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# Lattice Thermal Conductivity of *m*GeTe•*n*Sb<sub>2</sub>Te<sub>3</sub> Phase-Change Materials: A First-Principles Study

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**Abstract:** As the most promising materials for phase-change data storage, the pseudobinary mGeTe•nSb<sub>2</sub>Te<sub>3</sub> (GST) chalcogenides have been widely investigated. Nevertheless, an in-depth understanding of the thermal-transport property of GST is still lacking, which is important to achieve overall good performance of the memory devices. Herein, by using first-principles calculations and Boltzmann transport theory, we have systematically studied the lattice thermal conductivity along the out of plane direction of both stable hexagonal and meta-stable rock-salt-like phases of GST, and good agreement with available experiments has been observed. It is revealed that with the increase of the n/m ratio, the lattice thermal conductivity of hexagonal GST increases due to the large contribution from the weak Te-Te bonding, while an inverse trend is observed in meta-stable GST, which is due to the increased number of vacancies that results in the decrease of the lattice thermal conductivity. The size effect on thermal conductivity is also discussed. Our results provide useful information to manipulate the thermal property of GST phase-change materials.

Keywords: phase-change materials; *m*GeTe•*n*Sb<sub>2</sub>Te<sub>3</sub>; lattice thermal conductivity; first-principles

## 1. Introduction

Due to the fast and reversible phase transition between amorphous and crystalline states, the pseudo-binary mGeTe•nSb<sub>2</sub>Te<sub>3</sub> (GST) chalcogenides have been widely investigated for application in phase-change memory devices, which is considered as the next-generation non-volatile memory [1–6]. The GST compounds are also considered as potential thermoelectric materials [7–10]. Since the 1960s, the  $(GeTe)_x(AgSbTe_2)_{1-x}$  (TAGS) system, which amounts to GST with Ag filling vacancies, has been reported to have high figure of merit (ZT) values of 1.7 for TAGS-80 and 1.4 for TAGS-85, and the latter exhibits greater mechanical stability [10]. Usually, materials with a ZT value higher than 1 can be considered as good thermoelectric materials. One reason that makes GST a good thermoelectric material is due to its low thermal conductivity (k). For data storage applications, since the set and reset processes of phase-change memory devices are controlled by heat, understanding the heat transfer in these compounds is especially important. The thermal conductivity of a material is an essential property to characterize its heat transfer performance, which is usually divided into two parts, i.e., electronic ( $k_e$ ) and lattice ( $k_l$ ) thermal conductivity. In metals, electronic thermal conductivity contributes more than the lattice thermal conductivity, but in semiconductors, lattice plays a much more important role. Therefore, it is helpful to gain a better understanding for thermal transport properties of materials if we can distinguish the contributions from phonons and electrons individually, which, unfortunately, is not easy to achieve from experiments.

Even though the GST materials have been widely studied owing to their potential applications in data storage and thermoelectric materials, there still remains debate over their structure. Petrov et al. [11] proposed an atomic stacking sequence of Te-Sb-Te-Ge-Te-Ge-Te-Sb- for GST225.



Later, in 2002, Kooi and De Hosson [12] proposed a stacking sequence of Te-Ge-Te-Sb-Te-Te-Sb-Te-Gewith Sb and Ge atoms exchanging their positions. Besides these two ordered stacking sequences, the Ge and Sb atoms randomly occupying the same layers were also found [13]. Recent work shows that the Kooi structure is the most stable at low temperatures below 125 K, but above 125 K, the ferro phase is more stable [14]. The different stacking sequences could influence the lattice thermal conductivity. For instance, in the case of  $Ge_2Sb_2Te_5$ , the Kooi structure has a lower lattice thermal conductivity than the Petrove structure [15]. Although there are few theoretical works on the study of the lattice thermal conductivity of hexagonal  $Ge_2Sb_2Te_5$  [15–17] and  $Ge_1Sb_2Te_4$  [7], a comprehensive understanding on both the stable and meta-stable phases of  $mGeTe nSb_2Te_3$  chalcogenides is still lacking.

