Unique Melting Behavior in Phase-Change Materials for Rewritable Data Storage

Zhimei Sun,[1,*] Jian Zhou,[2] and Rajeev Ahuja[1]

[1]*Condensed Matter Theory Group, Department of Physics, Uppsala University, Box 530, SE-751 21, Uppsala, Sweden*
[2]*Materials Chemistry, Department of Materials Science and Engineering, Royal Institute of Technology, SE-100 44 Stockholm, Sweden*

$Ge_2Sb_2Te_5$ (GST) is a technologically very important phase-change material for rewritable optical and electrical storage because it can be switched rapidly back and forth between amorphous and crystalline states for millions of cycles by appropriate pulsed heating. However, an understanding of this complicated phenomenon has not yet been achieved. Here, by *ab initio* molecular dynamics, we unravel the reversible phase transition process of GST. The melting of rocksalt-structured GST is unique in that it forms two-dimensional linear or tangled clusters while keeping order in the perpendicular direction. It is this specific character that results in the fast and reversible phase transition between amorphous and crystalline and hence rewritable data storage.

Phase-change (PC) materials based on chalcogenide alloys have been widely studied for data storage in current multimedia applications, such as optical and electrical memory devices (DVD-RW, DVD-RAM) [1–6]. Of particular interest is $Ge_2Sb_2Te_5$ (GST), which exhibits the best performance when used in DVD-RAM in terms of speed and stability. GST has two crystalline states: low-temperature metastable cubic (c) and high-temperature hexagonal. By annealing, the as-deposited amorphous (a) GST thin film crystallizes to a rocksalt structure at ∼140 °C and finally transforms to a hexagonal structure at ∼310 °C [7]. With further increasing temperatures, the hexagonal structure melts at ∼623 °C [7]. In contrast, the complete crystallization to a rocksalt structure of the melt-quenched amorphous bits in a crystalline matrix can be achieved in 10 nanoseconds (ns) by laser heating [8]. The $a \leftrightarrow c$ phase transition is ultimately fast and reversible as can be realized by pulsed heating (in ns). The principle of phase-change optical or electrical recording is simple. By applying an appropriate laser beam or high electrical pulse, a PC material is heated to above its melting temperature and then rapidly quenched into the amorphous state (write). An amorphous mark against the crystalline background is a recorded bit. The information recorded can be read easily because the amorphous and crystalline states are very different in optical or electrical properties. To switch the amorphous mark back to its crystalline state (erase), another appropriate laser beam or electrical pulse is applied. The material in its amorphous state is then heated to just above its glass-transition temperature, resulting in the rearrangement of atoms back into the cubic state. Therefore, understanding the nature of $a \leftrightarrow c$ phase transition is the key point to tuning the properties of GST and searching new PC materials with better performances. However, the paradoxical situation is that PC materials have been commercially used but the phase-change mechanism behind the utilization is unclear due to the structure complexity and extremely fast $a \leftrightarrow c$ phase transforma-

tion. So far, the crystal structure and phase-change mechanisms of PC compounds are still important open subjects.

Based on the extended x-ray absorption fine structure spectroscopy (XAFS) analysis, Kolobov *et al.* [9] suggested that the amorphization of $Ge_2Sb_2Te_5$, i.e., the order-disorder transition, is due to an umbrella flip of Ge atoms from an octahedral position into a tetrahedral position, which results in the fast DVD performance and repeatable switching over millions of cycles. WeŁnic *et al.* [10] attributed this transition mainly to the changes of electronic configurations of Te and Sb by means of static *ab initio* calculations. Using a rate equation model describing the generation and collapse of amorphous regions in thin crystalline films, Kohary *et al.* [11] observed that the amorphous spot collapse is assisted by the motion of certain crystal facets. Very recently, Baker *et al.* [12] reported significant concentrations of Ge-Ge bonds in a-GST by a new extended XAFS study of local bonding. In our previous Letter [13], we have shown that the most stable configuration of c-GST has a stacking sequence of Te-Ge-Te-Sb-Te-v-Te-Sb-Te-Ge- in the [111] direction, wherein "v" represents vacancy layers. Furthermore, we proposed that vacancies are highly ordered and layered and result from fcc symmetry. In the present Letter by *ab initio* molecular dynamics (AIMD) which has been proved to be a very accurate and valuable tool for theoretical study of materials at high temperatures [14,15], we have unraveled the reversible $a \leftrightarrow c$ phase transition process for the first time. Our results show a remarkable agreement with the storage process of write and erase, and hence reveal the unique melting behavior of GST.

