University of Wollongong

Research Online

Australian Institute for Innovative Materials -
Papers

Australian Institute for Innovative Materials

1-1-2018

Enhancement of thermoelectric figure of merit by the insertion of multi-walled carbon nanotubes in α -MgAgSb

Jingdan Lei
Henan University

De Zhang
Henan University

Weibao Guan
Henan University

Zheng Ma
Henan University

Zhenxiang Cheng
University of Wollongong, Henan University, cheng@uow.edu.au

See next page for additional authors

Follow this and additional works at: <https://ro.uow.edu.au/aiimpapers>

Part of the [Engineering Commons](#), and the [Physical Sciences and Mathematics Commons](#)

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

Enhancement of thermoelectric figure of merit by the insertion of multi-walled carbon nanotubes in α -MgAgSb

Abstract

Hybrid materials provide an efficient alternative route on improving the thermoelectric performance compared with doping elements. Especially, the insertion of carbon nanotubes plays an effective role in modulating the electrical transport properties and phonon scattering simultaneously. We fabricated a multi-walled carbon nanotube (MWCNTs) doped α -MgAgSb-based hybrid material and researched its thermoelectric properties in detail. The introduced MWCNTs enhanced carrier transport due to the metallic character of MWCNTs and phonon dispersion by the additional interfaces of insertions. The results showed that the electrical conductivity in α -MgAgSb/CNTs was remarkably enhanced especially at MgAg_{0.97}Sb_{0.99}/0.15 wt. % CNTs boosting to 1.6 times than that of CNTs-free MgAg_{0.97}Sb_{0.99}. In addition, the thermal conductivity ($\kappa_{0.1}$) of MgAg_{0.97}Sb_{0.99}/0.1 wt. % CNTs was reduced to 0.85 κ_0 . As a result, the ZT value at room temperature was efficiently improved from 0.55 to 0.83, 1.5 times higher, and a high ZT value of 1.05 at 375 K was obtained. In addition, the dimensionless material factor B^* increased from 0.98 to 1.49 at the doping level of 0.1 wt. % CNTs at 300 K, which revealed that MWCNTs significantly enhanced the thermoelectric performance of α -MgAgSb.

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Lei, J., Zhang, D., Guan, W., Ma, Z., Cheng, Z., Wang, C. & Wang, Y. (2018). Enhancement of thermoelectric figure of merit by the insertion of multi-walled carbon nanotubes in α -MgAgSb. *Applied Physics Letters*, 113 (8), 083901-1-083901-5.

Authors

Jingdan Lei, De Zhang, Weibao Guan, Zheng Ma, Zhenxiang Cheng, Chao Wang, and Yuanxu Wang

Enhancement of thermoelectric figure of merit by the insertion of multi-walled carbon nanotubes in α -MgAgSb

Jingdan Lei, De Zhang, Weibao Guan, Zheng Ma, Zhenxiang Cheng, Chao Wang, and Yuanxu Wang

Citation: *Appl. Phys. Lett.* **113**, 083901 (2018); doi: 10.1063/1.5042265

View online: <https://doi.org/10.1063/1.5042265>

View Table of Contents: <http://aip.scitation.org/toc/apl/113/8>

Published by the [American Institute of Physics](#)

Articles you may be interested in

Enhanced thermoelectric efficiency in topological insulator Bi₂Te₃ nanoplates via atomic layer deposition-based surface passivation

Applied Physics Letters **113**, 083904 (2018); 10.1063/1.5030674

Low lattice thermal conductivity in arc-melted GeTe with Ge-deficient crystal structure

Applied Physics Letters **113**, 083902 (2018); 10.1063/1.5043359

Enhanced thermoelectric performance realized in AgBiS₂ composited AgBiSe₂ through indium doping and mechanical alloying

Applied Physics Letters **112**, 213905 (2018); 10.1063/1.5034388

A practical field guide to thermoelectrics: Fundamentals, synthesis, and characterization

Applied Physics Reviews **5**, 021303 (2018); 10.1063/1.5021094

Revisiting lattice thermal transport in PbTe: The crucial role of quartic anharmonicity

Applied Physics Letters **113**, 073901 (2018); 10.1063/1.5040887

Ultrahigh Hall mobility and suppressed backward scattering in layered semiconductor Bi₂O₂Se