In this work, we have performed comprehensive first-principle calculations to systematically study the lattice thermal conductivity of both stable hexagonal and meta-stable rock-salt-like Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub>, Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>, and Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>. The lattice thermal conductivity is obtained by solving the Boltzmann Transport Equation (BTE) using the information of interatomic force constants (IFCs) obtained from first principles calculations. This approach has been a proven success in obtaining reliable results in many materials [18–20]. Our calculated results reveal an interesting variation trend in the thermal conductivity with varying chemical compositions of GST alloys, and the results agree well with the reported experimental data. Furthermore, we have also studied the size effect on lattice thermal conductivity. The present work will contribute to the fundamental understanding of thermal conductivity, and hence better tuning heat transfer performance of GST phase change materials.

#### 2. Materials and Methods

Our theoretical calculations were performed using the projector augmented-wave method (PAW) [21] in conjunction with the generalized gradient approximation (GGA) [22] of Perdew-Burke-Ernzerhof functional (PBE) [23], as implemented in the Vienna *ab initio* simulation package (VASP) code [24]. Pseudopotentials with electronic configurations of Ge  $4s^24p^2$ , Sb  $5s^25p^3$ , and Te  $5s^25p^4$  were used. For stable hexagonal GST (*h*-GST) phases, the *k*-points of  $9 \times 9 \times 5$  were automatically generated with  $\Gamma$  symmetry. The geometry convergence was achieved with the cutoff energy of 400 eV. The convergence criteria for ion relaxation and electronic loop was  $1 \times 10^{-6}$  eV, based on the total energy difference. The van der Waals corrected D2 functional [25] was applied to hexagonal GST. For meta-stable rock-salt-like GST (*c*-GST) phases, *k*-points of  $7 \times 7 \times 3$  were used. The Phonopy package [26] was used to obtain the harmonic interatomic force constants (IFCs). The supercell approach with a  $3 \times 3 \times 2$  supercell and  $3 \times 3 \times 2$  *k*-point was used for *h*-GST phases, and a  $2 \times 2 \times 2$  supercell and  $\Gamma$  *k*-point was used for *c*-GST phases. The third-order anharmonic IFCs were calculated by using supercell approach with a  $3 \times 3 \times 2$  supercell and  $\Gamma$  *k*-point in real space for both phases, and a cutoff for the interaction range is set by including the third nearest neighbor atoms. The ShengBTE package [27] was used to obtain the third-order IFCs and solve the Boltzmann transport equation (BTE).

#### 3. Results and Discussion

Among the pseudo-binary mGeTe•nSb<sub>2</sub>Te<sub>3</sub> compounds, the Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> (GST124), Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> (GST225), and Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> (GST147) have been widely studied for phase change memory. Even though GST materials have been widely studied due to their application in data storage and thermoelectric materials, there still remains debate over their structure [11–14,28–30]. Here we used the most stable atom stacking sequence below 125 K proposed by Kooi [12] (the structures are illustrated in Figure 1). The stable GST phases have a hexagonal structure, and the atom stacking sequence for *h*-GST124, *h*-GST225, and *h*-GST147 are Te-Ge-Te-Sb-Te-Te-Sb- (Figure 1a), Te-Ge-Te-Sb-Te-Te-Sb-Te-Ge-(Figure 1b), and Te-Ge-Te-Sb-Te-Te-Sb-Te-Te-Sb- (Figure 1c), respectively. Besides the stable hexagonal structure, GST phases also have a meta-stable rock-salt phase, and these stoichiometric compounds inevitably contain vacancies. Both theoretical and experimental studies indicate that vacancies prefer ordering on the (111) plane [31–34]. In order to study the effect of vacancy on thermal conductivity, we rebuilt the rock-salt structure in terms of hexagonal stacking based on the (111)