The present AIMD use canonical *NVT* (constant number, volume, and temperature) ensembles which are implemented in the Vienna *ab initio* simulation package [16]. The interatomic forces were computed quantum mechanically using projector augmented wave potentials [17] within the local-density approximation. The temperatures were controlled using the algorithm of Nosé [18,19]. *k*

points of $3 \times 3 \times 1$ are automatically generated with the origin at Gamma point, and Gaussian smearing was applied. The k points of $3 \times 3 \times 2$ have also been tested at 1500 K. Because the difference is minute we used the k points of $3 \times 3 \times 1$ to save CPU time. The ensemble of 108-atom plus 12 vacancies was melted and equilibrated at high temperatures from 600 to 2000 K for 2000 steps, with each time step for 3 femtoseconds (fs) at temperatures below 1500 K and 2 fs at 2000 K. The amorphous structures snapshot at 1500 and 2000 K were then crystallized at 600 K for 17 000 (17k) and 20 000 (20k) time steps to get the fcc structure.

The supercell of rocksalt-structured GST consisting of 108 atoms and 12 vacancies is constructed based on our previous Letter [13]. The size of the supercell is fixed to the equilibrium volume of 3100.68 $\mathring{A}^3$ throughout the calculations. Figure 1 shows the radial distribution function (RDF) for GST at temperatures from 600 to 2000 K. It is clear that the structure starts to lose its long-range order between 1200 and 1500 K, and the RDF shows an amorphous solid or liquid character. To see the details of atomic motions, we show in Fig. 2 the ion trajectories of atoms projected onto the $(11\bar{2})$ planes over a 6 picosecond (ps) period for temperatures below 1500 K and 4 ps above 1800 K, starting with an equilibrium $T = 0$ K configuration. It is obvious that atoms vibrate only around their initial configurations below 800 K. At around 1000 K, atoms travel far away from their equilibrium positions in the (111) plane but without any disordered area. At around 1200 K, atoms travel farther away from their initial positions with some areas showing complete disorder. It is noted that the supercell at around 1500 K is still locally ordered from the ion trajectories although according to the
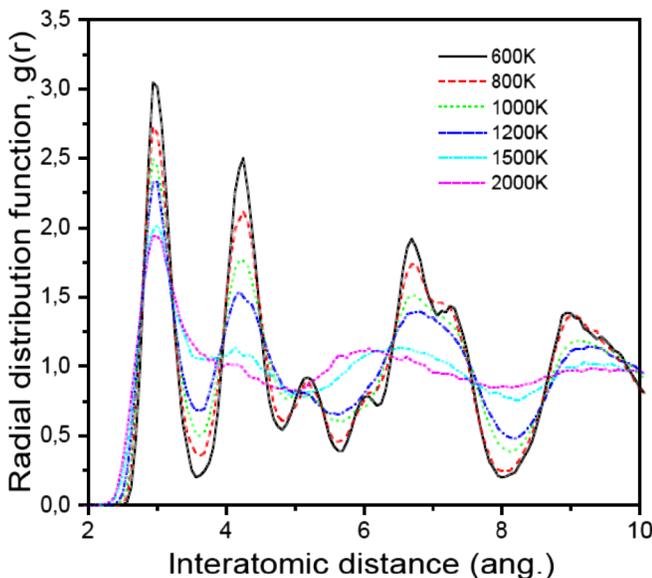
RDF (Fig. 1) it is amorphous. Above 1800 K, the structure is completely disordered in two dimensions by forming linear and tangled clusters while keeping order in the perpendicular direction, forming a striking contrast to conventional melting.

