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Abstract

SnTe, with the same rock-salt structure as PbTe, is a potentially attractive thermoelectric material. Pristine SnTe has poor thermoelectric performance because of its very high hole concentration resulting from intrinsic Sn vacancies, which leads to a high thermal conductivity and a low Seebeck coefficient. In this work, the thermoelectric properties of SnTe were modified by doping with different contents of gadolinium and silver. It is found that SnTe doped with optimal gadolinium (i.e. Gd_{0.06}Sn_{0.94}Te) exhibited extraordinarily low lattice thermal conductivity that is close to the theoretical minimum. The drastic reduction of lattice thermal conductivity is attributed to the formation of nanoprecipitates, which strongly scatter phonons by mass fluctuation between a second phase and matrix coupled with mesoscale scattering via grain boundaries. Further doping Gd_{0.06}Sn_{0.94}Te with Ag leads to a higher Seebeck coefficient due to the decreased carrier concentration and adjusted phase composition. Optimal Ag doping leads to a 3 times and 2 times enhancement of the figure of merit (ZT) in comparison with SnTe and Gd_{0.06}Sn_{0.94}Te, respectively, i.e. a ZT of ~ 1.1 was obtained for 11 atom% Ag-containing Gd_{0.06}Sn_{0.94}Te at 873 K.

Keywords

snte, ag, gd, free, lead, thermoelectrics, doping, performance, thermoelectric, enhancement

Disciplines

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Lead-free SnTe-based thermoelectrics: enhancement of thermoelectric performance by doping with Gd/Ag†

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SnTe, with the same rock-salt structure as PbTe, is a potentially attractive thermoelectric material. Pristine SnTe has poor thermoelectric performance because of its very high hole concentration resulting from intrinsic Sn vacancies, which leads to a high thermal conductivity and a low Seebeck coefficient. In this work, the thermoelectric properties of SnTe were modified by doping with different contents of gadolinium and silver. It is found that SnTe doped with optimal gadolinium (*i.e.* Gd_{0.06}Sn_{0.94}Te) exhibited extraordinarily low lattice thermal conductivity that is close to the theoretical minimum. The drastic reduction of lattice thermal conductivity is attributed to the formation of nanoprecipitates, which strongly scatter phonons by mass fluctuation between a second phase and matrix coupled with mesoscale scattering *via* grain boundaries. Further doping Gd_{0.06}Sn_{0.94}Te with Ag leads to a higher Seebeck coefficient due to the decreased carrier concentration and adjusted phase composition. Optimal Ag doping leads to a 3 times and 2 times enhancement of the figure of merit (*ZT*) in comparison with SnTe and Gd_{0.06}Sn_{0.94}Te, respectively, *i.e.* a *ZT* of ~ 1.1 was obtained for 11 atom% Ag-containing Gd_{0.06}Sn_{0.94}Te at 873 K.

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Introduction

Thermoelectric materials, which can generate electricity from waste heat or be used as solid state Peltier coolers, could play an important role in energy saving and environmental issues.¹ The thermoelectric conversion efficiency is governed by the figure of merit (*ZT*) defined as $ZT = \alpha^2 \sigma T / (\kappa_{\text{lat}} + \kappa_{\text{el}})$, where α , σ , T , κ_{lat} and κ_{el} denote the Seebeck coefficient, electrical conductivity, absolute temperature, lattice thermal conductivity and electronic thermal conductivity, respectively.^{2,3} Significant improvement in the power factor ($\alpha^2 \sigma$) coupled with low lattice thermal conductivity is necessary for enhancing the performance of present thermoelectric materials. An approach to obtaining high power factors involves manipulation of the density of states through band engineering, including band convergence/degeneracy^{4–6} or introduction of resonant impurity levels near the

Fermi level.^{7,8} Methods to block the propagation of phonons include the introduction of point defects,^{9,10} second phase nanoprecipitates^{11,12} and mesoscale grain boundaries.^{13–15}

