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Local structure of liquid $\text{Ge}_1\text{Sb}_2\text{Te}_4$ for rewritable data storage use

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Abstract

Phase-change materials based on chalcogenide alloys have been widely used for optical data storage and are promising materials for nonvolatile electrical memory use. However, the mechanism behind the utilization is unclear as yet. Since the rewritable data storage involved an extremely fast laser melt-quenched process for chalcogenide alloys, the liquid structure of which is one key to investigating the mechanism of the fast reversible phase transition and hence rewritable data storage, here by means of *ab initio* molecular dynamics we have studied the local structure of liquid $\text{Ge}_1\text{Sb}_2\text{Te}_4$. The results show that the liquid structure gives a picture of most Sb atoms being octahedrally coordinated, and the coexistence of tetrahedral and fivefold coordination at octahedral sites for Ge atoms, while Te atoms are essentially fourfold and threefold coordinated at octahedral sites, as characterized by partial pair correlation functions and bond angle distributions. The local structure of liquid $\text{Ge}_1\text{Sb}_2\text{Te}_4$ generally resembles that of the crystalline form, except for the much lower coordination number. It may be this unique liquid structure that results in the fast and reversible phase transition between crystalline and amorphous states.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Phase-change (PC) materials based on chalcogenide alloys, for example $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST225) and $\text{Ge}_1\text{Sb}_2\text{Te}_4$ (GST124), are technologically important materials, used for optical data storage, such as in compact disks (CD) and digital versatile disks (DVD), and are promising candidate materials for nonvolatile electronic memory use [1–7]. Both optical and electrical data storage types rely on the extremely fast and reversible phase transition between the crystalline and amorphous states, that exhibit a pronounced difference in

optical and electrical properties. The principle of PC optical and electrical recording is simple. By applying an high energy laser beam, 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 have a large difference in optical and/or electrical properties. To switch the amorphous mark back to its crystalline state (erase), another low energy laser beam 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 the reversible phase transition between crystalline and amorphous

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states is the key point for tuning the properties of GST and for searching for new PC materials with better performances. However, a full understanding of the phase-change mechanism behind the utilization has not yet been achieved although PC materials are at present commercially used. Therefore, the structure and phase-change mechanism of the PC compounds are still important open subjects and topics of debate.

Recently, different models for amorphous or liquid GST have been proposed; nevertheless, a common agreement has not yet been achieved. Kolobov *et al* [8] has proposed an amorphous model for GST225 based on extended x-ray absorption fine structure spectroscopy (EXAFS) analysis. It was suggested that the order–disorder transition is due to an umbrella-flip of Ge atoms from an octahedral position into a tetrahedral position. However, in comparison to the amorphous model proposed by Kolobov *et al* [8] for GST225, that of Baker *et al* [9] gave different interpretations of EXAFS data, and more recently, Kohara *et al* [10] suggested an even-number ring structure from reverse Monte Carlo models fitted to x-ray diffraction data. On the other hand, WeŁnic *et al* [11] proposed a spinel structure for amorphous GST124 from static *ab initio* calculations. Therefore, further investigations are necessary to obtain deeper understanding of the amorphous or liquid structure of GST, which will reveal the reversible phase transition and help us search for better performance PC materials. Fortunately, in this respect, *ab initio* molecular dynamics (AIMD) provides an appropriate way, based on the previous successful studies [11–13]. Here by means of AIMD, we explore the local structure of liquid GST124 alloy in order to shed light on the rapid phase-change mechanism of GST alloys.

2. Methods

Ab initio molecular dynamics (AIMD) implemented in the Vienna *ab initio* simulation package [14] was used in the present work. The interatomic forces were computed quantum mechanically using projector augmented wave potentials [15] within the local density approximation. Only one k point (Gamma) was used for the electronic structure calculations. Gaussian smearing was applied and an energy cutoff of 136.4 eV was chosen. The initial configuration is a metastable cubic GST124 supercell that contains 27 Ge, 54 Sb and 108 Te atoms plus 27 vacancies, where Ge, Sb and vacancies are randomly placed in one sublattice and Te atoms occupy the other sublattice. Before AIMD simulations we performed structure optimization for this supercell. After optimization, the supercell size is $18.19 \times 18.34 \times 18.34 \text{ \AA}^3$, which is a distorted rocksalt structure (orthorhombic). A density of $0.0305 \text{ atoms \AA}^{-3}$ close to the experimental value for the amorphous phase [16] is used in the calculations. Firstly the ensemble of 189 atoms plus 27 vacancies was melted and thermalized at 3000 K for 3 ps, where the temperature was controlled using the algorithm of Nosé [17, 18]. Then the liquid was gradually quenched down to the final temperatures of 1000 K over a period of 30 ps at a quenching rate of $6.67 \times 10^{13} \text{ K s}^{-1}$. Finally the structure obtained was rethermalized at 1000 K, which is well above the melting temperature of