Figures 3(a) and 3(b) show the mean square displacement averaged over atoms, $\langle \Delta R^2 \rangle(t)$, for GST at 1500 and 2000 K, respectively. Note that in the $[1\bar{1}0]$ and $[01\bar{1}]$ directions, atoms move farther away from their initial configurations as a function of simulation times, while in the [111] direction atoms vibrate around a constant value of ~ 0.02 $\mathring{A}^2$ away from their initial configurations. So far, the general feature of melting of GST is unique in that it forms two-dimensional linear and tangle cluster where atoms behave like liquid or amorphous in the {111} planes. While parallel to the [111] direction, they are essentially vibrating around their initial configurations. It has been known that chalcogenide alloys containing one or more elements from group VI are typically good glass formers, which is mainly attributed to the group VI elements forming predominately twofold-coordinated covalent chemical bonds that can produce linear, tangled, polymer like clusters in the melt.

Table I lists a summary of the estimated coordination numbers and average nearest neighbor distances (R_{mean}) for various atom pairs in the liquid structure of GST obtained from 2000 K, where R_{min} and R_{max} are the minimum and maximum nearest neighbor distances, respectively. It is seen that there are significant concentrations of Ge-Ge and Te-Te homopolar bonds, while in the cubic state only Te-Sb and Te-Ge bonds exist. The estimated total coordination numbers for Ge, Sb, and Te in the liquid are 3.75, 3.08, and 2.58, respectively. Furthermore, the tetrahedral coordination of Ge suggests sp^3 hybridization of Ge in the liquid structure and a full coordination of Sb with a

FIG. 1 (color online). Radial distribution function of Ge$_2$Sb$_2$Te$_5$ at temperatures from 600 to 2000 K.
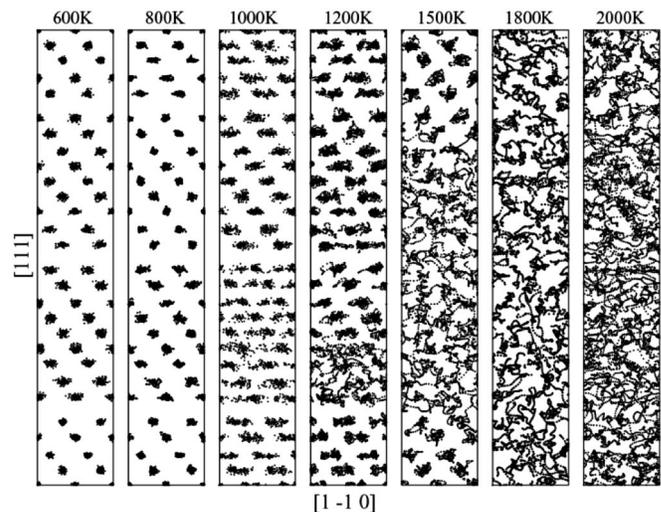
FIG. 2. Ion trajectories of atoms for Ge$_2$Sb$_2$Te$_5$ in the temperature range from 600 to 2000 K.
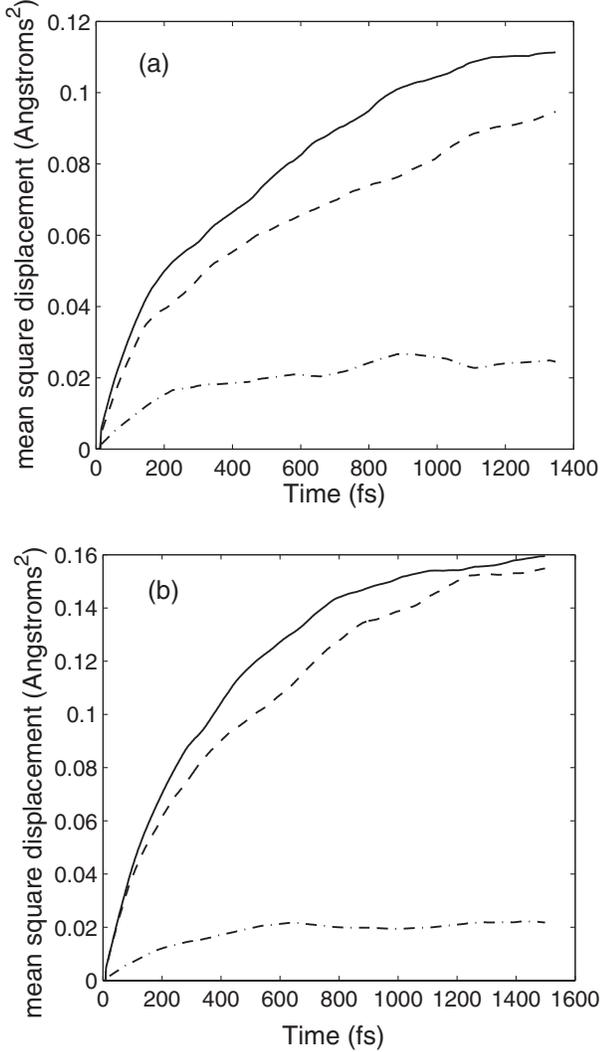
FIG. 3. The mean square displacement averaged over atoms for $Ge_2Sb_2Te_5$. (a) 1500 K. (b) 2000 K, wherein the solid line, dashed line, and dash-dotted line represent the $[1\bar{1}0]$ (R_x), $[01\bar{1}]$ (R_y), and $[111]$ (R_z) directions, respectively.

