

Unique amorphous structure of Ge₂Sb₂Te₅ alloy

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ABSTRACT

By *ab initio* molecular dynamics simulations, we unraveled the unique network structure of amorphous Ge₂Sb₂Te₅, which shows similar structural ordering as its cubic form. Furthermore, the highest ordering around Te is expected and the arrangement of the Te-Te bond is similar to that in cubic Ge₂Sb₂Te₅ as characterized by the pair distribution functions and bond angle distributions. Therefore, the reversible phase transition between amorphous and cubic forms would involve the movement of not only Ge but also Sb atoms. Finally, high density of the sample will induce higher ordering of amorphous Ge₂Sb₂Te₅ and an over coordinated system.

Key words: Ge₂Sb₂Te₅, unique amorphous structure, *ab initio* molecular dynamics

1. INTRODUCTION

Ge₂Sb₂Te₅ (GST) is technologically important phase-change material for rewritable data storage applications. Currently it is considered as the most promising candidate material for nonvolatile electronic memories.¹⁻³ Both optical and electrical data storage rely on the extremely fast and reversible phase transition between the crystalline (rocksalt structure) and amorphous states of GST. The pronounced optical or electrical contrast indicates that the local atomic arrangement of the amorphous state differs considerably from that of its crystalline state. However, the fact that the atomic rearrangement required for recrystallization of amorphous GST proceeds within a few nanoseconds⁴ indicates that these two states should have similar local atomic arrangements. Therefore, a full understanding of the local atomic arrangements of GST is necessary to reveal the reversible phase change mechanism behind the utilization and thus to identify new phase-change materials with better performance. However, the mechanism has not been fully understood as yet although many efforts have been made.⁵⁻¹⁴ Here by *ab initio* molecular dynamics (AIMD) simulations, we investigated the local atomic arrangements of amorphous Ge₂Sb₂Te₅ (*a*-GST) to shed light on the fast reversible phase change between amorphous and crystalline states of GST alloys.

2. CALCULATION METHODS

The calculations methods used in the present work are implemented in the Vienna *ab initio* simulation package.¹⁵ Details of the *ab initio* and AIMD simulations have been reported previously.¹¹⁻¹⁴ Two supercells of GST have been used. One contains 243 atoms with an experimental density of 0.0297 atoms/Å³ [16] (refers to as *La*-GST), the other contains 108 atoms with a theoretically calculated density of 0.0348 atoms/Å³ through our static *ab initio* calculations of GST at 0K (refers to as *Ha*-GST). For the melt and quench process, the supercells were firstly melted and thermalized at 5000K for 3 ps, and then it was quenched down to 300 K by a continuous quenching route with a constant cooling rate of 333 K ps⁻¹. The structural results presented in this paper are averaged over the configurations gathered during the 3 ps at 300 K.

3. RESULTS & DISCUSSION

Fig. 1 shows the pair distribution functions (PDFs) for *Ha*-GST and *La*-GST. It is seen in Fig 1 that the density shows no significant effects on the features of PDFs. The Te-Te pair function (Fig. 1a) is rather interesting by showing a very broad first peak at ~ 4.1 Å and a second peak at ~ 6.09Å which are comparable to the second and third

neighbor distances of cubic (*c*)-GST, respectively. This shows a high ordering of the Te-Te bond in *a*-GST which resembles that of its cubic form because there is no Te-Te bonds existing as the first nearest neighbor in *c*-GST. The Te-Sb and Te-Ge (Fig. 1a) pair function show very sharp first peaks at $\sim 2.9 \text{ \AA}$ and $\sim 2.8 \text{ \AA}$ which correspond to the average bond lengths of Te-Sb and Te-Ge in *a*-GST, respectively. In addition, the Te-Sb pairs show broad second peaks at $\sim 6.02 \text{ \AA}$ and $\sim 6.28 \text{ \AA}$ for *Ha*-GST and *La*-GST, respectively; while the Te-Ge pairs show broad second peaks at $\sim 5.94 \text{ \AA}$ and $\sim 6.12 \text{ \AA}$ for *Ha*-GST and *La*-GST, respectively. Compared with the third nearest neighbor distance or lattice constant of *c*-GST ($\sim 6.02 \text{ \AA}$), the results indicate that high density induces higher ordering in *a*-GST. A close study on the Ge-Ge, Ge-Sb and Sb-Sb PDFs shows the similar trends as that of Te-Te, Te-Sb and Te-Ge, although these three types of bonds are not existed in its cubic form. Furthermore, the analysis of PDFs demonstrates a medium range ordering in *a*-GST and shows higher ordering around Te atoms.