Lead chalcogenides are the most studied thermoelectric materials with high *ZT* values between 1.4 and 2.2,^{4,12,14–16} although concerns about Pb (*e.g.* toxicity) limit their large scale application. An alternative is SnTe, which is a lead-free environmentally friendly semiconductor with the same rock-salt structure and the same multiple valence bands (light- and heavy-hole bands) as PbTe, suggesting that it is a good thermoelectric material. SnTe has rarely been investigated however, because of our inability to control its very high level of intrinsic Sn vacancies (10^{20} to 10^{21} cm^{−3}), which leads to a low Seebeck coefficient and a high thermal conductivity.^{17,18} Other concerns about SnTe are its small band gap (~ 0.18 eV at 300 K) and the large energy separation (0.3–0.4 eV at 300 K) between its light and heavy hole bands, which significantly suppress the contribution of heavy holes to the Seebeck coefficient at high temperature.^{19–21} Attempts at modifying the valence band structure of SnTe to improve its *ZT* value have been made recently. Zhang *et al.*⁷ reported a resonant level near the Fermi level of SnTe that was introduced by indium doping, and found a notable enhancement of the Seebeck coefficient. In conjunction with a successful reduction of the thermal conductivity through refinement of the microstructure by ball milling, they reported a *ZT* of 1.1 around 873 K. Han *et al.*^{22,23} reported a *ZT* of 0.9–1 for SnTe–AgSbTe₂ alloys. Recently, an exciting *ZT* of

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† Electronic supplementary information (ESI) available: Densities, temperature dependent diffusivity (*D*), heat capacity (*C_p*), Lorenz number (*L*) of Gd_{*x*}Sn_{1–*x*}Te and Ag_{*y*}Gd_{0.06}Sn_{0.94}Te, and STEM/STEM EDS spectra of Gd_{0.06}Sn_{0.94}Te and Ag_{0.11}Gd_{0.06}Sn_{0.94}Te. See DOI: 10.1039/c6ta01994c

~ 1.4 at 923 K was achieved for SnTe through codoping of In/Cd together with introduction of CdS nanostructures.²⁴

In this paper, we present the promising thermoelectric performance of highly dense lead-free SnTe co-doped with Gd/Ag (*i.e.* $\text{Ag}_y\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$, $0 \leq y \leq 0.15$) fabricated by a simple solid reaction in sealed tubes, followed by the spark plasma sintering (SPS) technology. The lattice thermal conductivity of SnTe was first optimized through the introduction of nanoprecipitates by doping Gd into SnTe. In conjunction with the adjustment of the phase composition *via* further doping of Ag into $\text{Gd}_x\text{Sn}_{1-x}\text{Te}$, the carrier concentration was reduced accompanied by the enhancement of the Seebeck coefficient. A promising ZT of ~ 1.1 was achieved at 873 K for our optimized sample (*i.e.* $\text{Ag}_{0.11}\text{Gd}_{0.06}\text{SnTe}_{0.94}$), which is comparable to that of state-of-the-art Mg-,²⁵ Cd-,¹⁰ and In-⁷ alloyed SnTe-based materials.

Experimental section

Materials

Tin (Sigma Aldrich, 99.8%), tellurium (Sigma Aldrich, 99.8%), gadolinium (Sigma Aldrich, 99%) and silver (Sigma Aldrich, 99.9+%) were used for synthesis without any further purification.

Sample preparation

Ingots (~ 6 g) of $\text{Gd}_x\text{Sn}_{1-x}\text{Te}$ and $\text{Ag}_y\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ were synthesized by mixing appropriate ratios of high-purity Sn, Te, Gd and Ag in quartz tubes in an argon filled glovebox. The tubes were flame-sealed under vacuum and slowly heated to 1173 K over 10 h, held at this temperature for 15 h, and then quenched in an ice water bath. The resultant ingots were crushed into fine powders and then densified by the SPS method at 773 K for 5 min in a 20 mm-diameter graphite die under an axial compressive stress of 50 MPa in a vacuum. Highly dense ($>95\%$ of theoretical density) disk-shaped pellets were obtained.

Characterization

Electrical properties. The obtained highly dense pellets were cut into bars with a dimension of $8 \times 3 \times 3 \text{ mm}^3$ to be used for the simultaneous measurement of the Seebeck coefficient and the electrical conductivity on an Ozawa RZ2001i (Japan) instrument under a helium atmosphere from room temperature to 823–873 K.

Thermal conductivity. Highly dense pellets were cut and polished into $\Phi 10 \times 1 \text{ mm}^3$ disks for the thermal diffusivity measurements. The samples were coated with a thin layer of graphite to minimize errors from the emissivity of the material. The thermal conductivity was calculated from $\kappa = DC_p d$, where the thermal diffusivity coefficient (D) was measured using the laser flash diffusivity method in a Linseis LFA1000 (Germany), and the specific heat capacity (C_p) was indirectly derived from a representative sample (DSC 204) over the range of 323–573 K, and then simulated to 873 K based on the Debye module. The density (d) was measured by the Archimedes method.

