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Tailoring Phase Transition Temperature to Achieve High-Performance Cubic GeTe-based Thermoelectrics

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Abstract: GeTe is highly sought-after due to its versatility as high-performance thermoelectrics, phase change materials, as well as ferroelectric Rashba semiconductor. Compared to most thermoelectric materials, it has an additional degree of freedom of rhombohedral-cubic phase transition at 673 K. At this temperature, the lattice thermal conductivity approaches theoretical minimum due to ferroelectric instability while the high-energy Σ and low-energy L bands converge to give outstanding electronic properties. Therefore, modulation of the phase transition temperature allows simultaneous and synergistic tuning of electronic and thermal transport properties to achieve high zT . In this work, Sn alloying together with Bi, Sb doping is used to suppress the phase transition to achieve a pure cubic structure with lattice thermal conductivity of around 0.4 W/mK and peak zT of 1.7 at 723 K with average zT of 1.23 between 400 and 800 K. Furthermore, Vickers hardness of

270, and Young's modulus of 63.5 GPa in $\text{Ge}_{0.4}\text{Sn}_{0.4}\text{Bi}_{0.02}\text{Sb}_{0.12}\text{Te}$ is by far the highest amongst binary chalcogenides. More importantly, the high quality factor achieved in this work enables ample room for further zT improvements. The fundamental insights drawn from this work provide a pathway towards engineering GeTe-based alloys to achieve high zT at any temperature of interest.

Keywords: Thermoelectrics, GeTe, Electronic transport, Thermal transport, Phase transition, Band gap

1. Introduction

In order for thermoelectric materials to be commercially viable for energy harvesting or cooling devices, decades of efforts have been dedicated to improve the dimensionless figure of merit $zT = S^2\sigma T/(\kappa_L + \kappa_e)$, where S , σ , κ_L and κ_e are the Seebeck coefficient, electrical conductivity, lattice and electronic contributions to the total thermal conductivity, respectively. However, for practical devices, the mechanical properties such as hardness, Young's modulus, and even coefficient of thermal expansion are important parameters that cannot be overlooked.¹ Furthermore, thermoelectrics can be classified as low, medium, and high temperature thermoelectrics in terms of application temperature used. For instance, Bi_2Te_3 and Mg_3Sb_2 -based compounds which have a peak zT around room temperature are currently the most prominent low-temperature thermoelectric materials.² On the other hand, PbTe or SnSe is arguably considered as the most prominent medium-temperature thermoelectric materials in addition to TAGS (Te-Ag-Ge-Sb) compounds (which are the alloys of GeTe-AgSbTe_2).³⁻⁶ Lastly, SiGe is a famous example of high-temperature thermoelectric material that has found applications in NASA (National Aeronautics and Space Administration) space probe. The criteria to determine whether a compound belongs to low, medium, or high-temperature thermoelectric material are largely dependent on the temperature range where the highest value of zT occurs. In order to achieve a high zT , several strategies such as band convergence, nanostructuring and magnetic inclusions are widely employed to improve power factor.⁷⁻¹⁵ Moreover, to induce phonon scattering, complex crystal structure, large lattice anharmonicity and defect engineering such as nanocomposites, dislocation and strain have also been extensively leveraged to reduce lattice thermal conductivity.¹⁶⁻²⁰

Among the prominent thermoelectric compounds, GeTe has been overlooked for decades, and was mainly used as an alloy in TAGS compounds despite the fact that GeTe has a similar or even superior electronic band structure to PbTe.²¹ A pervasive problem hindering widespread attention to this compound is its high concentration of holes in pristine GeTe (p-type) as well as the difficulty in achieving n-type GeTe via doping.^{22, 23} Counter-doping strategies to optimize the carrier concentration have been employed with a great degree of successes.^{16, 23-43} However, only one n-type GeTe-based alloy GeTe-AgBiSe₂ was reported to date.²² Comprehensive summary on latest progresses, challenges, and future potential of GeTe can be found in a recent perspective.⁴⁴

Despite all the challenges, GeTe has recently gained popularity amongst the research community. This is due to its versatility not only as a good thermoelectrics, but also as a popular phase-change material as well as an emerging class of ferroelectric Rashba semiconductor. More interestingly, GeTe has a rather unique feature of rhombohedral-cubic phase transition at around 673 K.¹⁶ From the perspective of thermoelectrics properties, this presents a unique opportunity to synergistically achieve ideal electronic and thermal performances via band-convergence and lowering lattice thermal conductivity near the phase transition temperature.¹⁶