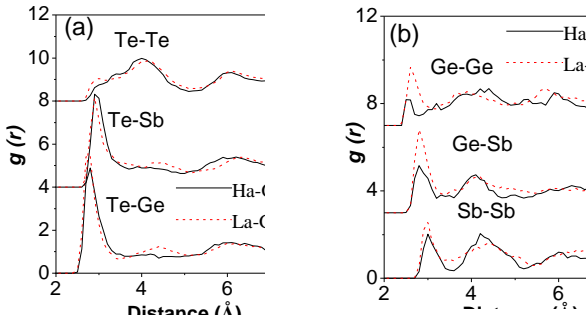


Fig. 1 The calculated pair distribution function $g(r)$ in *Ha*-GST (solid line) and *La*-GST (dash line) at 300 K.

By integrating the first peaks of PDFs around the constitute elements, we obtained the average total coordination numbers (CN). In *Ha*-GST, the total CNs around Ge, Sb and Te are 5.64, 6.24 and 4.86, respectively, which shows a picture of slightly over coordinated Ge and Te and under coordinated Sb compared to *c*-GST. In *La*-GST, the total CNs around Ge, Sb and Te are 5.33, 5.67 and 4.26, respectively, which shows a picture of under coordinated system in contrast to *Ha*-GST. Further investigation on the amorphous structures shows multifold coordinated Ge, Sb and Te in *a*-GST. Fig. 2 (a) and (b) show the fraction distribution of CNs around Ge, Sb and Te in *Ha*-GST and *La*-GST, respectively. It is seen in *Ha*-GST (Fig. 2a), fivefold and sixfold coordination dominate Ge and Sb, while fivefold coordination predominates Te. In addition, there are contributions from as high as sevenfold coordination for Ge and Sb and as low as threefold coordination for Te and Sb. On the other hand, in *La*-GST, Ge is dominated by fourfold and fivefold coordination with contributions from sixfold and threefold, Sb is dominated by fourfold, fivefold and sixfold coordination, and Te is predominated by threefold and fourfold coordination with significant contribution from twofold coordination. This clearly shows a picture of multifold coordinated amorphous system and high density will induce slightly over coordinated amorphous phase.

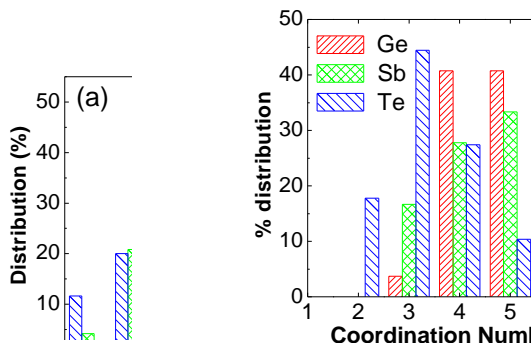


Fig. 2 Fraction distribution of coordination numbers around Ge, Sb and Te atoms in (a) *Ha*-GST and (b) *La*-GST.