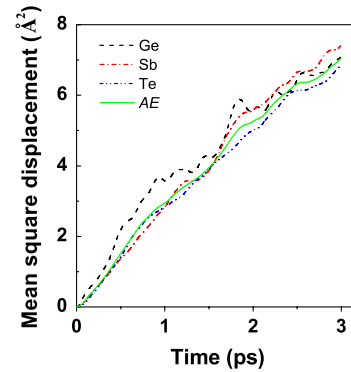


Figure 1. Mean square displacement versus time for Ge (dash), Sb (dash–dot) and Te (dash–dot–dot) atoms as well as for all elements (AE, solid curve) of liquid GST124.

GST124, for another 3 ps. The structural results presented in this work are thus averaged over the configurations gathered over 3 ps at the final temperature.

3. Results and discussion

Figure 1 shows the mean square displacement as a function of time for separate species and all atoms. It is clear that the system is liquid from the linear asymptotic growth of the mean square displacement. To quantify the dynamics of various species in GST124, we extracted the diffusion coefficient, D , from the atomic displacement as a function of time [19]. For partial atomic diffusion coefficients, we obtained $D_{\text{Ge}} \sim 4.04 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $D_{\text{Sb}} \sim 5.28 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, and $D_{\text{Te}} \sim 4.06 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The atomic mobilities of Ge and Te atoms in liquid GST124 are quite close, while Sb shows a slightly higher mobility, which is in contrast to the case for GeTe liquid where Ge atoms exhibit much higher mobility compared to Te atoms [19]. To our knowledge no experimental data on the partial self-diffusion coefficient of liquid GST124 have been reported so far. Furthermore, the calculated values of the partial diffusion coefficient indicate that all atoms diffuse in a coupled state.

Figure 2 shows the reduced partial pair correlation functions for liquid GST124. The maxima of the Te–Ge and Te–Sb pair correlation functions locate at 2.80 and 2.99 Å, comparable to the experimental values of 2.61 and 2.85 Å for Te–Ge and Te–Sb bond lengths [8], respectively. For Te pair correlation functions, the most important contributions come from the Te–Ge and Te–Sb correlations, while the Te–Te correlation is the least important, showing a rather broad first peak around 4.0 Å corresponding to the second-nearest neighbors. Similarly, in the case of Ge and Sb partial pair correlations, Ge–Te and Sb–Te correlations dominate over the partial quantities while the homopolar bonds Ge–Ge, Sb–Sb and Ge–Sb are least important.

The partial and total coordination numbers (Z) for each element are estimated from integrating the partial pair correlation functions (figure 1) and the results are given in table 1. It is clear that for liquid GST124, the major contribution to the total $g(r)$ for Ge is due to the Ge–Te bonds

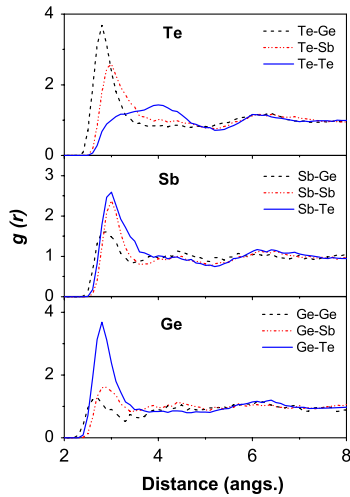


Figure 2. Calculated partial pair correlation function $g(r)$.

Table 1. The estimated average coordination number (Z) for various pairs of atoms in the liquid (1000 K) and crystalline GST124. The cutoff radii for Te–Sb, Sb–Sb, Te–Ge, Te–Te, Ge–Ge and Ge–Sb bonds are 3.5 Å, 3.4 Å, 3.3 Å, 3.0 Å, 2.9 Å and 3.0 Å, respectively.

	With Ge	With Sb	With Te	Z_{total}
Ge	0.29	0.60	3.59	4.48
Sb	0.30	1.25	3.54	5.09
Te	0.90	1.77	0.54	3.21

($Z_{Ge-Te} = 3.59$). In addition, a relatively low proportion of Ge–Ge and Ge–Sb bonds coexist ($Z_{Ge-Ge} = 0.29$, $Z_{Ge-Sb} = 0.60$). Homopolar Ge–Ge bonds in amorphous GST225 have been reported by Baker *et al* [9] from extended XAFS study of local bonding. In total, the average coordination number for Ge atoms in liquid (Z_{Ge}) GST124 is equal to 4.48, which probably suggests a mixture of multifold or defectively octahedrally coordinated Ge atoms in liquid. The results probably exclude the possibility of purely tetrahedrally bonded Ge as suggested in [8] for amorphous GST225. Similarly, the major contribution to the coordination of Sb atoms is from the Sb–Te bonds, with minor contributions from homopolar Sb–Sb and Sb–Ge bonds. In total, the coordination for Sb atoms is 5.09, showing a picture of defectively octahedral coordination. As for Te atoms, there are a rather high proportion of Te–Te bonds in the liquid, while no Te–Te bonds are observed in the crystalline phase. The total average coordination of Te in the liquid is 3.21, which is rather lower compared to the value of 4.5 for the crystalline state, suggesting a picture of even more defectively octahedrally coordinated Te atoms.

