High Thermoelectric Performance Achieved in Sb-doped GeTe by Manipulating Carrier Concentration and Nanoscale Twin Grains

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Abstract: Lead-free and eco-friendly GeTe shows a promising candidate for mid-temperature thermoelectric application. However, a low Seebeck coefficient due to its intrinsically high holes concentration that induced by Ge vacancies, and a relatively high thermal conductivity result in an inferior thermoelectric performance of pristine GeTe. However, extrinsic atoms Sb, Bi, and Y could play a crucial role in regulating the holes concentration of GeTe because of their relatively high solubility. Here we investigate the thermoelectric performance of the GeTe upon Sb doping, and demonstrate a high maximum $zT$ value up to 1.88 could be achieved in Ge$_{0.90}$Sb$_{0.10}$Te as a result of the significant suppression in thermal conductivity while holding a high power factor. Where the maintained high power factor is due to the markable enhancement in $S$, which could be attributed to the significant suppression of holes concentration and the valence band convergence upon Sb doping; while the low thermal conductivity stems from the suppression of electronic thermal conductivity due to the increase in electrical resistivity and the lowering of lattice thermal conductivity through strengthening the phonons scattering by the lattice distortion, dislocations, and twin boundaries. Aside from the excellent thermoelectric performance, Ge$_{0.90}$Sb$_{0.10}$Te also shows good reproducibility, as well as thermal stability. This work confirms the Ge$_{0.90}$Sb$_{0.10}$Te is a superior thermoelectric material for practical application.

Keywords: GeTe; Sb-doping; optimizing carrier concentration; and nanoscale twin grains

1 Introduction

Thermoelectric (TE) materials can convert heat directly into available electricity based on the Seebeck effect, providing an alternative way to utilize fossil energy more
The thermoelectric material performance can be estimated by the dimensionless figure of merit $zT = S^2T/\rho\kappa$, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $T$ is the absolute temperature, and $\kappa$ is the thermal conductivity, which usually stems from the crystal lattice vibrations ($\kappa_l$) and the charge carriers drift ($\kappa_e$). Hence, a good thermoelectric material should have a large $\sigma$ and $S$ along with a low $\kappa$.

In recent decades, IV-VI semiconductors with a narrow band gap have made a great progress in terms of theory and TE performance, showing a bright prospect in TE application [5–8]. For example, the maximum $zT$ exceeds 2.5 has been attained in PbTe-based TE materials [9–12], however, the toxicity of Pb limits its commercialization [13]. GeTe is an eco-friendly counterpart in the family of IV-VI semiconductors, which also exhibits an excellent TE performance [13,14]. Differently, it undergoes ferroelectric structural transition, which transforms from low-temperature rhombohedral phase (R$\bar{3}$m, the primitive cell could be regarded as a slightly distorted cubic along <111> direction) into high-temperature cubic one (Fm$\bar{3}$m) with Curie temperature between 600–700 K [15]. It is believed that such a slight symmetry-breaking is conducive to converging of the splitting valence bands and reducing the $\kappa_l$.

Additionally, some elements such as Sb, Bi, and Y generally have a high doping limit in GeTe, for instance, the doping limit for Sb exceeds 10%. Undoubtedly, such features are beneficial to adequately optimize the electronic transport properties, and in turn, yield a high $zT$, e.g., the maximum $zT$ over 2 is attainable in (Bi, Cu), (Bi, Pb), (Sb, Pb) and (Sb, In) codoping systems [16–20].
However, the pristine GeTe commonly exhibits an inferior TE performance due to its low $S$ and high $\kappa$, i.e., the large number of Ge vacancies causes a high holes concentration ($\sim 10^{21}$ cm$^{-3}$), a low $S$ ($\sim 34 \mu$V K$^{-1}$), and a high $\kappa$ ($\sim 8$ W m$^{-1}$ K$^{-1}$) at room temperature [21]. To suppress Ge vacancies and holes concentration, Cu interstitials and Sb/Bi/Y substitutions were introduced into GeTe matrix in order to offset the excess holes or increase the formation energy of Ge vacancy, for example, the holes concentration approaching to $\sim 10^{20}$ cm$^{-3}$ could be obtained by Sb/Bi/Y doping, and the available maximum $zT$ is up to 1.7–1.85 [22–25]. Aside from holes concentration optimization, the resonant doping and valence band alignment could also increase the $S$. It has been demonstrated that In/Ga/Ti doping could arise the resonant level around the Fermi level [26–29], and Mn/Cd/Zn doping could decrease the split energy between light and heavy valence bands for GeTe [17,30,31]. Popularly, a strategy, combining the carrier concentration optimization with band alignment or resonant doping, is used to optimize the electronic transport properties [26,27,32,33].