Applied Physics Letters **113**, 072106 (2018); 10.1063/1.5042727

AIP | Conference Proceedings

**Get 30% off all
print proceedings!**

Enter Promotion Code **PDF30** at checkout

Enhancement of thermoelectric figure of merit by the insertion of multi-walled carbon nanotubes in α -MgAgSb

Jingdan Lei,¹ De Zhang,¹ Weibao Guan,¹ Zheng Ma,¹ Zhenxiang Cheng,^{1,2} Chao Wang,^{1,a)} and Yuanxu Wang^{1,b)}

¹*Institute for Computational Materials Science, School of Physics and Electronics, Henan University, Kaifeng 475004, China*

²*Institute for Superconducting and Electronic Materials, University of Wollongong, Squires Way, North Wollongong 2522, Australia*

(Received 30 May 2018; accepted 31 July 2018; published online 20 August 2018)

Hybrid materials provide an efficient alternative route on improving the thermoelectric performance compared with doping elements. Especially, the insertion of carbon nanotubes plays an effective role in modulating the electrical transport properties and phonon scattering simultaneously. We fabricated a multi-walled carbon nanotube (MWCNTs) doped α -MgAgSb-based hybrid material and researched its thermoelectric properties in detail. The introduced MWCNTs enhanced carrier transport due to the metallic character of MWCNTs and phonon dispersion by the additional interfaces of insertions. The results showed that the electrical conductivity in α -MgAgSb/CNTs was remarkably enhanced especially at MgAg_{0.97}Sb_{0.99}/0.15 wt. % CNTs boosting to 1.6 times than that of CNTs-free MgAg_{0.97}Sb_{0.99}. In addition, the thermal conductivity ($\kappa_{0.1}$) of MgAg_{0.97}Sb_{0.99}/0.1 wt. % CNTs was reduced to 0.85 κ_0 . As a result, the ZT value at room temperature was efficiently improved from 0.55 to 0.83, 1.5 times higher, and a high ZT value of 1.05 at 375 K was obtained. In addition, the dimensionless material factor B* increased from 0.98 to 1.49 at the doping level of 0.1 wt. % CNTs at 300 K, which revealed that MWCNTs significantly enhanced the thermoelectric performance of α -MgAgSb. Published by AIP Publishing. <https://doi.org/10.1063/1.5042265>

Developing non-polluting energy materials has been a top priority in recent years, such as thermoelectric (TE) materials. TE materials tend to be favored by researchers as a promising power source due to converting heat into electricity.^{1–4} The performance of a thermoelectric material is described by the dimensionless figure of merit $ZT = S^2\sigma T/\kappa$, where σ is the electric conductivity, S is the Seebeck coefficient, κ is the thermal conductivity, and T is the absolute temperature, respectively. Excellent thermoelectric performance expects lower κ and higher $S^2\sigma$, the so called power factor. However, it impedes the pursuit of high ZT because that σ , S , and κ are highly interdependent.^{5,6} α -MgAgSb has been shown as a promising room-temperature thermoelectric material recently.⁷ Plentiful efforts to improve the TE performance of α -MgAgSb have been devoted to individually enhance electric conductivity^{8–12} or reduce thermal conductivity^{13,14} through doping chemical elements. Generally, enhancing electric conductivity σ through increasing carrier concentration designed by a traditional doping element always boosts carrier thermal conductivity (κ_c) simultaneously. Therefore, thermal conductivity κ deteriorates due to the excess carriers, where κ is constituted of lattice thermal conductivity κ_l and carrier thermal conductivity κ_c ($\kappa = \kappa_l + \kappa_c$). However, hybrid materials provide a promising alternative strategy for higher TE efficiency. For instance, TE performance is markedly enhanced in such a multi-walled carbon nanotube (MWCNTs) doped Cu₂Se-based TE material,¹⁵ Bi₂Te₃-based TE material,^{16,17} SnSe-based TE material,¹⁸ and so on. CNTs are outstanding low

dimensional structure materials with excellent electrical and thermal transport properties, which can carry currents upon 10^9 A cm⁻² and possess a thermal conductivity over 2000 W m⁻¹ K⁻¹.^{19,20} In addition, interfacial engineering like CNTs doped in thermoelectric materials is designed to not only modulate the carrier transport properties but also weaken thermal conductivity rationally by means of additional interfaces and larger grain boundaries between CNTs and matrix materials.