TABLE I. The estimated coordination number and average nearest neighbor distance (R_{mean}) for various atom pairs in the liquid structure of $Ge_2Sb_2Te_5$ at 2000 K, wherein R_{min} and R_{max} are the minimum and maximum nearest neighbor distance, respectively.

Atom	Bond	Coordination	R_{mean} (Å)	R_{min} (Å)	R_{max} (Å)
Ge	Ge-Te	2.96	2.80_3	2.37	3.06
	Ge-Ge	0.67	2.65	2.22	2.91
	Ge-Sb	0.12	2.76	2.72	2.80
Sb	Sb-Te	2.71	2.96_0	2.51	3.20
	Sb-Sb	0.25	2.77	2.72	2.84
	Sb-Ge	0.12	2.76	2.72	2.80
Te	Te-Ge	1.12	2.80_2	2.37	3.06
	Te-Sb	1.03	2.95_5	2.51	3.22
	Te-Te	0.43	2.81	2.51	2.99

Obviously, the anisotropic factor is so small that it can not induce the two-dimensional melting of GST.

Using the amorphous structures of fcc GST at 1500 and 2000 K, we have performed the crystallization (erase) process of GST at 600 K, whose structure evolution with increasing time are given in Figs. 4(a) and 4(b), respectively. It is seen that the amorphous area decreases with increasing time and both structures are back to their original ones in the end except for a twin that is normal phenomenon during annealing. The total time used for this crystallization process is 54 and 60 ps for the amorphous structure of 1500 and 2000 K, respectively. The amorphous structure crystallizes pretty fast due to its unique amorphous structure of forming linear and tangled clusters in melting.

In conclusion, by *ab initio* MD simulations, we have unraveled the structure evolution of GST with temperatures and the reversible phase transformation between the amor-

total coordinate number 3.08. The estimated total coordination number of ~2.58 for Te in the liquid is generally a mixture of two- and three-coordinated atoms according to the present calculations. Coincidently, a coordination number close to 2.5 has been reported in liquid Te, which was attributed to the lone-pair electrons effect [20].

One issue needs to be addressed is that constant volume AIMD using the equilibrium volume at 0 K will induce pressures at high temperatures, which could influence the melting character if the stress is very anisotropic. To clarify whether this unique melting is induced by pressure or not, we have calculated the pressure and stress matrix for GST at high temperatures. The results show that the pressure is not high, with the highest value of 2.7 GPa at 2000 K. The stresses are far from anisotropic, for example, at 2000 K the stress values of σ_{xx}, σ_{yy}, σ_{zz}, σ_{xy}, σ_{yz}, and σ_{zx} are 2.7, 2.6, 2.9, -0.44, -0.34, and -0.30 GPa, respectively.

FIG. 4. Structural evolutions at 600 K in the crystallization process for amorphous $Ge_2Sb_2Te_5$. (a) the amorphous structure obtained at 1500 K. (b) the amorphous structure obtained at 2000 K.

phous and rocksalt-structured crystalline states. The melting of GST is unique in that atoms form two-dimensional linear and tangled clusters while only vibrating around their initial configurations in the perpendicular direction. Thus this unique melting behavior is responsible for the fast and reversible phase transition between amorphous and crystalline. This rule can be applied to all the other phase-change materials in the Ge-Sb-Te system.

*To whom all correspondence should be addressed.
Email address: zhimei.sun@fysik.uu.se

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