Admittedly, a high doping limit of extrinsic atoms will bring about a significant lattice disorder, resulting in atomic mass and lattice strain fluctuation that endow a low $\kappa_l$ by the reinforcement of phonons scattering [34]. For example, the room temperature $\kappa_l$ is in the range of 1.0–1.5 W m$^{-1}$ K$^{-1}$ for GeTe systems with about 10 at% Sb/Bi/Pb introduction, which is much lower than that of the pristine GeTe (2.7 W m$^{-1}$ K$^{-1}$) [35,36]. Obviously, the $\kappa_l$ would be further suppressed in codoping systems, for instance, $\sim 0.5$ W m$^{-1}$ K$^{-1}$ was attained in Ge$_{0.88-y}$Sb$_{0.08}$Pb$_y$Te and Ge$_{0.85}$Bi$_{0.05}$Sb$_{0.10}$Te alloys at room temperature [37]. Surely, it is not always true for simply attributing the reduction
in $\kappa_l$ to the atomic mass and lattice strain fluctuation induced by the point defects. With
the substitution of extrinsic atoms on Ge sites, the evolution of microstructures is
complicated, such as precipitates [19,23,38,39], stacking faults [36,40,41], inversion
domain and twin [15,23,42−44], as well as herringbone domain structure might occur
[42], which also play an important role in strengthening the phonons scattering. In brief,
doping/alloying is an indispensable strategy for the enhancement of TE performance of
GeTe through properly regulating the electronic and phonons transport properties,
which is benefited from the various options of extrinsic atoms and their relatively high
solubility in GeTe matrix.

Here, we systematically investigate the TE performance of Ge$_{1-x}$Sb$_x$Te ($x = 0, 0.05,$
0.10, 0.15, and 0.20), which were prepared by the solid-state reaction and spark plasma
sintering (SPS) route. It demonstrates that a maximum $zT$ as high as 1.88 at 773 K could
be attained in Ge$_{0.90}$Sb$_{0.10}$Te with good reproducibility and thermal stability. With Sb
substitution on Ge sites, the $S$ is greatly improved due to the reduction in holes
concentration and valence band convergence. Moreover, a significantly reduced $\kappa$ is
attained, which originates from both the decrease in $\kappa_e$ and $\kappa_l$. TEM observations verify
the existence of nanoscale twins and dislocations in the matrix, which together with
point defects (Sb substitutions and residual Ge vacancies) result in a low $\kappa_l$, i.e., $\sim 0.89$
W m$^{-1}$ K$^{-1}$ in Ge$_{0.90}$Sb$_{0.10}$Te at 773K. This work confirms Ge$_{0.90}$Sb$_{0.10}$Te is a reliable
candidate for TE application.

2 Experimental Section

Polycrystalline samples Ge$_{1-x}$Sb$_x$Te ($x = 0, 0.05, 0.10, 0.15, 0.20$) were prepared
through a solid-state reaction followed by spark plasma sintering (SPS) procedure.

High-purity (> 4N) elements of Ge, Sb, and Te were weighted in the corresponding mole ratio and flame-sealed in quartz tubes under a vacuum lower than $5 \times 10^{-4}$ Pa. The tubes were heated to 1173 K and soaked for 6 h, both of heating and cooling rate is 1 K min$^{-1}$. These as-synthesized ingots were hand-ground into fine powders and then consolidated into cylindrical bulks by SPS at 823 K for 3 min under a uniaxial pressure of ~ 50 MPa in a vacuum (< 10 Pa). The relative density for these sintered samples is no less than 95%. Rectangular-shaped specimens (~ 2 mm × 2 mm × 10 mm) and square-shaped pellets (~ 6 mm × 6 mm × 1.5 mm) were cut off for electrical and thermal transport properties measurements, respectively.