planes along the [111] direction. The atomic stacking sequences for *c*-GST124, *c*-GST225, and c-GST147 are Te-Ge-Te-Sb-Te-v-Te-Sb-(Figure 1d), Te-Ge-Te-Sb-Te-V-Te-Sb-Te-Ge-(Figure 1e), and Te-Ge-Te-Sb-Te-v-Te-Sb-Te-v-Te-Sb-(Figure 1f), respectively. Where v represents a vacancy layer. Note that the meta-stable rock-salt-like structure calculated here does not correspond to that which is relevant for the memory switching (in which vacancies are disordered). As a first step, we have optimized all the structures and compared our calculated results with the experiments. The calculated lattice parameters for *c*-GST and *h*-GST are in good agreement with the available experimental results (summarized in Table 1). The calculated lattice parameter *a* for *h*-GST124, *h*-GST225, and *h*-GST147 is a = 4.305 Å, a = 4.293 Å, and a = 4.317 Å, respectively, agreeing well with the experimental values of 4.272 Å [35], 4.223 Å [13], and 4.236 Å [36], respectively, but the lattice constant along the *c* direction is significantly overestimated. The Te-Te bond length is calculated to be 4.041 Å, 4.059 Å, and 3.984 Å for the above three GST alloys, respectively, which are much larger than the experimental data of 3.748 Å [35], 3.753 Å [13], and 3.691 Å [36]. This is because the GGA functionals cannot accurately describe the long-range electron correlations. In hexagonal GST phases, the bond between the Te-Te layer is van der Waals-like bonding, which is a long-range electron correlation and might play an important role in thermal transport property. We thus introduced a van der Waals corrected D2 functional [25] to describe the weak bonding between Te-Te, which has been proven to be effective and reliable for GST225 [7,37]. The calculated bond lengths of Te-Te using van der Waals correction functionals are 3.844 Å, 3.843 Å, and 3.829 Å for h-GST124, h-GST225, and h-GST147, respectively, which is now in excellent agreement with previous experiments [13,35,36], indicating that the D2 functional is a proper method to describe the Te-Te weak bonding in the layered GST phases. For meta-stable rock-salt-like phases, a vacancy layer is in between the two neighboring Te atomic layers. The distances between two Te atoms  $d_{Te-v-Te}$  are calculated to be 4.273 Å, 4.286 Å, and 4.250 Å for the *c*-GST124, *c*-GST225, and *c*-GST147, respectively, which is obviously much larger than the length of the van der Waals-like bonded Te-Te in the hexagonal phases.

Compound	Lattice	GGA (Å)	PBE-D2 (Å)	Exp (Å)
<i>c</i> -Ge <sub>1</sub> Sb <sub>2</sub> Te <sub>4</sub>	а	4.295		4.27 <sup>1</sup>
	С	43.092		13.96 <sup>1</sup>
	d <sub>Te-v-Te</sub>	4.273		
c-Ge <sub>2</sub> Sb <sub>2</sub> Te <sub>5</sub>	а	4.286		4.26 <sup>2</sup>
	С	53.580		17.40 <sup>2</sup>
	d <sub>Te-v-Te</sub>	4.286		
c-Ge₁Sb₄Te <sub>7</sub>	а	4.304		
	С	75.595		
	d <sub>Te-v-Te</sub>	4.250		
<i>h</i> -Ge <sub>1</sub> Sb <sub>2</sub> Te <sub>4</sub>	а	4.305	4.221	4.272 <sup>1</sup>
	С	42.141	41.314	41.686 <sup>1</sup>
	d <sub>Te-Te</sub>	4.041	3.844	$3.748^{-1}$
<i>h</i> -Ge <sub>2</sub> Sb <sub>2</sub> Te <sub>5</sub>	а	4.293	4.213	4.223 <sup>2</sup>
	С	17.550	17.185	17.239 <sup>2</sup>
	d <sub>Te-Te</sub>	4.059	3.843	3.753 <sup>2</sup>
<i>h</i> -Ge <sub>1</sub> Sb <sub>4</sub> Te <sub>7</sub>	а	4.317	4.230	4.236 <sup>3</sup>
	С	24.474	24.084	23.761 <sup>3</sup>
	d <sub>Te-Te</sub>	3.984	3.829	3.691 <sup>3</sup>

**Table 1.** Calculated lattice parameters of meta-stable rock-salt like and hexagonal mGeTe•nSb<sub>2</sub>Te<sub>3</sub> chalcogenides. Exp refers to experimental data from literature.