Herein, we try to introduce MWCNTs into an α -MgAgSb based TE material and expect that this route with a second nanophase in the α -MgAgSb matrix improving the electrical property and reducing thermal conductivity could work. As a result, we obtain an increased electric conductivity ($\sigma_{0.15}$) at a doping level of 0.15 wt. % CNTs ($\sigma_{0.15} \approx 1.6 \sigma_0$) comparing with this (σ_0) of pure α -MgAgSb. In addition, a doping level of 0.1 wt. % ($\kappa_{0.1}$) is achieved with a reduced thermal conductivity ($\kappa_{0.1} \approx 0.85\kappa_0$) in the hybrid material with CNTs. Eventually, we get a significantly enhanced ZT value approaching 1.05 at 375 K in the MWCNT doped α -MgAgSb-based TE material. A superior ZT of 0.83 is about 1.5 times higher than that of pure α -MgAgSb and 2 times as high as that in Ying *et al.*'s work at room temperature,⁸ which proves that CNT doping is an efficient way to improve thermoelectric performance in α -MgAgSb.

Figure 1 shows FESEM (Field Emission Scanning Electron Microscope) carried out on the freshly fractured surface of samples. Figure 1(a) indicates a typical crystallized morphology of MgAg_{0.97}Sb_{0.99} after the SPS system, dispersed flakes like Na_{0.015}Sn_{0.985}Se.¹⁸ Energy dispersive spectrometer (EDS) mapping showed in Figs. 1(b)–1(e) exhibits that Mg, Ag, and Sb are uniformly distributed throughout pure

^{a)}wangchao@vip.henu.edu.cn

^{b)}wangyx@henu.edu.cn

FIG. 1. (a)–(e) FESEM image and the element energy dispersive spectrometer (EDS) mapping of the MgAg_{0.97}Sb_{0.99} sample. (f) and (g) EDS spectrum and (h)–(l) FESEM images of the MgAg_{0.97}Sb_{0.99}/0.75 wt. % CNT hybrid material, respectively.

MgAg_{0.97}Sb_{0.99}. In addition, equal microstructure detection in hybrid material MgAg_{0.97}Sb_{0.99}/0.75 wt. % CNTs is operated. The EDS spectrum of a random selection CNT inclusion to clarify the microstructure in Fig. 1(g) shows a CNT coated by MgAg_{0.97}Sb_{0.99} and is coincident with the deeper observation in Fig. 2(c). These additional boundaries play a significant role in facilitating electrical transport and phonon scattering in the hybrid material. Furthermore, these CNT coated MgAg_{0.97}Sb_{0.99} sizes vary from a few hundred nm to several μm in length and dozens of nm to a few hundred nm in width showed in Figs. 1(i)–(l). Another morphology of the embedded CNT is indicated in Fig. 2(a), which proves that these

FIG. 2. TEM images of MgAg_{0.97}Sb_{0.99}/0.75 wt. % CNTs: (a)–(c) low magnification images and (d) high resolution TEM images.

dispersed short MWCNTs are harmonious with the matrix. Figure 2(d) is a high resolution TEM image of magnifying CNT coated MgAg_{0.97}Sb_{0.99}. The lattice of MgAg_{0.97}Sb_{0.99} and the surface of this CNT are distinguished by these red curves, showing a verification of Figs. 1(f) and 1(g).

Figure 3 exhibits temperature dependent thermoelectric properties for the MgAg_{0.97}Sb_{0.99}/x wt. % CNT (x = 0, 0.1, 0.15, 0.2, 0.25, 0.5, and 0.75) hybrid material. We can figure out that the electrical conductivity increases sharply with the increasing content of CNTs, increasing from 48 839 S m⁻¹ at pure MgAg_{0.97}Sb_{0.99} to 75 955 S m⁻¹ at x = 0.15 at room temperature in Fig. 3(a). The carrier mobility starts at 39 cm² V⁻¹ s⁻¹ then increases to 55 cm² V⁻¹ s⁻¹ simultaneously in Fig. 3(d). This phenomenon of increased electrical conductivity can also be found in composites of Cu₂Se and CNTs.¹⁵ Generally, the theoretical electrical conductivity of the hybrid material MgAg_{0.97}Sb_{0.99}/MWCNTs could be estimated by a parallel resistor model^{21,22}

$$\sigma_{\text{composite}} = M_{\text{MgAg}_{0.97}\text{Sb}_{0.99}} \sigma_{\text{MgAg}_{0.97}\text{Sb}_{0.99}} + M_{\text{MWCNTs}} \sigma_{\text{MWCNTs}}, \quad (1)$$