The crystal structure of sintered samples was analyzed using a PANalytical X-ray diffractometer (Cu Kα, λ = 0.154 nm) operated at 45 kV and 40 mA with a step size of 0.01313°. The high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and the energy-dispersive X-ray (EDS) mapping were performed on a probe-corrected transmission electron microscopy (TEM; FEI Titan G2) equipped with a super EDS system at 300 kV. The backscattered electron image (BSE) and EDS mapping scanning were employed with electron microscopy (SEM, FEI Helos G4) equipped with a super EDS system.

Room temperature carrier concentration ($\rho$) and mobility ($\mu_H$) were examined using a direct-current ($dc$) Hall effect measurement system (model 8404; Lakeshore Cryotronics, USA) at the excitation current up to 100 mA and magnetic field of 1.5 T. Electrical resistivity ($\rho$) and Seebeck coefficient ($S$) were measured by a static $dc$
method (LSR-3, Germany) under a helium (99.999%) atmosphere. The thermal conductivity ($\kappa$) is calculated by $\kappa = D \, d \, C_p$, where $D$ is the thermal diffusivity, $C_p$ is the specific heat, and $d$ is the volume density. The thermal diffusivity ($D$) was measured by a laser flash method (LFA 457; Netzsch, Germany); the specific heat ($C_p$) was estimated based on Dulong-Petit law, which is approximate to the measurement result; and the volume density ($d$) was determined by the Archimedes method.

### 3 Results and Discussion

Fig. 1 shows the XRD patterns of as-pulverized sintered Ge$_{1-x}$Sb$_x$Te samples. The major diffraction peaks of each sample could be indexed to the rhombohedral structure of GeTe (JCPDS 047–1079). Particularly, the presence of double peaks in the 2$\theta$ range of 23–27° and 41–45° further confirms the pristine GeTe is in rhombohedral phase. While the peaks located at ~ 27.3° and ~ 45.3° are corresponding to cubic Ge (JCPDS 065–0333). The obvious enlarged Ge peaks with rising the Sb content indicates that more Ge precipitates resides in the matrix, which is probably due to Sb atoms occupy on Ge sublattice sites. To examine the impact of Sb doping on the crystal structure of GeTe, we calculated lattice parameters of sintered Ge$_{1-x}$Sb$_x$Te samples and the results are shown in Fig. 1b, which shows the increase in lattice parameter $a$ while decrease in $c$ with rising Sb content, suggesting a smaller $c/a$ ratio. This phenomenon indicates that Sb doping could lower the structural transition temperature of GeTe and promote the occurrence of cubic phase, which is consistent with convergence of (024) and (220) diffraction peaks (Fig. 1a), also agrees with the observations in the Bi- and V-doped cases [24, 41].
Fig. 1 (a,b) Powder XRD patterns and lattice parameters $a$ and $c$ of Ge$_{1-x}$Sb$_x$Te. Where the black square (■) represents Ge precipitates.

We performed SEM and EDS to illustrate the microstructure evolution of GeTe upon Sb doping, as shown in Fig. 2. Fig. 2a shows a BSE image of the pristine GeTe, it can be seen that a small amount of nanoscale precipitates (dark contrast) is embedded into the host matrix (gray contrast). A BSE image of Ge$_{0.90}$Sb$_{0.10}$Te (Fig. 2b) shows that there are many micron-sized precipitates (dark contrast) in the matrix. The EDS mapping images for Ge$_{0.90}$Sb$_{0.10}$Te shown in Fig. 2d unveil the precipitates are Ge particles, which agree with the XRD characterization results. Moreover, the electron channeling contrast image (ECC) is taken on the region marked with the red dotted rectangle to characterize the microstructure of the matrix, as shown in Fig. 2c, which suggests that the matrix is comprised by the 2−10 micron-sized grains, and each grain exhibits lamellar configuration in the size range of 20−500 nm.
Fig. 2 BSE images of the pristine GeTe (a) and Ge$_{0.90}$Sb$_{0.10}$Te (b); (c) magnified ECC image of Ge$_{0.90}$Sb$_{0.10}$Te taken on the region marked by the red dotted rectangle in Fig. 2b; (d) elemental mapping images taken on the region that displayed in Fig. 2b.

