Atomistic origins of the phase transition mechanism in Ge$_2$Sb$_2$Te$_5$

Juarez L. F. Da Silva, Aron Walsh, Su-Huai Wei, and Hosun Lee

1 National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401, USA
2 Dept. of Applied Physics, Kyung Hee University, Suwon 446-701, South Korea

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Combined static and molecular dynamics first-principles calculations are used to identify a direct structural link between the metastable crystalline and amorphous phases of Ge$_2$Sb$_2$Te$_5$. We find that the phase transition is driven by the displacement of Ge atoms along the rocksalt [111] direction from the stable-octahedron to high-energy-unstable tetrahedron sites close to the intrinsic vacancy regions, which give rise to the formation of local 4-fold coordinated motifs. Our analyses suggest that the high figures of merit of Ge$_2$Sb$_2$Te$_5$ are achieved from the optimal combination of intrinsic vacancies provided by Sb$_2$Te$_3$ and the instability of the tetrahedron sites provided by GeTe.

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Ternary (GeTe)$_m$(Sb$_2$Te$_3$)$_n$ materials, in particular the Ge$_2$Sb$_2$Te$_5$ (GST) composition, have been considered as the most natural candidates for non-volatile memory applications through exploiting the fast and reversible resistance change between a metastable (m-GST) crystalline phase (low resistivity) and an amorphous (a-GST) phase (high resistivity). However, the mechanism of the phase transition is still under intense debate. The existing models have provided a preliminary understanding of the transition mechanism, but fail to provide a clear and direct structural link between the m-GST and a-GST phases, which play a key role in the understanding of the resolvable transition at an atomistic level. The m-GST (20% in GST) occupy the cation sites. It has been suggested that a-GST is characterized by the presence of 4-fold coordinated Ge atoms, in which the sum of the occurrences GeTe$_2$, Ge(SbTe$_3$), and Ge(GeTe$_5$) is about 66%. Ge−Ge and Ge−Sb bonds are found in those motifs, which is assumed to be due to disorder effects, since they are not present in the crystalline phases. Furthermore, a-GST shows a volume expansion of 6−7% compared with the m-GST phase, and it has a higher energy (28 − 40 meV/atom) with respect to m-GST. Theoretically, first-principles molecular dynamics (MD) starting from a liquid phase with slow cooling rates have been used to generate a metastable phase (RS-type structure), however, no direct transition path was identified to link the proposed m-GST and a-GST phases. Thus, a new approach that connects the two phases at the atomistic level becomes highly desirable. In this work, using first-principles methods, we will address the following open questions: Is there a dominant structure link between both phases? What are the roles of GeTe and Sb$_2$Te$_3$ in GST? We will show in this Letter that combined static (zero temperature) and MD (high-temperature) first-principles calculations can explain the phase transition mechanism between the m-GST and a-GST phases. Moreover, our study shows that generating the amorphous phase from a known crystalline phase provides a better understanding of the structural relationship between both phases. Thus, it provides a new avenue for further study of amorphous materials phase change transitions.

Our static total energy and MD calculations are based on the all-electron projected augmented wave (PAW) method and density functional theory (DFT) within the generalized gradient approximation (GGA-
PBE[24] as implemented in VASP. [25,26] To represent the metastable phase (RS-type structure), we employ a hexagonal (2×2×1) unit cell, in which the Te atoms are stacked along of the [0001] direction. [27] The MD calculations were performed employing cubic and hexagonal cells with 108 to 126 atoms. The total energies and equilibrium volumes for all structures in both crystalline and amorphous phases were obtained by full relaxation of the volume, shape, and atomic positions of the unit cell to minimize the quantum mechanical stresses and forces.

To understand the phase transition, we first established the crystal structure of the m-GST phase,[27] as shown in Fig. [1]. The obtained structure is consistent with experimental results and provides new insights into m-GST.[5, 9, 11, 12, 28] In this layered-structure the ordered intrinsic vacancies separate the building block units (GST), in which the Ge and Sb atoms are intermixed in.

We notice that tetrahedral Ge atoms can be obtained by shifting the octahedral Ge atoms in m-GST along the hexagonal c direction, i.e., there are two tetrahedral sites for each Ge atom, Fig. [1]. In order to identify the lowest energy tetrahedral sites, we calculated the energetics for the occupation of each site by Ge atoms. The lowest energy sites are located in the intrinsic vacancy regions, while the highest energy sites are located in the center of the GST building blocks, i.e., there is a strong preference for the four-fold Ge atoms to be located in or near intrinsic vacancy regions. Assuming that all the Ge atoms are shifted from their octahedron sites and occupy the lowest energy tetrahedral sites, we find that 50% of Ge will shift from the octahedra to tetrahedra along the [0001] direction, while the remaining 50% shift along of the opposite direction. The m-GST (shift) structure in which all Ge atoms occupy the tetrahedral sites according to the distribution of intrinsic vacancies and energy barriers is shown in Fig. [1], which leads to the formation of Ge–Ge bonds. This configuration is highly unstable, and the system will relax without energy barrier to a lower energy phase (see am-GST structure in Fig. [1]).

To provide a more direct structural link between the m-GST and a-GST phases, we first generated a-GST structures using first-principles MD simulations at high temperatures, T, using the same approach adopted in previous a-GST studies.[8,17,18,29] Secondly, we generated several amorphous structures from modified m-GST structures, in which a percentage of the Ge atoms (100%, 75%, 50%, 25%) are shifted from the tetrahedron sites to the lower energy octahedron sites (m-GST with shift Ge). The goal is to show that amorphous structures obtained in this way (am-GST in Fig. [1]) can preserve most of the structural features present in the a-GST generated by conventional MD calculations (a-GST in Fig. [1]), and therefore provide a direct structural link and solid evidence to support the mechanisms that determine the phase transition from m-GST to a-GST. The amorphous structures obtained by both approaches are shown in Fig. [1]. To quantify our analysis, we calculated the pair correlation (PC) functions, which are shown in Fig. [2]. For the a-GST structures, the PC functions were averaged over five structures, while the PC functions of the am-GST structures were calculated for ten structures with different initial occupation of the Ge tetrahedron sites; the structure that provided the best agreement with the a-GST PC functions is shown in Fig. [2].