Further insight into liquid GST124 is gained by analyzing the (first-neighbor) bond angle distributions, which are shown in figure 3. Maximal peaks are observed in the ranges $88^\circ < \theta < 97^\circ$, $85^\circ < \theta < 94^\circ$, and $86^\circ < \theta < 98^\circ$ for around Ge, Sb and Te atoms, respectively, in contrast to the first-neighbor bond angle at 90° for the crystalline states. In addition, angles at $\sim 60^\circ$ correspond to triangular rings, and a shoulder at $\sim 110^\circ$ gives a signature of the tetrahedral geometry. The fractional distribution of the coordination numbers for various species, as shown in figure 4, agrees with this picture. It is seen that

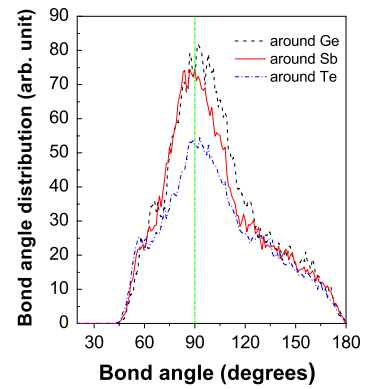


Figure 3. Bond angle distributions around Ge (dash), Sb (dash-dot), and Te (solid) atoms calculated for liquid GST124 at 1000 K. The dashed vertical line shows the position of 90° .

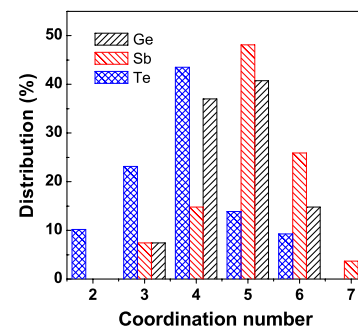


Figure 4. Distribution of coordination numbers for different species.

most Sb atoms are octahedrally and defectively octahedrally coordinated, and the average coordination of 5.09 is mainly a mixture of fourfold, fivefold, sixfold coordinations. Ge atoms are mostly fivefold and fourfold coordinated, while Te atoms are mostly fourfold and threefold coordinated at octahedral sites with contributions from even lower coordinations. The presence of multifold coordination and bond angles at $\sim 90^\circ$ in the liquid network is clearly seen from a snapshot structure of liquid GST124 as illustrated in figure 5. A close investigation of the structure shows that most fourfold Ge atoms are in a distorted tetrahedral environment. At this stage we may conclude that the liquid structure is similar to the crystalline form on average, but with important fluctuations around the mean.

4. Conclusion

On the basis of *ab initio* molecular dynamics study, liquid GST124 is essentially chemically ordered at 1000 K, with Ge–Te and Sb–Te as the dominant first-nearest neighbors, while Te–Te bonds are the second-nearest neighbors. The results show that the local structure of liquid GST124 is a picture of most Sb atoms being octahedrally coordinated, while there is coexisting tetrahedral coordination and fivefold coordination at octahedral sites for Ge atoms, the Te atoms essentially being fourfold and threefold coordinated at octahedral sites with contributions from twofold, fivefold and sixfold coordinations, as characterized by partial pair correlation functions and bond angle distributions. Although we cannot directly study

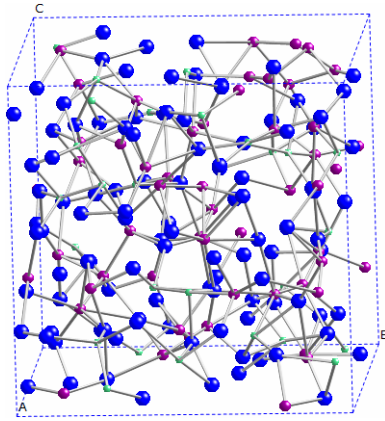


Figure 5. Snapshot of the liquid GST124 structure. The large black atoms represent Te, the middle light black atoms represent Sb and the small light grey atoms represent Ge.

a realistic amorphous structure since it is not possible to reproduce the experimental quench rates because of the limited timescales of *ab initio* molecular dynamics, the liquid structure of coexisting tetrahedral and octahedral coordination shown here will help us understand the pronounced optical and electrical contrast between the amorphous and crystalline structures and hence the high speed phase transition. The present results will shed light on the structure and thus working principles of phase-change recording technology.

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