Hall measurements. The carrier concentration and carrier mobility were determined by Hall coefficient measurements at room temperature with a PPMS-9 system. Four contact Hall-bar geometry was used for the measurement. At 300 K, the carrier concentration (N_p) and carrier mobility (μ) were estimated from the formulae: $N_p = 1/(eRH)$ and $\mu = \sigma RH$, where e and σ are the electronic charge and the electrical conductivity.

Electron microscopy and X-ray diffraction. (Scanning) transmission electron microscopy (S/TEM) and STEM energy dispersive spectroscopy (EDS) were performed using a JEOL ARM200F microscope with an accelerating voltage of 200 kV. The thin TEM specimens were prepared by conventional methods, including cutting, grinding, dimpling, and tripod polishing, with minimal duration of Ar-ion milling with a liquid N_2 cooling stage. Samples ground in an agate mortar were used for powder X-ray diffraction (XRD). The XRD patterns were obtained with Cu $K\alpha 1$ ($\lambda = 1.5418 \text{ \AA}$) radiation in a reflection geometry on an Inel diffractometer operating at 40 kV and 25 mA, and equipped with a position sensitive detector. High resolution synchrotron X-ray diffraction was applied on representative powders of $\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ at 300 K in the Australian Synchrotron.

Results and discussion

The strategy for enhancing the thermoelectric performance of SnTe consists of two rational steps. First, the lattice thermal conductivity of SnTe is reduced by introducing nanoprecipitates through Gd doping. The sample with the lowest thermal conductivity is then chosen for further improvement in electrical properties *via* adjusting the carrier concentration and phase composition by doping Ag into $\text{Gd}_x\text{Sn}_{1-x}\text{Te}$.

Doping with Gd

Fig. 1(a) presents the powder XRD patterns of sintered samples of $\text{Gd}_x\text{Sn}_{1-x}\text{Te}$ ($x = 0, 0.02, 0.04, 0.06$, and 0.08). The main Bragg reflections of all the samples correspond well to the rock-salt structure, indicating SnTe as the major phase. For Gd-doping samples with dopant concentration above 0.02, some very small peaks with the 2θ value around $30\text{--}33^\circ$ were observed, which

Fig. 1 (a) Powder XRD patterns of $\text{Gd}_x\text{Sn}_{1-x}\text{Te}$ ($x = 0\text{--}0.08$) samples; (b) powder synchrotron XRD pattern of the $\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ sample; (c) the lattice parameter as a function of x at room temperature.

indicates a low solubility limit for Gd in SnTe, *i.e.* smaller than 0.04. In order to identify these small peaks, a representative sample of $\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ was subjected to a high resolution synchrotron X-ray diffraction measurement at 300 K. They were indexed to Sn (200), GdTe_3 (113) and Sn (101) with the $2\theta = \sim 30.8^\circ$, $\sim 31.2^\circ$, and $\sim 32.1^\circ$, respectively, as shown in Fig. 1(b). The existence of GdTe_3 contributes a “Sn-rich” system to the matrix, and the excessive Sn is expected to precipitate once all the intrinsic Sn lattice vacancies are compensated.⁷ This can be confirmed by the changes of lattice parameter as shown in Fig. 1(c). The lattice parameter as a function of x increases gradually with increasing Gd content and then saturates at $x \geq 0.04$. The increased lattice parameters are attributed to the Sn self-compensation until $x \sim 0.04$. The result is close to that of Sn doped samples, which suggests that the limit for Sn compensation in SnTe is ~ 0.03 .¹⁰

Fig. 2(a) displays the total thermal conductivity, κ_{tot} , as a function of temperature for $\text{Gd}_x\text{Sn}_{1-x}\text{Te}$ ($x = 0, 0.02, 0.04, 0.06$, and 0.08). The thermal conductivities of these samples overall decrease with the increase of temperature. They also first gradually decrease and then increase with increasing Gd content, approaching the minimum value of $\sim 1.3 \text{ W m}^{-1} \text{ K}^{-1}$ at the optimal Gd dopant concentration (*i.e.* $x = 0.06$). The total thermal conductivity consists of the electronic thermal conductivity, κ_{el} and the lattice thermal conductivity, κ_{lat} . The electronic contribution can be evaluated by the Wiedemann–Franz formula $\kappa_{\text{el}} = L\sigma T$, where L , σ , and T are the Lorenz number, electrical conductivity, and absolute temperature, respectively. In our work, the L value is obtained from the accepted equation $L = 1.5 + \exp[-|\alpha|/116]$, where L is in $10^{-8} \text{ W } \Omega \text{ K}^{-2}$ and α in $\mu\text{V K}^{-1}$,²⁶ and the data details can be found in the ESI.†