In this work, we sought to leverage on this unique feature of ferroelectric phase transitions in GeTe, and demonstrate the versatility of tuning the phase transition temperature and band-gap so that we can simultaneously control electronic and thermal transport as well as the temperature at which the peak zT occurs. In our first series of samples, we study the effect of Sn alloying on the phase transition temperature in Ge_{1-x}Sn_xTe ($x = 0, 0.1, 0.2, 0.3, 0.4$, and 0.5). A pure cubic phase with no phase transition is realized for $x = 0.4$ and 0.5 in the temperature range of interest (*i.e.* 300 – 800 K). It is evident that our cubic Ge_{1-x}Sn_xTe has superior mechanical properties to pristine GeTe as well as those of other prominent compounds such as PbTe and Bi₂Te₃.⁴⁵⁻⁴⁷ Subsequently, Bi and Sb were used to counter-dope the cubic Ge_{0.5}Sn_{0.5}Te matrix to optimize the carrier concentration. As a result, a high average zT of 1.23 with a peak zT of 1.7 is achieved between 400 to 800 K. In addition, the trends of power factor and Seebeck coefficient points to a higher band-gap in Ge_{0.5}Sn_{0.5}Te (0.42 eV) than in GeTe (0.13 eV), which is also confirmed by density functional theory (DFT) calculations. Lastly, by analyzing the quality factor B , it can be deduced that by further optimizing the carrier concentration, the performance of this compound can reach a zT beyond 2. We propose that by synergistically tuning both phase transition temperature and band-gap, it would be possible to unlock tremendous potential of GeTe to compete with other prominent compounds like Bi₂Te₃, PbTe, PbSe, PbS, SnSe, SnTe and SiGe across all temperature ranges.⁴⁸⁻⁵¹

2. Results and discussion

Due to the larger ionic radius of isovalent Sn^{2+} than Ge^{2+} , the addition of Sn into GeTe system results in a larger lattice parameter, as shown in the X-ray diffraction (XRD) peaks in Figure 1(a). Upon increasing the Sn content, the peak gradually shifted to the lower angles, indicative of larger lattice parameters, according to Bragg's law. In addition to peak shifts, adding more Sn into GeTe causes gradual distortion from rhombohedral structure to cubic structure. The room temperature XRD peaks of both $\text{Ge}_{0.6}\text{Sn}_{0.4}\text{Te}$ and $\text{Ge}_{0.5}\text{Sn}_{0.5}\text{Te}$ can be indexed to cubic structure, in sharp contrast to the pristine rhombohedral GeTe. The observation from the XRD data is consistent with the differential scanning calorimetry (DSC) data (Figure 1(b)) which show that the endothermic peak, corresponding to rhombohedral-cubic phase transition, shifted to lower temperatures with the increase of Sn content. In contrast, no endothermic peak is observed for $\text{Ge}_{0.6}\text{Sn}_{0.4}\text{Te}$ and $\text{Ge}_{0.5}\text{Sn}_{0.5}\text{Te}$, signifying that the rhombohedral phase in these samples are fully suppressed. The origin of this cubic phase stabilization can be associated with the larger ionic radius of Sn^{2+} (118 pm) than Ge^{2+} (73 pm) which results in a higher Tolerance factor, thus stabilizing the cubic phase. In addition, the larger unit cell brought about by the introduction of Sn also contributes to low lattice thermal conductivity.¹⁷ Furthermore, the cubic phase stabilization has also been ascribed to high configurational entropy, albeit without exhaustive explanation about its origin.^{22, 39, 52} As our samples consists of 5 different elements (Ge, Sn, Bi, Sb, and Te), the configurational entropy becomes high. The configurational entropy of mixing can be expressed as:

$$\Delta S = -N_A k_B \sum x_i \ln x_i \quad (1)$$

Where N_A , k_B and x_i being the Avogadro number, Boltzmann constant, and the mole fraction of each of the elements, respectively. The entropy estimation method employed here is similar to previous reports⁵³⁻⁵⁵. The ΔS for all samples in this work ranges from 5.76 J/molK for pristine GeTe to 10.47 J/molK for $\text{Ge}_{0.39}\text{Sn}_{0.39}\text{Bi}_{0.02}\text{Sb}_{0.20}\text{Te}$. The configurational entropy ΔS and the corresponding calculated T_c as well as experimental T_c from DSC are summarized in Table 1. In order to probe deeper into the role of configurational entropy in stabilizing the cubic GeTe phase, the difference in enthalpy of formation of rhombohedral and cubic GeTe was examined. At constant pressure, the enthalpy change in a system can be formulated as:

$$\Delta H = \Delta E + P\Delta V \quad (2)$$

In addition, at a constant temperature, the enthalpy can be related to entropy via:

$$\Delta H = \Delta G + T\Delta S \quad (3)$$

where ΔE , P , ΔV , ΔG and T represent the change in internal energy of a system, pressure, and change in volume, Gibbs free energy and absolute temperature, respectively. At the rhombohedral – cubic structural phase transition temperature, by definition, $\Delta G = 0$ (both rhombohedral and cubic phase are equally stable at the phase transition temperature). Therefore, the enthalpy difference between the cubic phase and the rhombohedral phase can be expressed in terms of entropy change as:

$$\Delta H = T_C \Delta S \quad (4)$$

where T_C is the phase transition temperature. Theoretical and experimental reports have shown that the enthalpy of formation of cubic GeTe is estimated to be 40 – 50 meV/atom higher than those of rhombohedral GeTe.⁵⁶ Therefore, increasing ΔS has a direct implication in shifting the tendency for the cubic phase to be stabilized at lower temperature. In other words, the increase in ΔS should directly manifest in lower T_C (Table 1). It is noteworthy that the disappearance of experimental T_C for the samples with high Sn fraction ($x = 0.4$ and 0.5) is ascribed to unit cell volume increase, as shown in equation 2. The increase in volume reduces the $\Delta H_{\text{cubic-rhombohedral}}$ and therefore further reduces the T_C .

Figure 1. (a) XRD patterns of pristine GeTe and Sn-doped GeTe samples. (b) DSC graphs, showing endothermic peak shifts as Sn content increases. (c) XRD patterns of Bi and Sb doped Ge_{0.5}Sn_{0.5}Te samples. (d) Variable temperature XRD patterns for Ge_{0.4}Sn_{0.4}Bi_{0.02}Sb_{0.12}Te sample.

Figure 1(c) shows the XRD patterns of various Sb and Bi doped Ge_{0.5}Sn_{0.5}Te samples (Ge_{0.49-x}Sn_{0.49-x}Bi_{0.02}Sb_{2x}Te). All peaks can be indexed to the cubic structure. Just like in the case of pristine GeTe, the elemental Ge peaks can be observed at around 2θ of 28°. The elemental Ge peaks can be attributed to Ge agglomeration in the sample, which results in Ge-vacancies in the GeTe matrix phase and therefore high concentration of holes. This is confirmed by data from X-ray Fluorescence (XRF), which shows persistently higher Te-atomic percentage than its nominal composition, (Table 2 and Figure S1). On the other hand, no other secondary phase can be observed for all Sb and Bi doped samples up to 723 K, and the cubic phase is observed in the entire temperature range measured, as shown in the variable temperature XRD peaks in Figure 1(d). The benefits of suppressing the phase transition in this compound can be clearly

observed in Figure 2(a), showing the thermal elongation profile of cubic $\text{Ge}_{0.4}\text{Sn}_{0.4}\text{Bi}_{0.02}\text{Sb}_{0.12}\text{Te}$ compared to pristine GeTe. Notwithstanding higher coefficient of thermal expansion, $\text{Ge}_{0.4}\text{Sn}_{0.4}\text{Bi}_{0.02}\text{Sb}_{0.12}\text{Te}$ does not have any kinks at 700 K as compared to pristine GeTe which has negative thermal expansion near 700 K. Hence, when subject to high temperature gradient (*i.e.* 400 – 800 K), $\text{Ge}_{0.49-x}\text{Sn}_{0.49-x}\text{Bi}_{0.02}\text{Sb}_{2x}\text{Te}$ samples are expected to experience less thermal stress unlike the pristine GeTe.

Compound	ΔS (J/molK)	T_C calculated (K)*	T_C experimental (K)
GeTe	5.76	670	650
$\text{Ge}_{0.9}\text{Sn}_{0.1}\text{Te}$	7.11	542	620
$\text{Ge}_{0.8}\text{Sn}_{0.2}\text{Te}$	7.84	492	530
$\text{Ge}_{0.7}\text{Sn}_{0.3}\text{Te}$	8.30	465	490
$\text{Ge}_{0.6}\text{Sn}_{0.4}\text{Te}$	8.56	450	N.A.
$\text{Ge}_{0.5}\text{Sn}_{0.5}\text{Te}$	8.64	447	N.A.
$\text{Ge}_{0.43}\text{Sn}_{0.43}\text{Bi}_{0.02}\text{Sb}_{0.12}\text{Te}$	10.16	380	N.A.
$\text{Ge}_{0.41}\text{Sn}_{0.41}\text{Bi}_{0.02}\text{Sb}_{0.16}\text{Te}$	10.34	373	N.A.
$\text{Ge}_{0.39}\text{Sn}_{0.39}\text{Bi}_{0.02}\text{Sb}_{0.20}\text{Te}$	10.47	368	N.A.
$\text{Ge}_{0.40}\text{Sn}_{0.40}\text{Bi}_{0.02}\text{Sb}_{0.12}\text{Te}$	10.07	383	N.A.

