_0^\infty \frac{\chi^n}{1 + e^{\chi - \eta}} d\chi \quad (3)$$

$$\eta = \frac{E_f}{k_B T} \quad (4)$$

In the above equations, k_B is the Boltzmann constant, e the electron charge and E_f the Fermi energy. Meanwhile, acoustic phonon scattering ($r = -1/2$) has been assumed as the main carrier scattering mechanism. The Lorenz number can be obtained as shown in **Figure 1S** by applying the calculated reduced Fermi energy η and scattering parameter r into Eq. (1).