where σ and M are the electrical conductivity and ratio of constituent materials, respectively. In Fig. 3(a), the electrical conductivity of hybrid material MgAg_{0.97}Sb_{0.99}/MWCNTs should have increased with the MWCNT doped content, as a result of which $\sigma_{\text{MgAg}_{0.97}\text{Sb}_{0.99}}$ decreases after MWCNT addition. As we know, electrical conductivity σ in the single-phase thermoelectric material is contingent on the carrier concentration (n) and mobility (μ), and the relationship is

$$\sigma = ne\mu. \quad (2)$$

As shown in Fig. 3(d), μ decreases from 55 cm² V⁻¹ s⁻¹ at MgAg_{0.97}Sb_{0.99}/0.15 wt. % MWCNTs to 38 cm² V⁻¹ s⁻¹ at the MWCNT content 0.75 wt. %. We assume this phenomenon to be caused mainly by that grain boundary scattering which plays a leading role in MgAg_{0.97}Sb_{0.99}/0.75 wt. % CNTs that oppose the excellent electrical conductivity of CNTs.^{23,24} The carrier mobility has been expressed as

$$\mu = q\tau/m^*, \quad (3)$$

where q is the electron charge, τ is the relaxation time, and m^* is the effective mass. The carrier scattering on the grain boundaries imposes dominated influences on the relaxation time τ compared with ionized impurity scattering. Additionally, the effective mass m^* of MgAg_{0.97}Sb_{0.99}/0.15 wt. % CNTs is merely 1.7 m_e calculated by the measured Seebeck coefficient and carrier concentration and the others are listed in Table I

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

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

$$m^* = \frac{h^2}{2k_B T} \left[\frac{n}{4\pi F_{1/2}(\eta)} \right]^{2/3}, \quad (6)$$

where η is the reduced Fermi energy, $F_n(\eta)$ is the n th order Fermi integral, e is the electron charge, k_B is the Boltzmann

FIG. 3. TE properties as a function of temperature: (a) electrical conductivity, (b) Seebeck coefficient, (c) power factor, (d) room temperature carrier concentration and mobility, (e) total thermal conductivity, and (f) lattice thermal conductivity.

TABLE I. Effective mass m^* of the $\text{MgAg}_{0.97}\text{Sb}_{0.99}/x$ wt. % CNT ($x=0, 0.1, 0.15, 0.2, 0.25, 0.5$, and 0.75) hybrid material.

x wt. % CNTs	0	0.1	0.15	0.2	0.25	0.5	0.75
m^*	2.19	2.08	1.70	1.81	2.05	2.08	2.15

constant, h is the Planck constant, and r is the scattering factor considered as $-1/2$ at room temperature.

From Snyder's work² and the changeless carrier concentration of all hybrid materials in Fig. 3(d), we could infer that the Seebeck coefficient of $\alpha\text{-MgAg}_{0.97}\text{Sb}_{0.99}/\text{MWCNTs}$ is mainly contingent on effective mass m^* . Meanwhile, the effective mass m^* has been calculated and listed in Table I, where m^* of all hybrid materials decreases with the MWCNT content and then increases. As shown in Fig. 3(b), the Seebeck coefficient decreases from $\text{MgAg}_{0.97}\text{Sb}_{0.99}/0.1$ wt. % CNTs to $\text{MgAg}_{0.97}\text{Sb}_{0.99}/0.15$ wt. % CNTs and recovers relatively after the CNT content of 0.2 wt. %. Hybrid materials doped slight CNT $\text{MgAg}_{0.97}\text{Sb}_{0.99}/x$ wt. % CNTs ($x=0.1$ and 0.15) achieve optimal power factors above $20 \mu\text{W cm}^{-1} \text{K}^{-2}$ owing to the dominated Seebeck coefficient and electrical conductivity in Fig. 3(c), respectively. However, the power factor in other hybrid materials increasing the content of CNTs could not match the CNT-free $\text{MgAg}_{0.97}\text{Sb}_{0.99}$.