*: T_C is calculated based on $\Delta H_{\text{cubic-rhombohedral}}$ from literature : 40 meV.⁵⁶

Table 1. Configurational entropy, calculated and experimental T_C of samples with different alloying compositions.

In addition to thermal elongation profile, nano-indentation tests shown in Figure 2(b) suggest superior microhardness and Young's modulus of $\text{Ge}_{0.4}\text{Sn}_{0.4}\text{Bi}_{0.02}\text{Sb}_{0.12}\text{Te}$ to the pristine GeTe and other prominent thermoelectric compounds, as shown Figure 2(c) and (d). The superior mechanical properties in this system may be linked to its high configurational entropy (*i.e.* chemical disorder brought about by different atomic species leads to an increased energy barrier to move dislocations, stacking faults, and other kind of defects and hence enhances the stiffness and hardness of the alloy).⁵³

Compound	Ge (at%)	Sn (at%)	Bi (at%)	Sb (at%)	Te (at%)
GeTe	46.69	-	-	-	53.31
$\text{Ge}_{0.5}\text{Sn}_{0.5}\text{Te}$	23.25	22.05	-	-	55.70

$\text{Ge}_{0.43}\text{Sn}_{0.43}\text{Bi}_{0.02}\text{Sb}_{0.12}\text{Te}$	21.41	19.27	0.92	3.64	54.76
$\text{Ge}_{0.41}\text{Sn}_{0.41}\text{Bi}_{0.02}\text{Sb}_{0.16}\text{Te}$	21.34	18.07	0.85	4.00	55.73
$\text{Ge}_{0.39}\text{Sn}_{0.39}\text{Bi}_{0.02}\text{Sb}_{0.20}\text{Te}$	21.14	17.74	0.89	4.69	55.55
$\text{Ge}_{0.40}\text{Sn}_{0.40}\text{Bi}_{0.02}\text{Sb}_{0.12}\text{Te}$	19.21	17.35	0.91	5.93	56.60

Table 2. Elemental composition of pristine GeTe, $\text{Ge}_{0.5}\text{Sn}_{0.5}\text{Te}$, and $\text{Ge}_{0.49-x}\text{Sn}_{0.49-x}\text{Bi}_{0.02}\text{Sb}_{2x}\text{Te}$ from X-ray Fluorescence (XRF) showing persistent excess anion.

Figure 2. (a) Thermal elongation vs temperature of the cubic $\text{Ge}_{0.4}\text{Sn}_{0.4}\text{Bi}_{0.02}\text{Sb}_{0.12}\text{Te}$ as compared to pure GeTe from ³⁸ (b) Nano-indentation profile showing load vs displacement that can be used to obtain microhardness and Young's modulus. (c) The microhardness of $\text{Ge}_{0.4}\text{Sn}_{0.4}\text{Bi}_{0.02}\text{Sb}_{0.12}\text{Te}$ in comparison to other prominent thermoelectric compounds.^{45-47, 57-60} (d) Young's modulus of $\text{Ge}_{0.4}\text{Sn}_{0.4}\text{Bi}_{0.02}\text{Sb}_{0.12}\text{Te}$ as compared to literatures.^{29, 45, 61-63}

The cubic structure of $\text{Ge}_{0.4}\text{Sn}_{0.4}\text{Bi}_{0.02}\text{Sb}_{0.12}\text{Te}$ is further confirmed by the selected area electron diffraction (SAED) pattern of TEM image (Figure 3(a)), which can be indexed to reflections from cubic planes. The lattice parameter estimated from the SAED pattern is about $6.10 \text{ \AA}$, in close agreement with the lattice parameter of $6.16 \text{ \AA}$ obtained from the XRD, (supplementary Table S1). Figure 3(b) shows the electron backscatter diffraction (EBSD) image of the sample $\text{Ge}_{0.4}\text{Sn}_{0.4}\text{Bi}_{0.02}\text{Sb}_{0.12}\text{Te}$. Large grain sizes up to 10's of micrometers can be seen for most grains. This is due to the long annealing time (3 days at 923 K) before the sintering, which tends to maximize the crystallinity and hence the intrinsic mobility of the sample. Figure 3(c) illustrates the phase change from rhombohedral to cubic upon Sn alloying.