The electrical transport properties of the samples Ge$_{1-x}$Sb$_x$Te are shown in Fig. 3. From Fig. 3a, we can see that the $\rho$ of all the samples increases with rising the temperature, showing a degenerate semiconductor behavior. Typically, for the pristine GeTe, the $\rho$ is $\sim 1.26 \times 10^{-6}$ $\Omega$ m at 323 K, which increases to $\sim 5.11 \times 10^{-6}$ $\Omega$ m at 773 K. As Sb substitution on Ge sites could generate a donor type point defect and increase the formation energy of Ge vacancy, the $\rho$ increases with increasing the Sb content. For example, the $\rho$ at 323 K increases from $\sim 1.26 \times 10^{-6}$ $\Omega$ m for the pristine GeTe to 5.01 $\times 10^{-5}$ $\Omega$ m for the sample Ge$_{0.80}$Sb$_{0.20}$Te. The abnormal change in $\rho$ $\sim T$ curves shows a signature of structural phase transition, the transition temperature could be moved to a lower temperature with rising the Sb content, which is also observed in Bi-doped GeTe system, and makes it possible to enhance the TE performance by controlling the distortion degree of the crystal structure from cubic to rhombohedral.
The Hall measurement was carried out on the samples Ge\(_{1-x}\)Sb\(_x\)Te, as shown in Fig. 3b. It clearly shows that the carrier concentration and mobility could be significantly suppressed upon Sb doping, which is mainly due to the generation of the charged substitutional point defects. For example, the room temperature carrier concentration gradually declines from \(\sim 9.02 \times 10^{20}\) to \(\sim 2.01 \times 10^{20}\) cm\(^{-3}\) as the Sb content increases from \(x = 0\) to \(x = 0.15\), then rises to \(\sim 2.55 \times 10^{20}\) cm\(^{-3}\) when \(x = 0.20\), indicating that the doping limit of Sb in GeTe is about 15 at\%, and the doping efficiency is greatly reduced when the Sb content exceeds 10 at\%; while the room temperature carrier mobility monotonically drops from 53 cm\(^2\) V\(^{-1}\) s\(^{-1}\) for the pristine GeTe to 5.9 cm\(^2\) V\(^{-1}\) s\(^{-1}\) for the sample Ge\(_{0.80}\)Sb\(_{0.20}\)Te. Both the declined carrier concentration and mobility lead to the increase in \(\rho\) for the Sb-doped GeTe system.

Fig. 3c shows the temperature-dependent Seebeck coefficient (\(S\)) of the samples Ge\(_{1-x}\)Sb\(_x\)Te. The positive \(S\) suggests that all the samples have a p-type conductive behavior, and the inability of single Sb doping in inversing such conductive behavior. As expected, the \(S\) is greatly improved upon Sb doping, which increases from \(\sim 31 \mu V\) K\(^{-1}\) for the pristine GeTe to \(\sim 119 \mu V\) K\(^{-1}\) for Ge\(_{0.90}\)Sb\(_{0.10}\)Te, and further to \(\sim 173 \mu V\) K\(^{-1}\) for Ge\(_{0.80}\)Sb\(_{0.20}\)Te at 323 K. And a maximum \(S\) up to 249 \(\mu V\) K\(^{-1}\) at 574 K is attained in Ge\(_{0.80}\)Sb\(_{0.20}\)Te.

To find out underlying reason of the enhanced \(S\) of GeTe upon Sb doping, the Pisarenko curve based on a two-valence-band model is plotted in Fig. 3d, and the representative data from the literatures are inserted for comparison. It can be seen that the data for the pristine GeTe fall exactly on the Pisarenko curve, while the data for the
Sb-doped samples lie above the curve, indicating that the valence band convergence could be induced by Sb doping. According to the results of band structure calculations, the apex of heavy valence band is higher than that of the light one for the rhombohedral GeTe, which inverses for the cubic GeTe. As mentioned above, Sb doping promotes the structural transition of GeTe from rhombohedral to cubic, leading to the band convergence by decreasing the split energy between the heavy and light valence bands. Overall, the greatly enhanced $S$ in the Sb-doped GeTe samples could be attributed to the valence band convergence and the holes concentration suppression, as the $S$ is inversely coupled with the carrier concentration.