The lattice thermal conductivity κ_{lat} is then calculated by subtracting κ_{el} from κ_{tot} , and the results are shown in Fig. 2(b). A significant decrease in κ_{lat} has been achieved in the $\text{Gd}_x\text{Sn}_{1-x}\text{Te}$ ($x = 0\text{--}0.08$) samples compared to the pristine SnTe. The κ_{lat} as a function of x decreases with increasing Gd concentration and then increases in a similar way to the total thermal conductivity, which suggests that there is an optimal dopant concentration for the formation of nanoprecipitates to achieve the strongest phonon scattering.²⁷ $\text{Gd}_x\text{Sn}_{1-x}\text{Te}$ samples doped with 4 atom%

and 6 atom% Gd have a similar κ_{lat} , $\sim 0.6 \text{ W m}^{-1} \text{ K}^{-1}$, and the $\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ is chosen for further Ag incorporation due to its overall lower thermal conductivity. The $\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ sample has a κ_{lat} of $\sim 1.6 \text{ W m}^{-1} \text{ K}^{-1}$ at 323 K, decreases to the minimum ($\sim 0.63 \text{ W m}^{-1} \text{ K}^{-1}$) with temperature increasing to 573 K, and reaches $\sim 0.81 \text{ W m}^{-1} \text{ K}^{-1}$ at 873 K. The lower lattice thermal conductivity is close to the theoretical minimum, κ_{min} ($\sim 0.5 \text{ W m}^{-1} \text{ K}^{-1}$) for SnTe-based materials.²⁸ This value is also comparable to $0.6 \text{ W m}^{-1} \text{ K}^{-1}$ of the Hg-doped SnTe sample reported by Tan *et al.*⁹

To understand the origin of the lower lattice thermal conductivity, the microstructures and chemical compositions of the $\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ sample were investigated by TEM, STEM and EDS. Fig. 3(a) shows low-magnification images of high-density nanoscale precipitates with a wide range of size ($\sim 2\text{--}30 \text{ nm}$) and dark contrast. These nanoprecipitates are shown with two morphologies (red circles for the bigger ones and yellow squares for the smaller ones). Their size distribution was counted, and most of them are in the range of 2 to 6 nm as shown in Fig. 3(b). These nanoprecipitates are the main cause of phonon scattering due to mass fluctuation between the precipitates and the matrix, especially targeting the medium wavelength phonons.²⁹ The inset of Fig. 3(a) is the selected area diffraction (SAD)

Fig. 2 (a) Total thermal conductivity (κ_{tot}); (b) lattice thermal conductivity (κ_{lat}) as a function of temperature for SnTe with different Gd contents.

Fig. 3 Electron microscopy image of the $\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ specimen. (a) Low-magnification image of the specimen along the $[0\text{--}11]$ zone axis shows both larger nanoprecipitates (red circles) and smaller nanoprecipitates (dashed yellow rectangles) in the matrix. The inset shows the corresponding SAD pattern. (b) Histograms of the precipitate size for $\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$, with the inset showing the corresponding area used to analyse the nanoprecipitate size. (c) HRTEM image of one of the smaller nanoprecipitates, with the inset presenting the IFFT image of the dashed yellow rectangle, showing that the Moiré patterns exist on the surface between the nanoprecipitate and the matrix. (d) HRTEM image of a larger nanoprecipitate. Dislocation arrays with a periodic spacing of $\sim 2 \text{ nm}$ were observed and are highlighted by red arrows, with the inset showing the morphology of a larger nanoprecipitate.