Figure 3. (a) SAED (selected area diffraction) TEM pattern showing reflections from planes that can be indexed to cubic phase (inset: low magnification TEM image showing the absence of the Herringbone structure, which is only observed in rhombohedral GeTe). (b) EBSD (electron backscatter diffraction) pattern showing large grain size in the order of 10's of micrometers. (c) Illustration showing rhombohedral to cubic phase change by alloying Sn .

The resistivity vs temperature profile of pristine GeTe, $\text{Ge}_{0.5}\text{Sn}_{0.5}\text{Te}$, and various levels of Bi and Sb doped $\text{Ge}_{0.49-x}\text{Sn}_{0.49-x}\text{Bi}_{0.02}\text{Sb}_{2x}\text{Te}$ samples is shown in Figure 4(a). It is noteworthy that the resistivity of the pristine GeTe as well as $\text{Ge}_{0.49-x}\text{Sn}_{0.49-x}\text{Bi}_{0.02}\text{Sb}_{2x}\text{Te}$ samples peaks at temperatures around 700 K whereas the resistivity of $\text{Ge}_{0.5}\text{Sn}_{0.5}\text{Te}$ sample increases without reaching any plateau at the maximum measurement temperature of 823 K. Similar trends can be observed from the Seebeck coefficients vs temperature in Figure 4(b) as well as the corresponding power factor in Figure 4(c). The underlying reason for the observed trend is attributed to the larger band-gap of $\text{Ge}_{0.5}\text{Sn}_{0.5}\text{Te}$ than GeTe, which prevents bipolar conduction at high temperature, as supported by the DFT electronic band structure calculation shown in Figure 5(a) and (b), respectively. At 700 K, the plateau in resistivity and Seebeck starts to occur for GeTe. This is due to the thermally activated charge carriers from valence band to conduction band, which corresponds to an energy of $3 k_B T$ (approximately 0.19 eV). Consequently, the number of electrons increases, which contributed to the reduction in Seebeck (*i.e.* holes have positive Seebeck, electrons have negative Seebeck). Therefore, the experimentally inferred band gap for pristine GeTe is around 0.19 eV, similar to literature reports on pristine GeTe.⁶⁰ Interestingly, the DFT calculation underestimated the band-gap of GeTe (0.13 eV) by a factor of about 1.5 in comparison with experimental value (0.19 eV), which is commonly observed for DFT calculated band gaps.⁶⁴

On the other hand, the band gap for $\text{Ge}_{0.5}\text{Sn}_{0.5}\text{Te}$ estimated from DFT is around 0.42 eV, which explains the absence of plateau in Seebeck and resistivity even at 823 K. In addition, for $\text{Ge}_{0.49-x}\text{Sn}_{0.49-x}\text{Bi}_{0.02}\text{Sb}_{2x}\text{Te}$ samples, both Seebeck and resistivity reach the maximum at around 700 K as well. This can be attributed to the fact that Bi doping introduces impurity states due to Bi p-orbital near the conduction band, which effectively lowers the band gap.⁶⁰ Experimentally, this is evident from the shift in the peak of power factor to lower temperature as the Bi-doping level increases (Figure S2). This points to the possibility to achieve facile control of band-gaps in GeTe by controlling the amount of Bi dopant. It is noteworthy that the band gap calculated by the DFT method using experimental lattice parameters may result in underestimation in the band gap compared with the ideal crystal.

The power factor vs temperature trend for pristine GeTe stands out compared to $\text{Ge}_{0.49-x}\text{Sn}_{0.49-x}\text{Bi}_{0.02}\text{Sb}_{2x}\text{Te}$ samples, as shown in Figure 4(c). Notably, the prominent peak in power factor at around 700 K for GeTe is absent in $\text{Ge}_{0.49-x}\text{Sn}_{0.49-x}\text{Bi}_{0.02}\text{Sb}_{2x}\text{Te}$ samples. This can be ascribed to the absence of