**Fig. 3** Electrical properties of Ge$_{1-x}$Sb$_x$Te: (a) electrical conductivity; (b) carrier concentration and mobility as a function of the Sb content $x$ at room temperature; (c) Seebeck coefficient; (d) Pisarenko plot. 

Fig. S1 shows the temperature-dependent power factor ($PF$) of the samples
Ge$_{1-x}$Sb$_x$Te. The maximum $PF$ as high as $\sim 4.74 \times 10^{-3}$ W m$^{-1}$ K$^{-2}$ at 773 K is attained in the pristine GeTe. Expectedly, the high $PF$ is maintained when the Sb content not exceeds 10 at% due to the greatly enhanced $S$, in spite of evident increase in $\rho$. The maximum $PF$ up to $\sim 3.23 \times 10^{-3}$ W m$^{-1}$ K$^{-2}$ achieved in Ge$_{0.90}$Sb$_{0.10}$Te is comparable to V-, Y-, Bi-, and Sb-doped counterparts [22,24,25,41].

Fig. 4a shows the temperature-dependent thermal conductivity ($\kappa$) of the samples Ge$_{1-x}$Sb$_x$Te. The $\kappa$ is greatly reduced over the whole temperature range (323–773 K) upon Sb doping, which decreases from $\sim 7.40$ W m$^{-1}$ K$^{-1}$ for the pristine GeTe to 1.61 W m$^{-1}$ K$^{-1}$ for the sample Ge$_{0.90}$Sb$_{0.10}$Te at 323 K. To understand the details in regard to the great reduction of $\kappa$, the $\kappa$ is generally divided into two parts of electronic thermal conductivity ($\kappa_e$) and lattice thermal conductivity ($\kappa_l$). The $\kappa_e$ is calculated according to the Wiedemann-Franz law, $\kappa_e = L \rho^{-1} T$, where $L$ is the Lorentz number estimated on the basis of a two-valence-band model (Fig. S2). As shown in Fig. 4b, it is observed that the $\kappa_e$ for GeTe could be remarkably suppressed upon Sb doping due to the significant decrease in $\rho$. For example, the $\kappa_e$ as high as 5.07 W m$^{-1}$ K$^{-1}$ at 323 K is attained in the pristine GeTe, which dramatically drops to 0.43 W m$^{-1}$ K$^{-1}$ for Ge$_{0.90}$Sb$_{0.10}$Te. The $\kappa_l$ is obtained by subtracting $\kappa_e$ from $\kappa$, i.e., $\kappa_l = \kappa - \kappa_e$. The temperature-dependent $\kappa_l$ of the Ge$_{1-x}$Sb$_x$Te is plotted in Fig. 4c. It indicates that the $\kappa_l$ of GeTe could be substantially suppressed upon Sb doping, e.g., a highest $\kappa_l$ up to $\sim 2.33$ W m$^{-1}$ K$^{-1}$ at 323 K is attained in the pristine GeTe, which decreases to $\sim 1.19$ W m$^{-1}$ K$^{-1}$ for the sample Ge$_{0.90}$Sb$_{0.10}$Te.
Fig. 4 Temperature-dependent thermal properties of Ge$_{1-x}$Sb$_x$Te: (a) thermal conductivity; (b) electronic thermal conductivity; (c) lattice thermal conductivity.