Fig. 4 (a) Electrical conductivity; (b) Seebeck coefficient; (c) power factor; (d) ZT as a function of temperature for $Gd_xSn_{1-x}Te$ ($x = 0–0.08$) samples.

pattern along the $[0–11]$ orientation with an aperture that captures both the matrix and the precipitates. Two sets of Bragg diffraction spots indicate the presence of lattice mismatch between the matrix and the nanoprecipitates. To investigate the distribution of elements in $Gd_{0.06}Sn_{0.94}Te$, electron energy loss spectroscopy (EELS) elemental mapping was performed and the images are shown in Fig. S1 in the ESI.† The images clearly demonstrate that the bigger nanoprecipitates (labelled with red circles) are rich in Sn, while the smaller ones (labelled with yellow squares) are rich in Gd, and Te is uniformly distributed. The high resolution TEM (HRTEM) image in Fig. 3(c) shows a Gd-rich nanoscale precipitate (square with dashed yellow lines) embedded in the matrix. Moiré fringes are observed at interfaces due to the lattice overlap of $GdTe_3$ and the matrix,⁹ which can be identified by its inverse fast Fourier transform (IFFT) image inserted in Fig. 3(c). Other positions of Moiré patterns are observed in grain boundaries (Fig. S2†). The Moiré patterns indicate that the grains in precipitates and the matrix are highly crystalline, with clean interfaces and/or boundaries where obscured dislocations exist.³⁰ The Moiré patterns could deteriorate electrical properties, although they provide sufficient atomic strains to scatter heat-carrying phonons.

In addition to Moiré patterns, dislocation arrays with a periodic spacing of ~ 2 nm were observed in Sn-rich larger nanoprecipitates, as shown by the typical HRTEM image in Fig. 3(d). These dislocation arrays target intermediate wavelength phonons which cannot be scattered sufficiently by the smaller nanoprecipitates.³⁰ It is known that phonons in a material carry most of the heat and have a spectrum of wavelengths and mean free paths (MFP), each of which contributes to the total thermal conductivity. In our case, the long MFP phonons are mainly scattered by mesoscopic particles around 500 nm in size that are obtained through sintering as shown in Fig. S2.†²⁹ The medium MFP phonons, giving

predominant contributions to the lattice thermal conductivity, are scattered by the dislocation arrays together with nanoprecipitates based on mass fluctuation. Therefore, in Gd-doped SnTe samples, the phonons were effectively scattered from nano- to micro-length scales.

Fig. 4 shows the temperature dependence of thermoelectric properties of $Gd_xSn_{1-x}Te$ ($x = 0–0.08$). The room temperature electrical conductivity of the pristine SnTe is ~ 6300 S cm^{-1} . It systematically decreases with dopant content x increasing from 0 to 0.04, and then nearly remains unchanged at ~ 2500 S cm^{-1} when $x \geq 0.06$ [Fig. 4(a)]. The decrease in the electrical conductivity is ascribed to the reduced hole concentration. Moreover, the introduced nanoprecipitates, Moiré fringes and dislocation arrays also significantly influence carrier mobility.

The Seebeck coefficients of $Gd_xSn_{1-x}Te$ ($x = 0–0.08$) samples as a function of temperature are presented in Fig. 4(b). The undoped sample possesses a low Seebeck coefficient of ~ 26 $\mu V K^{-1}$ at room temperature because of its high hole concentration as mentioned above. With increase of dopant concentration x , their room temperature Seebeck coefficients changed slightly, however, they increase faster at high temperature, which is attributed to the increasing contribution of the heavy-hole Σ band at high temperature due to the thermal excitation.²⁹ The contribution of the heavy-hole band at high temperature can be enhanced once a significant number of Sn vacancies were removed.¹⁰ The maximal Seebeck coefficient of 160 $\mu V K^{-1}$ is obtained from $Gd_{0.06}Sn_{0.94}Te$ at 873 K, which is 60% enhancement over pristine SnTe.

Fig. 4(c) shows the temperature dependence of power factors for $Gd_xSn_{1-x}Te$ ($x = 0–0.08$) samples. Their power factors are deteriorated as a result of Gd incorporation into all temperatures due to their decreased electrical conductivities, although the Seebeck coefficient is significantly increased due to the compensation of Sn vacancies. Nevertheless, due to the benefit of the significant reduction in thermal conductivity, their ZT values are enhanced with increase of Gd content over the whole temperature range. A ZT of 0.6 at 873 K is obtained in $Gd_{0.06}Sn_{0.94}Te$, which represents $\sim 50\%$ improvement over undoped SnTe.