phase transition in $\text{Ge}_{0.49-x}\text{Sn}_{0.49-x}\text{Bi}_{0.02}\text{Sb}_{2x}\text{Te}$, which results in L-band dominated transport and no phase-transition induced band alignment. Figure 4(d) shows the trend of weighted mobility vs temperature of the samples in this work as compared to other GeTe-based compounds in the literatures. In all cases, the decreasing trend of weighted mobility vs temperature can be ascribed to acoustic phonon scattering. $\text{Ge}_{0.49-x}\text{Sn}_{0.49-x}\text{Bi}_{0.02}\text{Sb}_{2x}\text{Te}$ samples have a lower weighted mobility as compared with pristine GeTe as well as other literature data, which can be ascribed to both the reduction of effective mass (Figure S9) and enhanced defect scattering caused by multiple-dopants. Interestingly, $\text{Ge}_{1.01}\text{Te}$ reported by Jinfeng et al³⁵ stands out to be substantially higher than the rest of the literature data as well as data from this work, especially near room temperature. This can be largely credited to the difference in synthesis condition. Hitherto, the works of Jinfeng *et al* and Liu *et al*^{31,35} are the only reports on GeTe solid-state synthesis via ball-milling followed by spark plasma sintering. This is unlike the widely-used melt-quenching-annealing-spark plasma sintering in most other literatures. Pair correlation function of the molten state of GeTe shows prevalent homopolar Ge-Ge bonds⁶⁵, which justifies the tendency to form elemental Ge agglomerates via melt synthesis. On the contrary, ball-milling obviates the need to melt the GeTe phase and thus minimize the excess holes concentration without the need of additional doping, that can lead to high intrinsic mobility.

Figure 4. (a) Resistivity vs temperature (b) Seebeck vs temperature (c) power factor of all samples in this work. (d) Weighted mobility of pristine GeTe, as well as the $\text{Ge}_{0.4}\text{Sn}_{0.4}\text{Bi}_{0.02}\text{Sb}_{0.12}\text{Te}$ as compared to other GeTe-based compounds from other literatures.

The total density of states (DOS) as well as partial density of states (PDOS) of pristine cubic GeTe and $\text{Ge}_{0.5}\text{Sn}_{0.5}\text{Te}$ is shown in Figure 5(c) and (d), respectively. In order to elucidate the reasons why Sn alloying causes the increase in the band-gap, the PDOS of pristine GeTe which reveals contributions from Ge $4s^2$ lone pairs near the valence band maximum (VBM) was examined. Based on the simple ligand-field theory, the lattice expansion via the introduction of Sn into GeTe essentially reduced the repulsive force between the Ge $4s^2$ lone pairs and the surrounding Te-ligands. Thus lowered the energy of the Ge $4s^2$ lone pairs and VBM, resulting in enlarged band gap and suppressed bipolar effect at high temperatures.¹⁸

Figure 5. Electronic band structure of (a) pristine cubic GeTe (b) cubic Ge_{0.5}Sn_{0.5}Te. Total density of states (DOS) and partial DOS for (c) pristine GeTe and (d) Ge_{0.5}Sn_{0.5}Te.

The thermal transport properties of pristine GeTe and cubic Ge_{0.49-x}Sn_{0.49-x}Bi_{0.02}Sb_{2x}Te samples are presented in Figure 6. The pristine GeTe shows a minimum total thermal conductivity at around the phase transition temperature (650 K), which further reinforces the important role of this phase transition in realizing good thermoelectric properties. In contrast, the total thermal conductivity of cubic Ge_{0.49-x}Sn_{0.49-x}Bi_{0.02}Sb_{2x}Te stays roughly constant at just above 1 W/mK throughout the entire temperature range. In addition, the relatively high total thermal conductivity of Ge_{0.5}Sn_{0.5}Te originates from the high electronic contribution due to its low resistivity and a relatively high Lorenz number (Figure S3 and S4).

As shown in Figure 6(b), the lattice thermal conductivity of cubic $\text{Ge}_{0.49-x}\text{Sn}_{0.49-x}\text{Bi}_{0.02}\text{Sb}_{2x}\text{Te}$ is near the amorphous thermal conductivity limit of GeTe.²⁹ The low lattice thermal conductivity in the cubic phase is largely due to ferroelectric instability (shown in Figure S5) which softens the polar optical phonons to the extent that they scatter the acoustic phonons, and therefore leads to large anharmonicity.¹⁶ In addition, high configurational entropy in our samples may have also contributed to lowering of lattice thermal conductivity, as was observed for Ag_9GaSe_6 .⁵⁵ Furthermore, it can also in part attributed to a larger unit cell due to mass and size/strain fluctuations brought about by point defects introduced by Sn, Bi, and Sb atoms.^{17, 66} The Debye-Callaway model (Figure 6(b)) shows Umklapp (U) – dominated scattering for pristine GeTe while point defects (PD) are mainly responsible for the trend and magnitude of lattice thermal conductivity observed for cubic $\text{Ge}_{0.49-x}\text{Sn}_{0.49-x}\text{Bi}_{0.02}\text{Sb}_{2x}\text{Te}$. It is noteworthy that the grain boundaries (GB) scattering (red dotted line) does not result in further lowering of lattice conductivity, revealing that the scattering mechanism in these samples is dominated by point defects rather than grain boundaries. This is also consistent with the large grain sizes observed in Figure 3(b). The physical parameters used for Debye-Callaway model for cubic $\text{Ge}_{0.49-x}\text{Sn}_{0.49-x}\text{Bi}_{0.02}\text{Sb}_{2x}\text{Te}$ is shown in Table S2.