Figure 3(e) presents a temperature dependent total thermal conductivity of hybrid material $\text{MgAg}_{0.97}\text{Sb}_{0.99}/x$ wt. % CNTs ($x=0, 0.1, 0.15, 0.2, 0.25, 0.5$, and 0.75). All the sample hybrid $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ with CNTs achieve a reduced thermal conductivity than that of CNT-free $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ at room temperature. Especially, $\text{MgAg}_{0.97}\text{Sb}_{0.99}/x$ wt. % CNTs ($x=0.1$ and 0.15) exhibit a significant reduction of thermal conductivity in the entire temperature range due to the increased $\alpha\text{-MgAgSb}/\text{CNTs}$ interfaces, which causes a lattice phonon dissipation as well as carrier scattering simultaneously. However, the thermal conductivity deteriorates in hybrid materials $\text{MgAg}_{0.97}\text{Sb}_{0.99}/x$ wt. % CNTs ($x=0.2, 0.25, 0.5$, and 0.75), which may be caused mainly by the excellent thermal transport property $2000\text{--}6000 \text{ W m}^{-1} \text{K}^{-1}$ of CNTs.²⁵ The introduction of MWCNTs into MgAgSb has not affected the morphology of the matrix shown from SEM images. However, we can find the inserted MWCNTs have been coated by many tiny grains, which has been justified by

the TEM images in Fig. 2. It is these emergent grains that enhance phonon scattering and prevent the linear increase in thermal conductivity with the increased MWCNT content. It is well known that the total thermal conductivity (κ_{total}) consists of the lattice thermal conductivity (κ_{lattice}), the carrier thermal conductivity (κ_{carrier}), and the bipolar thermal conductivity (κ_{bipolar}), a relationship $\kappa_{\text{total}} = \kappa_{\text{lattice}} + \kappa_{\text{carrier}} + \kappa_{\text{bipolar}}$. We ignore the κ_{bipolar} because of the unreliability of the evaluated value on κ_{bipolar} . κ_{lattice} obtained by subtracting κ_{carrier} from κ_{total} is indicated in Fig. 3(f). Additionally, κ_{carrier} can be easily evaluated from the Wiedemann-Franz relationship ($\kappa_{\text{carrier}} = L\sigma T$), where L is the Lorenz number and L can be given as²⁶

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

The reduced Fermi energy η can be derived from the measured Seebeck coefficients. By applying the reduced Fermi energy η and scattering factor ($r = -1/2$) into Eq. (7), the Lorenz number L is calculated and then κ_{carrier} and κ_{lattice} could be estimated. We can figure out intuitively that the lattice thermal conductivity is dominated in hybrid material $\text{MgAg}_{0.97}\text{Sb}_{0.99}/\text{CNTs}$ in Fig. 3(f). κ_{lattice} of the hybrid material is significantly reduced due to the additional interfaces of CNTs and $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ as well as the multiscale grain boundaries than that in pure $\text{MgAg}_{0.97}\text{Sb}_{0.99}$. In addition, the dislocation strain at grain boundaries happens when CNTs are added into the matrix, which can contribute to scatter the phonon.²⁷

Figures 4(a) and 4(b) are ZT of hybrid materials $\text{MgAg}_{0.97}\text{Sb}_{0.99}/\text{CNTs}$ and comparison of $\text{MgAg}_{0.97}\text{Sb}_{0.99}/x$ wt. % CNTs ($x=0$ and 0.1), respectively. We obtain an improved ZT from 0.83 at room temperature to 1.05 at 375 K in hybrid material $\text{MgAg}_{0.97}\text{Sb}_{0.99}/0.1$ wt. % CNTs. Normalized thermoelectric properties at this content are inserted in Fig. 4(b) contrasting with those of pure $\text{MgAg}_{0.97}\text{Sb}_{0.99}$. It is distinct that the electrical conductivity increases sharply when 0.1 wt. % MWCNTs are introduced into the matrix ($\sigma_{0.1} \approx 1.3 \sigma_0$). In addition, the ZT of $\text{MgAg}_{0.97}\text{Sb}_{0.99}/0.1$ wt. % CNTs is 1.5 times higher than that of $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ due to the reduced thermal conductivity

FIG. 4. (a) Temperature dependent ZT of MgAg_{0.97}Sb_{0.99}/CNTs, (b) Comparison of ZT and normalized thermoelectric properties of MgAg_{0.97}Sb_{0.99}/x wt. % CNTs (x = 0 and 0.1), (c) ZT values at room temperature for elements doping in α-MgAgSb compared with the MgAg_{0.97}Sb_{0.99}/CNT hybrid material (fabricated by mechanical alloying is marked with the white background contrasting with the yellow background of the solid phase reaction), and (d) normalized ZT_{0.1}/ZT₀ and B*_{0.1}/B*₀ ratios at 300 K of MgAg_{0.97}Sb_{0.99}/0.1 wt. % CNTs compared with MgAg_{0.97}Sb_{0.99}, respectively.