Further doping with Ag

To further improve the thermoelectric properties of SnTe, an optimized Gd-doped SnTe sample (*i.e.* $Gd_{0.06}Sn_{0.94}Te$) was

Fig. 5 (a) Powder XRD patterns of $Ag_yGd_{0.06}Sn_{0.94}Te$ ($y = 0–0.15$) samples, with the inset showing enlarged powder XRD patterns in the range of 38° to 43° (2θ deg.); (b) lattice parameter and (c) carrier concentration as a function of y at room temperature.

selected to dope with different contents of Ag. The XRD patterns of the resultant samples ($\text{Ag}_y\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$, $y = 0, 0.03, 0.05, 0.07, 0.09, 0.11, 0.13$ and 0.15) show the NaCl-type structure as the main phase [Fig. 5(a)]. A trace of the Ag_4Sn phase is detected in the samples with dopant concentration above 0.05 (*i.e.* $y \geq 0.05$). The absence of GdTe_3/Sn , which was detected in the $\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ sample, suggests that doping Ag into $\text{Gd}_x\text{Sn}_{1-x}\text{Te}$ changes the crystal structure and the composition of $\text{Gd}_x\text{Sn}_{1-x}\text{Te}$. Fig. 5(b) shows the lattice parameter as a function of Ag concentration y for $\text{Ag}_y\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ samples. The lattice parameter decreases gradually with increasing Ag content, and then slightly increases at $y > 0.05$. The drastic decrease in the lattice parameter also suggests that Ag reacted with Sn to produce Ag_4Sn , not substituted Sn. This is supported by the fact that the Ag^+ radius (0.126 nm) is larger than that of Sn^{2+} (0.093 nm), and the cell parameters of Ag_4Sn ($a = b = 2.966 \text{ \AA}$, $c = 4.782 \text{ \AA}$) are much smaller than that of SnTe ($a = 6.319 \text{ \AA}$).

The trend of the room temperature Hall carrier concentration (N_p) as a function of y is in a good agreement with that of the lattice parameter [Fig. 5(c)]. The hole concentration in the undoped $\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ sample is up to $\sim 3.6 \times 10^{21} \text{ cm}^{-3}$, but it clearly decreases to $\sim 1.4 \times 10^{20} \text{ cm}^{-3}$ with doped Ag concentration increasing from 0 to 0.07 and then increases to $\sim 5 \times 10^{20} \text{ cm}^{-3}$ with further increase of Ag content to 0.15. The decreased Hall carrier concentration is attributed to the fact that Gd is a donor dopant for SnTe, and doping of Gd into SnTe leads to the decrease of electrical conductivity. Below the critical dopant concentration (*i.e.* $y < 0.07$), the formation of Ag_4Sn could boost the homogenous distribution of Gd in SnTe, however, the formation of Ag_4Sn above the critical dopant concentration ($y \geq 0.07$) leads to Sn vacancies and an increase of the hole concentration.

To demonstrate that Ag doping led to the homogenous distribution of Gd in SnTe, $\text{Ag}_y\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ samples were characterized with TEM. Fig. 6(a) shows the typical low-magnification image of the $\text{Ag}_{0.11}\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ specimen. In comparison with the Gd-doped SnTe sample in Fig. 3, only one type of

uniform nanoprecipitate (red arrows) is observed in the SnTe matrix, and only one set of Bragg diffraction spots appears in the inset SAD pattern taken with an aperture that captures both the matrix and the nanoprecipitates. This result suggests no distinguishable difference between the matrix and the nanoprecipitates, owing to their small lattice mismatch. Most of the nanoscale precipitates in this sample are in the range of 5 to 7 nm [Fig. 6(b)]. The HRTEM image in Fig. 6(c) depicts a coherent nanoscale precipitate (circled with the dashed red line) that is embedded in the matrix. No defects or discontinuities in lattice fringes are observed at the matrix/precipitate interface, confirming coherently strained nanoscale endotaxial precipitates.