The spectral thermal conductivity and phonon relaxation time shown in Figure 6(c) (bottom and top, respectively) exhibit a signature of point defect dominated scattering which results in attenuation of the spectral thermal conductivity at high frequency, as shown by the blue area under the curve. This suggests that there is ample room to further reduce the total lattice thermal conductivity by engineering the grain size, lattice strain, or dislocations to scatter low-frequency and mid-frequency phonons.^{17, 66}

Lastly, the temperature-dependent lattice thermal conductivity attenuation caused by substitution of Sn, Bi, and Sb atoms on Ge sites is presented in Figure 6(d). The attenuation factor for $\text{Ge}_{0.49-x}\text{Sn}_{0.49-x}\text{Bi}_{0.02}\text{Sb}_{2x}\text{Te}$ is calculated with respect to pristine GeTe (represented by dotted horizontal line) via:

$$\Delta\kappa_L = 1 - \frac{\kappa_L}{\kappa_{L(\text{GeTe})}} \quad (5)$$

For $\text{Ge}_{0.5}\text{Sn}_{0.5}\text{Te}$, the attenuation factor lies around 0.6 at room temperature and gradually drops to negative near the phase transition temperature at 700 K. This can be explained by the absence of structural phase transition in $\text{Ge}_{0.5}\text{Sn}_{0.5}\text{Te}$ and therefore, the lattice thermal conductivity near 700 K is actually higher than those of pristine GeTe, consistent with the trend observed in Figure 6(b). Additionally, $\text{Ge}_{0.49-x}\text{Sn}_{0.49-x}\text{Bi}_{0.02}\text{Sb}_{2x}\text{Te}$ lies around 0.8 for the entire temperature range except the dip in 700 K due to pristine GeTe phase transition. Such a high level of attenuation in lattice thermal conductivity for $\text{Ge}_{0.49-x}\text{Sn}_{0.49-x}\text{Bi}_{0.02}\text{Sb}_{2x}\text{Te}$ even at high temperature can be explained by the average interdopant distance $l_{ad} =$

$n^{-1/3}$. As the concentration of dopants is high in $\text{Ge}_{0.49-x}\text{Sn}_{0.49-x}\text{Bi}_{0.02}\text{Sb}_{0.2x}\text{Te}$, the attenuation level is high even for high frequency phonons.⁶⁷

Figure 6. (a) total thermal conductivity (b) experimental and calculated lattice thermal conductivity (c) spectral thermal conductivity and relaxation time with Umklapp (U), point defect (PD) and grain boundary (B) phonon scatterings. (d) lattice thermal conductivity attenuation of pristine GeTe and cubic $\text{Ge}_{0.49-x}\text{Sn}_{0.49-x}\text{Bi}_{0.02}\text{Sb}_{0.2x}\text{Te}$ samples.

The combination of beneficial electronic properties as well as low thermal conductivity enables a peak zT of 1.7 to be achieved at 723 K for $\text{Ge}_{0.4}\text{Sn}_{0.4}\text{Bi}_{0.02}\text{Sb}_{0.12}\text{Te}$, as shown in Figure 7(a). In addition, a high average zT of 1.23 from 400 to 800 K (shown in Figure 7(b)) as well as superior mechanical properties (in Figure 2(c) and (d)) demonstrates good potential for practical device applications. It is noteworthy that the maximum zT in our compounds occurs at 723 K, not coinciding with phase transition at lower temperatures. This shows that all of our samples have excessive carrier concentration at low temperature (*i.e.* the doping efficiency of Bi and Sb are limited in reducing the number of holes), which leaves scope

for carrier concentration optimization to engineer high zT near room temperature. For instance, the room temperature Seebeck coefficient in this work lies right below $100 \mu\text{V/K}$, whereas the optimum doping to maximize zT is recently shown to be $202\text{--}230 \mu\text{V/K}$,⁶⁸ which suggests room for dramatic improvement in room temperature zT . Lastly, the high quality factor of 1.37 provides the possibility of further zT enhancements by carrier concentration optimization (Figure 7(c)).