and the almost unchanged Seebeck coefficient. The hybrid material by optimizing electrical and thermal conductivity synergistically is a more efficient route than monotonous element doping. As demonstrated in Fig. 4(c), the room temperature ZT value of CNTs by the solid phase reaction is distinctly higher than Na, Li, Yb, and Ca doped by mechanical alloying, especially higher than element Indium doped by the same way as the solid phase reaction. Furthermore, the thermal conductivities of MgAg_{0.97}Sb_{0.99}/CNTs do not deteriorate with the increased electrical conductivity due to the improved carrier mobility, which is one reason why the room temperature ZT value is higher than those of Na, Li, Yb, and Ca elements doped increasing electrical conductivity by the improved carrier concentration.

Material factor B was derived by Chasmar and Stratton and explored continuously to evaluate the performance of thermoelectric materials.^{28,29} Liu *et al.* redefined this parameter in view of the bipolar effect and a generalized B* was proposed³⁰

$$B^* = 0.06668 \frac{\mu(m^*/m_0)^{3/2} T^{3/2}}{\kappa_{\text{lattice}}} E_g, \quad (8)$$

where m^* , m_0 , μ , κ_{lattice} , E_g , and T are the carrier effective mass, free electron mass, carrier mobility, lattice thermal conductivity, band gap, and absolute temperature, respectively. Band gap E_g can be easily estimated from the Goldsmid relationship³¹

$$E_g = 2eS_{\text{max}}T_{\text{max}}, \quad (9)$$

where e is the electron charge and T_{max} is the temperature at which the maximum Seebeck coefficient S_{max} emerges. Generally, the dimensionless material factor B* is coincident with ZT on thermoelectric performance evaluation, which gets rid of highly interdependent electric conductivity and Seebeck coefficient. Since the bipolar effect is taken into account in B*, we just illustrate the relationship between B* with ZT of MgAg_{0.97}Sb_{0.99} and MgAg_{0.97}Sb_{0.99}/0.1 wt. %

CNTs at 300 K. At 300 K, ZT is improved from 0.55 to 0.83 at the CNT doping level of 0.1 wt. %, which is 1.46 times higher than that of CNT-free MgAg_{0.97}Sb_{0.99}. Corresponding to the ZT, B* increases to 1.52 times starting from 0.98 to 1.49 and normalized ZT_{0.1}/ZT₀, B*_{0.1}/B*₀ ratios are shown in Fig. 4(d). At room temperature, B* is equal to ZT. Both of them demonstrate the improved thermoelectric performance in α-MgAg_{0.97}Sb_{0.99} by CNT addition.

In summary, MgAg_{0.97}Sb_{0.99}/x wt. % CNT (x = 0, 0.1, 0.15, 0.2, 0.25, 0.5, and 0.75) hybrid materials are fabricated, as well as their thermoelectric properties are investigated in this work. The carrier mobility is distinctly boosted attributed to the typically metallic character of MWCNTs and the scattering mechanism is increased by the additional interfaces between MWCNTs with the MgAg_{0.97}Sb_{0.99} matrix and the multiscale grain boundaries in MgAg_{0.97}Sb_{0.99}/CNTs. Therefore, we achieved an enhanced electrical conductivity ($\sigma_{0.15} \approx 1.6\sigma_0$) in MgAg_{0.97}Sb_{0.99}/0.15 wt. % CNTs and a reduced thermal conductivity ($\kappa_{0.1} \approx 0.85\kappa_0$) at the level of 0.1 wt. % MWCNTs doped compared with those (σ_0 and κ_0) of pure MgAg_{0.97}Sb_{0.99}. More importantly, the improved ZT value 0.83 is 1.5 times higher than that of pure α-MgAgSb 0.55 at room temperature and approaches to 1.05 at 375 K in MgAg_{0.97}Sb_{0.99}/CNTs. Therefore, our work demonstrates that it is an efficiently alternative route to enhance TE performance in α-MgAgSb or other TE materials through the hybrid material with MWCNTs.

See [supplementary material](#) for experimental details and XRD pattern.