Our PC function analysis shows that for all the am-GST structures, the one in which 50% of the Ge atoms are shifted from the octahedron to the tetrahedron sites along the hexagonal [0001] direction and the rest 50%...
amorphization is a consequence of the Ge atoms moving to the lower coordination sites in the a-GST structures. Therefore, the smaller volume deformation observed in the experimental sample may indicate that the amorphization process in not complete, i.e. not all the Ge atoms are moved away from their stable octahedral sites.

Comparison of the total energies reveals that the a-GST structure is about 140 – 182 meV/atom higher in energy than the lowest energy m-GST structure, which corresponds to the energy limit between the fully amorphized (100% shift of the Ge atoms) and the ordered m-GST structure. Differential scanning calorimetry measurements obtained 28 – 42 meV/atom. We found that the calculated energy differences decrease by about 30 meV/atom if the intrinsic vacancies become disordered in m-GST. Furthermore, the energy difference could be much smaller (e.g. about 50 meV/atom) if only a fraction of the Ge atoms undergo site transitions. This again suggests that full scale amorphization of GST or a complete ordering of Ge, Sb, and intrinsic vacancies in m-GST may not be typical in the GST phases.

The averaged bond lengths calculated for both phases are summarized in Table I along with available experimental results. The calculated bond lengths deviate by about 3 – 6% from the experimental results; however, most of the error is due to the use of GGA in our calculations, which systematically overestimates the lattice constants by about 3%. Furthermore, it is important to notice that the nearest-neighbor distances are spread over a large range of values, e.g. Ge–Te is from 2.67 to 2.94 Å and Sb–Te is from 2.86 to 3.23 Å. We found a contraction in the averaged Ge–Te bond lengths in a-GST of up to 10% compared with m-GST, e.g. Ge–Te decreases from 2.87 – 3.24 Å (m-GST) to 2.67 – 2.94 Å (a-GST), while experimental measurements obtained a decrease of about 12%. Similar trends exist for Sb–Te.

To understand the relaxation effects introduced by the shift of Ge atoms from octahedron to tetrahedron sites, we calculated the potential energy path along the RS [111] direction for GeTe as a function of Ge shift from octahedron (perfect RS) to the tetrahedron (zincblende) sites. The results are shown in Fig. 3. As expected, the distorted RS structure has the lowest energy (54 meV lower than the perfect RS structure), in which the distortion is driven by Peierls-type level repulsion near the band edge. Unexpectedly, the zincblende (ZB) structure in which the Ge atoms occupy the tetrahedron sites with bond angles (Ge–Te–Ge) of 109.47°, is not a local minimum as would be expected based on the general trends for binary semiconductors. In fact, we found that the ZB structure relaxes without energy barrier to the ‘graphite-like’ or to the ‘long-Ge–Te’ structures, which have lower energies than the high-symmetry ZB phase. Thus, Ge at ideal tetrahedral sites are intrinsically unstable in GeTe, which drives the Ge atoms at tetrahedral sites in GST.
to move away and adopt a variety of lower symmetry coordination environments.

The variety of coordination environments found in the GeTe energy surface is remarkable. From Ge site occupation of (0.25,0.25,0.25) to (0.40,0.40,0.40), three structures have similar energies, i.e. ‘long-Ge–Te’, layered-ZB, and layered-RS. In ‘long-Ge–Te’, the Ge atoms form three short bonds (2.77 Å) and one long bond (4.68 Å) with the Te atoms. However, Ge is only three-fold coordinated in the layered structures with bond lengths of 2.76 Å, which is 2.90% (14.51%) smaller than the short (longer) Ge–Te bond lengths in the distorted RS structure. As the layered GeTe structures are lower in energy than the graphite-like phase and only about 100 meV/f.u. higher than the distorted RS structure, it indicates a strong tendency of Ge atoms to form four-fold motifs with three short Ge–Te bonds (about 2.76 Å) and bond angles of about 90°. Similar results, e.g. short bond lengths and average bond angles of about 90°, are observed by our calculations for a-GST, which is also consistent with previous MD results for a-GST[8, 17, 18] as well as by experimental observations.[5, 6, 19] Therefore, the inherent instability of Ge at the tetrahedral sites, low displacement energy, and unique coordination preferences of GeTe plays an important role in the formation of a-GST.

In summary, using first-principles calculations, we obtained a direct structural link between the meta-stable and amorphous GST phases, as well as the role of the parent compounds. The Sb2Te3 provides intrinsic lattice vacancies, while GeTe contributes its RS-type structure in which Ge displacements along the RS [111] direction can be realized at low energy cost. The instability at the tetrahedral sites leads to the generation of disordered GST structures in which the Ge atoms are mostly four-fold coordinated with three short Ge–Te bond lengths. As the displacement has the lowest energy near intrinsic vacancy sites, our analysis suggests that a high degree of amorphization can be achieved most easily when the system has a composition of (GeTe)2(Sb2Te3), i.e., is consistent with the observation that GST has the highest figure of merit of all Ge–Sb–Te compounds. Moreover, we show that generating amorphous materials directly from its crystalline counterpart provides a better approach to understand these type of phase transitions present in phase change materials.

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