To illustrate the low $\kappa$ of Ge$_{0.90}$Sb$_{0.10}$Te, its microstructural details is investigated by TEM. A typical bright-field TEM image, as shown in Fig. 5a, reveals the stacking lamellas are in alternate bright and dark contrast, and there exist fluctuation in contrast at the edges of the lamellas (marked with the yellow arrows). However, the elemental Ge, Sb, and Te are uniformly distributed in the host matrix according to the EDS mapping results (Fig. 5b), suggesting that the change in bright and dark contrast is unrelated to chemical compositions. A typical selected area electron diffraction (SAED) pattern of lamellas structure can only be indexed as the [1 $\bar{1}$ 2] zone axis with rhombohedral symmetry (see the inset in Fig. 5a), and a HRTEM image is obtained in the same zone axis, which matches with the lattice fringes of the (111) planes of
Moreover, the split diffraction spots far away from the transmitted beam are observed in the SAED pattern, together with the fast Fourier transform (FFT) image (the inset in Fig. 5c) demonstrates that the lamellar structure is caused by the twin grains, which is similar to the herringbone structure observed in Bi-/Sb-doped GeTe samples. Furthermore, the inverse FFT (IFFT) image discloses that there are dislocations at the boundaries of twin grains, which is resulted from the release of strain. Additionally, geometric phase analysis (GPA) is executed to calculate the distribution of strain in the matrix based on the HRTEM image (Fig. 5c), as shown in Fig. 5d, confirming that an obvious strain fluctuation distributes around the dislocations.

It is known that dislocations are very conducive to reducing the $\kappa_l$ by scattering the mid-frequency phonons. Overall, the low $\kappa_l$ of Ge$_{0.90}$Sb$_{0.10}$Te could be attributed to its complex microstructures such as point defects (Sb substitutions and residual Ge vacancies), dislocations, and twin boundaries.

The TE performance of GeTe is greatly enhanced upon Sb doping as a result of holes concentration optimization, band convergence, and the significant decrease in thermal conductivity. A highest $zT$ up to 1.88 is achieved in the sample Ge$_{0.90}$Sb$_{0.10}$Te (Fig. 6a), which is higher than Bi-/In-/Ti-doped counterparts (single extrinsic elemental doping systems) [24,29,45]. It demonstrates that elemental Sb is an outstanding dopant for enhancing the TE performance of GeTe.

More importantly, the high TE performance of Ge$_{0.90}$Sb$_{0.10}$Te is reproducible, which is verified by the repeatable $zT$ of the different batches samples, as shown in Fig. 6b. Additionally, the thermal cycling test was performed on a sample Ge$_{0.90}$Sb$_{0.10}$Te, the
electrical properties remain unchanged during the 2 times heating and cooling cycles (Fig. S3), suggesting an excellent stability of $\text{Ge}_{0.90}\text{Sb}_{0.10}\text{Te}$. These results indicate $\text{Ge}_{0.90}\text{Sb}_{0.10}\text{Te}$ has promising application in commercial TE devices.

**Fig. 5** The microstructure characterization of $\text{Ge}_{0.90}\text{Sb}_{0.10}\text{Te}$: (a) a low-magnification bright-field image, the inset is the SAED pattern taken on the marked region; (b) a HADDF image and the corresponding elemental mappings; (c) a HRTEM image from the marked region in Fig. 5a, the insets are the corresponding FFT images; (d) the distribution of strain calculated by GPA, the inset is the corresponding IFFT image.
Fig. 6 (a) $zT$ value of Ge$_{1-x}$Sb$_x$Te ($x = 0, 0.05, 0.10, 0.15, 0.20$); (b) $zT$ value of the different batches samples Ge$_{0.90}$Sb$_{0.10}$Te.

4 Conclusions

The Ge$_{1-x}$Sb$_x$Te samples were fabricated by the solid-state reaction followed by spark plasma sintering procedure. Sb doping not only leads to an optimized holes concentration approaching to $10^{20}$ cm$^{-3}$ but also results in valence band convergence for GeTe system. Also, the thermal conductivity is greatly reduced due to the suppression of both electronic and lattice thermal conductivity. Where the reduction in electronic thermal is due to the increase of electrical resistivity; while the decline in lattice thermal conductivity is caused by the modification in microstructures, that is, the phonons scattering is remarkably strengthened by substitutional point defects, dislocations, and twin boundaries. As a result, a maximum $zT$ up to 1.88 is achieved in Ge$_{0.90}$Sb$_{0.10}$Te. This work demonstrates Ge$_{0.90}$Sb$_{0.10}$Te is a promising candidate for TE commercial application.

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Electronic Supplementary Material

Supplementary material is available in the online version of this article at Fig. S1, Fig. S2 and Fig. S3.

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