This research was sponsored by the National Natural Science of China (Grant Nos. U1504511, 51571083, 51371076, and 11674083), the Science and Technology fund of Henan Province (Grant Nos. 182102210227, 162102210169, and 162300410224), and the Foundation of Henan Educational Committee (Grant No. 14A430029).

- ¹F. J. Disalvo, "Thermoelectric cooling and power generation," *Science* **285**, 703–706 (1999).
- ²G. J. Snyder and E. S. Toberer, "Complex thermoelectric materials," *Nat. Mater.* **7**, 105–114 (2008).
- ³X. Shi, J. Yang, J. R. Salvador, M. Chi, J. Y. Cho, H. Wang, S. Bai, J. Yang, W. Zhang, and L. Chen, "Multiple-filled skutterudites: High thermoelectric figure of merit through separately optimizing electrical and thermal transports," *J. Am. Chem. Soc.* **133**, 7837–7846 (2011).
- ⁴B. Yu, M. Zebarjadi, H. Wang, K. Lukas, H. Wang, D. Wang, C. Opeil, M. Dresselhaus, G. Chen, and Z. Ren, "Enhancement of thermoelectric properties by modulation-doping in silicon germanium alloy nanocomposites," *Nano Lett.* **12**, 2077–2082 (2012).
- ⁵Y. Pei, H. Wang, and G. J. Snyder, "Thermoelectric materials: Band engineering of thermoelectric materials," *Adv. Mater.* **24**, 6124–6124 (2012).
- ⁶T. Zhu, Y. Liu, C. Fu, J. P. Heremans, J. G. Snyder, and X. Zhao, "Compromise and synergy in high-efficiency thermoelectric materials," *Adv. Mater.* **29**(14), 1605884 (2017).
- ⁷Z. Liu, J. Mao, J. Sui, and Z. Ren, "High thermoelectric performance of α -MgAgSb for power generation," *Energy Environ. Sci.* **11**, 23–44 (2018).
- ⁸P. Ying, X. Liu, C. Fu, X. Yue, H. Xie, X. Zhao, W. Zhang, and T. Zhu, "High performance α -MgAgSb thermoelectric materials for low temperature power generation," *Chem. Mater.* **27**, 909–913 (2015).
- ⁹Z. Liu, Y. Wang, J. Mao, H. Geng, J. Shuai, Y. Wang, R. He, W. Cai, J. Sui, and Z. Ren, "Lithium doping to enhance thermoelectric performance of MgAgSb with weak electron-phonon coupling," *Adv. Energy Mater.* **6**, 1502269 (2016).
- ¹⁰Z. Liu, Y. Wang, W. Gao, J. Mao, H. Geng, J. Shuai, W. Cai, J. Sui, and Z. Ren, "The influence of doping sites on achieving higher thermoelectric performance for nanostructured α -MgAgSb," *Nano Energy* **31**, 194–200 (2017).
- ¹¹Z. Liu, Y. Zhang, J. Mao, W. Gao, Y. Wang, J. Shuai, W. Cai, J. Sui, and Z. Ren, "The microscopic origin of low thermal conductivity for enhanced thermoelectric performance of Yb doped MgAgSb," *Acta Mater.* **128**, 227–234 (2017).
- ¹²J. Shuai, H. S. Kim, Y. Lan, S. Chen, Y. Liu, H. Zhao, J. Sui, and Z. Ren, "Study on thermoelectric performance by Na doping in nanostructured $\text{Mg}_{1-x}\text{Na}_x\text{Ag}_{0.97}\text{Sb}_{0.99}$," *Nano Energy* **11**, 640–646 (2015).
- ¹³H. Zhao, J. Sui, Z. Tang, Y. Lan, Q. Jie, D. Kraemer, K. McEnaney, A. Guloy, G. Chen, and Z. Ren, "High thermoelectric performance of MgAgSb-based materials," *Nano Energy* **7**, 97–103 (2014).
- ¹⁴J. Sui, J. Shuai, Y. Lan, Y. Liu, R. He, D. Wang, Q. Jie, and Z. Ren, "Effect of Cu concentration on thermoelectric properties of nanostructured p-type $\text{MgAg}_{0.97-x}\text{Cu}_x\text{Sb}_{0.99}$," *Acta Mater.* **87**, 266–272 (2015).
- ¹⁵L. Zhao, S. M. K. N. Islam, J. Wang, D. L. Cortie, X. Wang, Z. Cheng, J. Wang, N. Ye, S. Dou, and X. Shi, "Significant enhancement of figure-of-merit in carbon-reinforced Cu_2Se nanocrystalline solids," *Nano Energy* **41**, 164–171 (2017).