Note: <sup>1</sup> Experiment in Reference [35]; <sup>2</sup> experiment in Reference [13]; <sup>3</sup> experiment in Reference [36].

The lattice thermal conductivity of the hexagonal phases is plotted in Figure 2. All the phonon models we calculated are stable, as shown in Figure 3. It is known that for layered chalcogenides, the out of plane lattice thermal conductivity was lower than the in-plane lattice thermal conductivity, making them good thermoelectric materials [4,7,38], so here we focus on the lattice thermal conductivity along the out of plane direction. At 300K, the calculated lattice thermal conductivity for h-GST225 is 0.42 Wm<sup>-1</sup> K<sup>-1</sup>, which is very close to the reported value of 0.6 Wm<sup>-1</sup> K<sup>-1</sup> by Siegert et al. [32], where the difference is due to the fact that the latter considered the electronic contribution to the thermal conductivity. Recently, theoretical works with similar approaches reported that the lattice thermal conductivity of GST225 along the out of plane direction was 0.6 Wm<sup>-1</sup> K<sup>-1</sup> [15] and 0.86  $Wm^{-1} K^{-1}$  [17], which agrees well with our value. For *h*-GST124, we got a value  $k_l = 0.6 \text{ Wm}^{-1} \text{ K}^{-1}$ , which is much lower than that of the reported value of 1.16 Wm<sup>-1</sup> K<sup>-1</sup>, where the electronic contribution is also included. However, when the authors removed the contribution from electrons by employing the Wiedemann–Franz law (WFL),  $k_l$  is reduced to around 0.7 Wm<sup>-1</sup> K<sup>-1</sup> [25], which is in good agreement with our calculated value. For GST147 at room temperature, our calculated lattice thermal conductivity is  $1.38 \text{ Wm}^{-1} \text{ K}^{-1}$ , close to the experimental data of  $1.2 \text{ Wm}^{-1} \text{ K}^{-1}$  [39], but being much higher than experimental data ( $0.49 \text{ Wm}^{-1} \text{ K}^{-1}$ ) from Shin and coworkers [40]. Obviously, there is large discrepancy among the different experimental results on the lattice thermal conductivity because of the different samples and measurement conditions. Nevertheless, our calculated values agree well with that of Konstantinov and coworkers [39]. Interestingly, it is also noticed that the lattice thermal conductivity increases when increasing the values of n/m ratios for hexagonal mGeTe•nSb<sub>2</sub>Te<sub>3</sub> chalcogenides. The cation disorder is not considered in the present work, which may slightly affect the thermal conductivity.



**Figure 1.** Structures for mGeTe•nSb<sub>2</sub>Te<sub>3</sub> phases: (a) stable Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub>, (b) stable Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>, (c) stable Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>, (d) meta-stable Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub>, (e) meta-stable Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>, (f) meta-stable Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>, *v* represents a vacancy layer. The Ge (red balls), Sb (blue balls), and Te (green balls) are indicated.



**Figure 2.** Calculated lattice thermal conductivity of *h*-GST phase-change materials along the out of plane direction.



**Figure 3.** Phonon dispersion relations and phonon density of states for hexagonal GST compounds: (a) GST225, (b) GST124, and (c) GST147.

To gain more insight into the observed thermal transport behavior, we have investigated the anharmonic scattering rates of *h*-GST phases at room temperature, as plotted in Figure 4. It is apparent that the anharmonic scattering rates of GST147 are the lowest, followed by GST124, and then GST225, indicating that the phonon lifetimes decrease in the sequence of GST147, GST124, and GST225. Based on this phonon-lifetime behavior of GST, it is easy to understand the above trend of the lattice thermal conductivity of *m*GeTe•*n*Sb<sub>2</sub>Te<sub>3</sub>. Finally, it is seen that the anharmonic scattering rate of GST147 is much lower than that of GST124 and GST225, which is the physical origin of the much larger lattice

thermal conductivity of GST147. This could be due to the fact that GST147 has a greater number of Te-Te weak bonds [41].



Figure 4. Anharmonic scattering rates for *h*-GST phases at 300 K vs. angular frequency.