Figure 7. (a) zT vs temperature of all samples. (b) Average zT in this work as compared to similar GeTe-based compounds in other literatures.^{25, 31, 33, 69, 70} (c) zT as a function of reduced Fermi potential for compounds with different quality factors.

In summary, Sn alloying has been proven to be effective in suppressing the phase transition of GeTe to achieve a pure cubic phase with low lattice thermal conductivity. Additional doping with Bi and Sb results in optimized carrier concentration of this compound, which results in a high zT of 1.7 at 723 K

and a high average zT of 1.23 between 400 and 800 K. In addition, the mechanical properties of $\text{Ge}_{0.49-x}\text{Sn}_{0.49-x}\text{Bi}_{0.02}\text{Sb}_{2x}\text{Te}$ are superior compared to previously reported thermoelectric compounds. Furthermore, we note that the band-gap of Sn alloyed GeTe is in fact higher than that of pristine GeTe. In other word, alloying with Sn in GeTe led to decrease in phase transition temperature but increase in band gap, providing an interesting avenue to tune overall average zT value over a wide temperature range via optimizing the carrier concentration.

Experimental Section

Synthesis

Bulk polycrystalline GeTe samples were prepared by mixing a stoichiometric amount of high-purity element (99.99%) at a high vacuum of 10^{-5} mbar in quartz ampoules. Samples were subsequently melted at 1223 K and were kept at this temperature for 12 hours, followed by quenching in ice water. Annealing was performed at 900 K for 72 hours. The final ingots were then hand ground into fine powder before being consolidated using plasma activated sintering (PAS) at 823 K for 10 minutes under a pressure of 50 MPa. The size of the graphite die was 12.7 mm in diameter. The sintering was done under 1 Pa vacuum. Extra caution was taken during the cooling down by slow cooling at 15 K/min and slowly releasing the pressure to the die to avoid cracking the sample. The final density of the pellets was tested using Archimedes method (~98% theoretical density). Pellets were then cut and polished into rectangular bars for electrical testing as well as square bars for thermal measurements.

Characterization

XRD patterns were collected using a Bruker D8-Advance X-ray powder diffractometer with Cu $K\alpha$ radiation. The high temperature Seebeck coefficient and electrical resistivity were measured using ZEM-3 from ULVAC. High temperature thermal conductivity was measured from LFA 457 Netzsch. The heat capacity used for thermal conductivity calculation was estimated using Dulong-Petit approximation. Microscopy analysis was done in field emission scanning electron microscopy FESEM (JEOL JSM 7600F). TEM was collected using JEOL 2010. The XRF data was collected using M4 Tornado Micro X-ray Fluorescence. Sound velocity measurement was conducted in the longitudinal mode using ultrasonic equipment (iThera Medical GmbH). The mechanical properties (Young's Modulus and hardness) were investigated using a nanoindentation system (Agilent G200 Nanoindenter XP) with a diamond Berkovich

tip. The hardness values were obtained by $H = P/A$ where P is the load on the tip and A is the calibrated area of the Berkovich tip versus indentation depth h . The Young's modulus values were obtained from $E = \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A}}$ where S is the applied stress.

Band Structures

DFT calculation was performed by using the generalized gradient approximation with the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional as implemented in Vienna Ab-initio Simulation Package (VASP).⁷¹ The projector augmented wave potentials were used to describe the electron-ion interaction. In the Brillouin zone sample of GeTe structure, the Monkhorst-Pack k-points mesh of $7 \times 7 \times 7$ was used and the kinetic cutoff energy was set to 520 eV. The lattice parameters and atomistic positions were fully optimized until the energy converge criterion to 10^{-7} eV. The optimized equilibrium lattice constant of cubic structure GeTe obtained in our calculation was 5.92589 angstrom. For band structure calculation, we considered the spin orbit coupling (SOC) effect with magnetic moment of $0.6 \mu_B$ along the z axis, where μ_B is Bohr magneton.

Conflict of Interests

The authors declare no competing financial interest.

Supporting Information

Supporting Information is available from the website.

Authors Information

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Table of Contents Graphics

The rhombohedral-cubic phase transition temperature of GeTe can be tailored via Sn-alloying, leading to high performance thermoelectric GeTe.

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