To further demonstrate the homogenous distribution of Gd in SnTe after Ag doping, elemental mapping of the $\text{Ag}_{0.11}\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ sample was carried out. The low magnification STEM image in Fig. 7(a) shows uniform nanoprecipitates with white contrast, which are proved to be an Ag rich area by mapping Ag [Fig. 7(b)]. In contrast, Sn, Te and Gd are uniformly distributed in both nanoprecipitates and the matrix, as shown in Fig. 7(c–e). Similar to the element mapping, the EDS spectra collected from the matrix and nanoprecipitates demonstrate that the matrix is SnTe doped with traces of Gd and Ag, and the nanoprecipitates have more Ag as shown in Fig. S5.†

Fig. 8 shows the temperature dependence of the thermoelectric properties of $\text{Ag}_y\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ ($y = 0\text{--}0.15$) samples with different Ag contents. Their electrical conductivities decrease with increasing temperature, as displayed in Fig. 8(a), indicating the typical behaviour of degenerate semiconductors. For all Ag/Gd codoped samples, their electrical conductivities are much lower than that of undoped SnTe. The room temperature electrical conductivity decreases from $\sim 6 \times 10^5 \text{ S m}^{-1}$ for pristine SnTe to $\sim 3 \times 10^5 \text{ S m}^{-1}$ for doped counterparts. Moreover, with increase of dopant Ag content, the room temperature σ values show a decreasing tendency, followed by an increase, which is consistent with the results expected with reduced carrier concentration [Fig. 5(c)]. It is important to note that the electrical conductivities of $\text{Ag}_y\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ samples show a turnover at $\sim 723 \text{ K}$, which suggests the occurrence of electron–hole bipolar effects in these samples with lower carrier concentrations at high temperature.¹⁰

Fig. 6 Electron microscopy of the $\text{Ag}_{0.11}\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ specimen. (a) Low-magnification image of the specimen along the [001] zone axis shows even nanoprecipitates in the matrix. The inset shows the corresponding SAD pattern. (b) Histogram of precipitate size for $\text{Ag}_{0.11}\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$. (c) HRTEM image of one of the nanoprecipitates.

Fig. 7 STEM EDS spectrum image of $\text{Ag}_{0.11}\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$. (a) Low magnification STEM image shows Ag-rich particles in the matrix; (b)–(e) corresponding EDS mapping of Ag, Gd, Sn, and Te elements, respectively. A whiter colour in the element maps corresponds to higher concentrations.

Fig. 8 Thermoelectric properties as a function of temperature for $\text{Ag}_y\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$: (a) electrical conductivity; (b) Seebeck coefficient; (c) power factor; (d) total thermal conductivity; (e) lattice thermal conductivity; (f) ZT .

Contrast to the behaviour of the electrical conductivity, the Seebeck coefficient (α) values of Gd/Ag doped samples increase in all temperature ranges without any evidence of deterioration [Fig. 8(b)]. Moreover, the room temperature Seebeck coefficient gradually increases with increasing Ag fraction, although the reduced N_p is expected to suppress the contribution of heavy holes to the Seebeck coefficient due to the higher Fermi level.¹⁰

This could be explained if the Gd could widen the band gap of SnTe. We could not resolve the band gap (E_g) of the $\text{Ag}_y\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ ($y = 0-0.15$) samples by diffuse infrared (IR) reflectance spectroscopy, as the present samples are highly self-doped (carrier concentration is of $\sim 10^{20}$ to 10^{21} cm^{-3}) due to the intrinsic Sn vacancies. In fact, the band gap is related to the Seebeck coefficient by the Goldsmid relation $E_g \approx 2e\alpha_{\text{max}}T_{\text{max}}$.³¹ The significant increase in the Seebeck coefficients of doped samples compared with pristine SnTe suggests that chemical doping effectively broadened the band gap of SnTe. The negligible difference in the Seebeck coefficients of $\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ and $\text{Ag}_y\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ ($y = 0-0.15$) samples demonstrates that Gd is an effective dopant to tune the band gap of SnTe.

Fig. 8(c) plots the power factors as a function of temperature for $\text{Ag}_y\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ ($y = 0-0.15$). With the benefits of the significant enhancement in the Seebeck coefficient and electrical conductivity at high temperature, the maximum power factor of $\sim 1800 \mu\text{W m}^{-1} \text{ K}^{-2}$ was reached in the $\text{Ag}_{0.11}\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ sample at 873 K.

The temperature dependence of the total thermal conductivity and the lattice thermal conductivity of $\text{Ag}_y\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ ($y = 0-0.15$) is shown in Fig. 8(d and e). The κ_{tot} values of all Gd/Ag codoped samples are significantly decreased due to the reduction in κ_{lat} . It should be noted that the κ_{lat} values of $\text{Ag}_y\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ samples are still relatively low compared to those of Cd¹⁰ and Hg⁹ doped SnTe. Typically, the κ_{lat} of $\text{Ag}_{0.11}\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ at room temperature is $1.8 \text{ W m}^{-1} \text{ K}^{-1}$, which is decreased to $\sim 0.6 \text{ W m}^{-1} \text{ K}^{-1}$ at 873 K. Fig. 8(f) presents the temperature dependence of ZT of $\text{Ag}_y\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ ($y = 0-0.15$). The highest ZT of ~ 1.1 at 873 K was achieved in $\text{Ag}_{0.11}\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$, which is $\sim 200\%$ improvement over the pristine SnTe.