For meta-stable rock-salt-like GST phases, although the atomic stacking sequence is similar with the hexagonal phases, the thermal transport behavior is quite different. The lattice thermal conductivity of the rock-salt like phases is plotted in Figure 5. It is seen that the  $k_1$  of GST147 is much lower than that of the GST124 and GST225, opposite to the trend observed in the hexagonal phases. This might be due to the fact that there is a vacancy layer between two adjacent Te atomic layers instead of van der Waals bonding. As we know, the defects in the crystal will increase the phonon scattering, and thus reduce the thermal conductivity. In mGeTe•nSb<sub>2</sub>Te<sub>3</sub> chalcogenides, when the n/m ratio increases, the vacancy concentration increases. For the GST147, GST124, and GST225, the vacancy concentrations are 28.6%, 25%, and 20%, respectively. The real meta-stable system is more complicated than our ideal model, therefore the vacancy ordering in these compounds will change when the samples are annealed under different conditions, hence resulting in large differences in thermal conductivity [32]. Nevertheless, although the calculated lattice thermal conductivity of rock-salt-like GST is overestimated, the observed relationship of lattice thermal conductivity for GST as a function of the n/m ratio is very useful. According to this relationship, one can estimate the possible trend of the lattice thermal conductivity for other GST compounds. For example, the lattice thermal conductivity of Ge<sub>3</sub>Sb<sub>2</sub>Te<sub>6</sub> is assumed to be larger than GST225, as the latter possesses more vacancy, which agrees well with the experimental observation [32].



**Figure 5.** The calculated lattice thermal conductivity of *c*-GST alloys, for which the structures are reconstructed based on the (111) plane and along the [111] direction of the rock-salt structure. Herein, *c* axis is along the out of plane direction.

Many materials, such as Si [42], usually show a strong size-dependent thermal conductivity. Since the GST chalcogenides have been shown to scale down to very small dimensions [43], it is interesting to see how size effect will influence the lattice thermal conductivity. Figure 6 plots the  $k_l$  of *h*-GST nanowires along the out of plane direction with different diameters. The construction of the nanowire and theory model is formulated in reference [27]. This method was successfully used [44]. Interestingly, the lattice thermal conductivity of GST chalcogenides shows a small size dependence. For nanowires with a diameter larger than 100 nm, the  $k_l$  is almost the same as that of the bulk phase. For GST124 and GST225, it is observed that the  $k_l$  decreases obviously only when the diameter is reduced down to 10 nm. In order to have a clear comparison for these three compounds, the normalized cumulative thermal conductivity for GST124, GST225, and GST147 is shown in Figure 6. It is interesting to see that the GST chalcogenides are more sensitive to size effect when the n/m ratio increases. For mGeTe•nSb<sub>2</sub>Te<sub>3</sub> chalcogenides, the phonon mean-free path (MFP) increases with the increasing n/m ratio. It is known that nanocrystallization could reduce the thermal conductivity owing to the boundary effect, as the phonons with larger MFPs than the boundary would be easily blocked. Therefore, due to the small MFPs of GST phases, it is not easy to reduce the thermal conductivity by reducing the size, as shown in Figure 7.



**Figure 6.** Calculated lattice thermal conductivities for *h*-GST nanowires at room temperature as a function of the diameter of nanowires.



Figure 7. Normalized cumulative thermal conductivity of h-GST phases at 300 K.

### 4. Conclusions

In conclusion, we have investigated the lattice thermal conductivity of both stable hexagonal and meta-stable rock-salt-like mGeTe•nSb<sub>2</sub>Te<sub>3</sub> chalcogenides by considering the intrinsic anharmonic phonon scattering. Our results show that for hexagonal GST, the lattice thermal conductivity increases when the n/m ratio increases, showing the large contribution of Te-Te weak bonding, while the trend is completely reversed for meta-stable phases. The lattice thermal conductivity of the GST chalcogenides shows a small size dependence and the material is more sensitive to size effect when the n/m ratio

increases. Our work contributes to the fundamental understanding on thermal transport of the GST phase change materials.

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