- ¹⁶K. T. Kim, Y. C. Si, E. H. Shin, K. S. Moon, H. Y. Koo, G. G. Lee, and G. H. Ha, "The influence of CNTs on the thermoelectric properties of a CNT/ Bi_2Te_3 composite," *Carbon* **52**, 541–549 (2013).
- ¹⁷F. Ren, H. Wang, P. A. Menchhofer, and J. O. Kiggans, "Thermoelectric and mechanical properties of multi-walled carbon nanotube doped $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ thermoelectric material," *Appl. Phys. Lett.* **103**, 221907 (2013).
- ¹⁸F. Chu, Q. Zhang, Z. Zhou, D. Hou, L. Wang, and W. Jiang, "Enhanced thermoelectric and mechanical properties of Na-doped polycrystalline SnSe thermoelectric materials via CNTs dispersion," *J. Alloy. Compd.* **741**, 756–764 (2018).
- ¹⁹B. Q. Wei, R. Vajtai, and P. M. Ajayan, "Reliability and current carrying capacity of carbon nanotubes," *Appl. Phys. Lett.* **79**, 1172–1174 (2001).
- ²⁰M. F. De Volder, S. H. Tawfik, R. H. Baughman, and A. J. Hart, "Carbon nanotubes: Present and future commercial applications," *Science* **339**, 535–539 (2013).
- ²¹H. Wang, S.-I. Yi, X. Pu, and C. Yu, "Simultaneously improving electrical conductivity and thermopower of polyaniline composites by utilizing carbon nanotubes as high mobility conduits," *ACS Appl. Mater. Interfaces* **7**, 9589–9597 (2015).
- ²²W. Yao, Y. Chao, S. Ming, S. Silong, and D. Yuan, "Individual adjustment of electrical conductivity and thermopower enabled by multiple interfaces in polyaniline-based ternary hybrid nanomaterials for high thermoelectric performances," *Adv. Mater. Interfaces* **5**, 1701168 (2018).
- ²³T. Yamada, H. Makino, N. Yamamoto, and T. Yamamoto, "Ingrain and grain boundary scattering effects on electron mobility of transparent conducting polycrystalline Ga-doped ZnO films," *J. Appl. Phys.* **107**, 123534 (2010).
- ²⁴Q. G. Zhang, B. Y. Cao, X. Zhang, M. Fujii, and K. Takahashi, "Influence of grain boundary scattering on the electrical and thermal conductivities of polycrystalline gold nanofilms," *Phys. Rev. B* **74**, 134109 (2006).
- ²⁵Z. Han and A. Fina, "Thermal conductivity of carbon nanotubes and their polymer nanocomposites: A review," *Prog. Polym. Sci.* **36**, 914–944 (2011).
- ²⁶A. F. May, E. S. Toberer, A. Saramat, and G. J. Snyder, "Characterization and analysis of thermoelectric transport in n -type $\text{Ba}_8\text{Ga}_{16-x}\text{Ge}_{30+x}$," *Phys. Rev. B* **80**, 125205 (2009).
- ²⁷H. S. Kim, S. D. Kang, Y. Tang, R. Hanus, and G. J. Snyder, "Dislocation strain as the mechanism of phonon scattering at grain boundaries," *Mater. Horiz.* **3**, 234–240 (2016).
- ²⁸R. P. Chasmar and R. Stratton, "The thermoelectric figure of merit and its relation to thermoelectric generators," *J. Electron. Control* **7**, 52–72 (1959).
- ²⁹D. Tuomi, "Thermoelectricity VII. The Seebeck quality factor, Q_s , a semiconductor characterization tool," *J. Electrochem. Soc.* **131**, 2101–2105 (1984).
- ³⁰W. Liu, J. Zhou, Q. Jie, Y. Li, H. S. Kim, J. Bao, G. Chen, and Z. Ren, "New insight into the material parameter B to understand the enhanced thermoelectric performance of $\text{Mg}_2\text{Sn}_{1-x-y}\text{Ge}_x\text{Sb}_y$," *Energy Environ. Sci.* **9**, 530–539 (2016).
- ³¹H. J. Goldsmid and J. W. Sharp, "Estimation of the thermal band gap of a semiconductor from Seebeck measurements," *J. Electron. Mater.* **28**, 869–872 (1999).