Table 1 compares the thermoelectric properties of $\text{Ag}_{0.11}\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ with those of In-, In/Se-, Bi/HgTe-, Bi/SrTe-, Cd/CdS-, In/Cd/CdS- and Mg-doped SnTe. It clearly shows that our sample has a medium electrical conductivity and a Seebeck coefficient, and the lowest lattice thermal conductivity in comparison with those previously reported SnTe-based materials. It has a ZT (~ 1.1 at 873 K) comparable to that of In-doped SnTe (~ 1.1 at 873 K),⁷ Cd/CdS-doped SnTe (~ 1.3 at 873 K),¹⁰ In/Cd-doped SnTe (~ 1.4 at 873 K)²⁴ at the same temperature.

Table 1 Comparison of thermoelectric properties of Gd/Ag doped SnTe with those of In-,⁷ In/Se-,³² Bi/HgTe-,⁹ Bi/SrTe-,³³ Cd/CdS-,¹⁰ In/Cd/CdS-²⁴ and Mg-²⁵ doped SnTe

Composition	$\sigma, 10^4 \text{ S m}^{-1}$	$\alpha, \mu \text{ V K}^{-1}$	$\alpha^2\sigma, 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$	$\kappa_{\text{lat}}, \text{ W m}^{-1} \text{ K}^{-1}$	ZT	Reference
$\text{In}_{0.0025}\text{Sn}_{0.9975}\text{Te}$ (873 K)	~ 7.0	~ 170	~ 2.0	~ 0.90	~ 1.1	7
$\text{In}_{0.015}\text{Sn}_{0.985}\text{Te}_{0.85}\text{Se}_{0.15}$ (855 K)	~ 6.4	~ 175	~ 1.9	~ 1.25	~ 0.8	32
$\text{Sn}_{0.98}\text{Bi}_{0.02}\text{Te}$ -3% HgTe (923 K)	~ 8.0	~ 185	~ 2.7	~ 0.70	~ 1.35	9
$\text{Sn}_{0.97}\text{Bi}_{0.03}\text{Te}$ -3% SrTe (823 K)	~ 7.0	~ 170	~ 2.0	~ 0.80	~ 1.2	33
$\text{SnCd}_{0.03}\text{Te}$ -2% CdS (873 K)	~ 4.5	~ 200	~ 1.8	~ 0.63	~ 1.3	10
$\text{Sn}_{0.97}\text{In}_{0.015}\text{Cd}_{0.015}\text{Te}$ -2% CdS (873 K)	~ 5.6	~ 200	~ 2.2	~ 0.60	~ 1.4	24
$\text{Sn}_{0.94}\text{Mg}_{0.06}\text{Te}$ (856 K)	~ 10.0	~ 175	~ 3.0	~ 0.78	~ 1.2	25
$\text{Ag}_{0.11}\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ (873 K)	~ 5.6	~ 180	~ 1.8	~ 0.59	~ 1.1	In this work

Conclusions

Lead-free high performance SnTe thermoelectric materials were rationally designed and prepared through chemical doping of Gd and Ag *via* two steps. The first step is doping Gd into SnTe to effectively reduce the lattice thermal conductivity *via* introduction of nanoprecipitates. The large mass contrast between the nanoprecipitates and the matrix, together with the increased grain boundaries from mesoscale grains the heat-carrying phonons strongly scattered from nano- to mesoscales. The second step is doping Ag into optimized $\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$ to improve the Seebeck coefficient and power factor by tuning its composition to reduce the carrier density. The maximum ZT of ~ 1.1 at 873 K was successfully obtained in $\text{Ag}_{0.11}\text{Gd}_{0.06}\text{Sn}_{0.94}\text{Te}$. Our research highlights the potential of SnTe-based thermoelectric materials by engineering their compositions to tune the electrical conductivity, Seebeck coefficient and thermal conductivity, as alternatives of lead chalcogenides in the near future.

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