The local structure of *a*-GST can be further analyzed by the (first-neighbor) bond angle distributions, which is shown in Fig. 3. For *Ha*-GST (Fig. 3a), sharp peaks centering at $\sim 92^\circ$, $\sim 87^\circ$ and $\sim 90^\circ$ are observed around Ge, Sb and Te, respectively, which reminisces the octahedral geometry of rocksalt structured GST225. In addition, there are small broad peaks at $\sim 166^\circ$ indicating a distorted octahedrally coordinated *Ha*-GST. For *La*-GST (Fig. 3b), sharp peaks centering at $\sim 94^\circ$, $\sim 88^\circ$ and $\sim 91^\circ$ are observed around Ge, Sb and Te, respectively, which also shows a distorted octahedrally coordinated *La*-GST considering the presence of small broad peaks at $\sim 164^\circ$. For both phases, there are small peaks at $\sim 60^\circ$, which indicates the presence of triangle rings in *a*-GST.

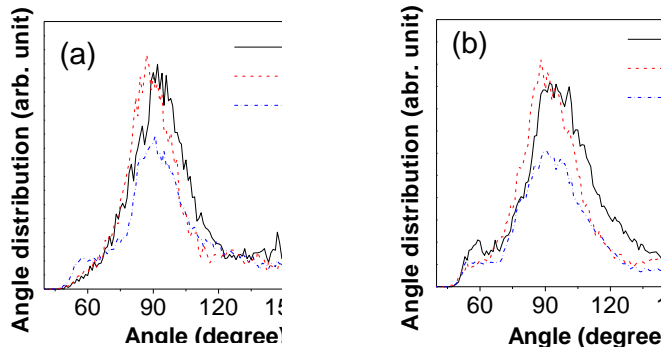


Fig. 3 Bond angle distributions calculated around Ge (solid), Sb (dash), and Te (solid dot) in (a) *Ha*-GST and (b) *La*-GST, where the cut off distance to calculated bond angle is 3.5\AA .

Furthermore, the angle distribution of various pairs of bonds with respect to the [111] crystallographic direction shown in Fig. 4 gives more information of *a*-GST. The most interesting phenomenon is the Te-Te pairs (Fig. 4a), which shows sharp peaks at $\sim 90^\circ$ for both *a*-GST phases. Compared with the vertical dashed line existed in *c*-GST, the arrangement of the Te-Te bonds in *a*-GST demonstrate the highest ordering resembling that in its cubic form. It is obvious that the amorphous structure of *a*-GST is unique in that the Te-Te bonds demonstrated the same chemical and structural ordering as that in its cubic structure. There is correlation in the Te-Sb and Te-Ge pairs which shows a high ordering (Fig. 4 a). Therefore, the highest ordering around Te in *a*-GST is expected. As seen in the angle distributions in Fig. 4 (b), there is also correlation in the Sb-Sb and Ge-Ge bonds shown by the rather sharp peaks. Compared to the corresponding angles of $\sim 36^\circ$, $\sim 90^\circ$ and $\sim 144^\circ$ existed in *c*-GST, the Sb-Sb and Ge-Ge bonds also show highly local ordering in *a*-GST which resembles that of its cubic structure. Furthermore, higher ordering in *Ha*-GST is expected shown by the sharper peaks in the angle distributions (Fig. 4b). The Ge-Sb bond seems more or less uncorrelated as seen in the broad distributed angles, where the peak position shifts from $\sim 140^\circ$ in *Ha*-GST to $\sim 90^\circ$ in *La*-GST.

4. CONCLUSION

On the basis of *ab initio* molecular dynamics study, we have shown that the local structure of *a*-GST generally resembles that of its cubic form as characterized by the pair distribution functions and bond angle distributions. The density shows no significant effect on the structure ordering of *a*-GST, but has obvious effect on the chemical ordering around the constitute elements as exhibited by the slightly over coordinated system in *Ha*-GST and under coordinated situation in *La*-GST. Furthermore, the highest ordering around Te atoms is expected and the arrangement of the Te-Te bond is quite similar to that of *c*-GST. In addition, the average total coordination number of Te in *Ha*-GST ($CN = 4.86$) is comparable to that in *c*-GST ($CN = 4.8$). Therefore, the reversible phase transition between amorphous and cubic forms would involve the movement of not only Ge but also Sb atoms.

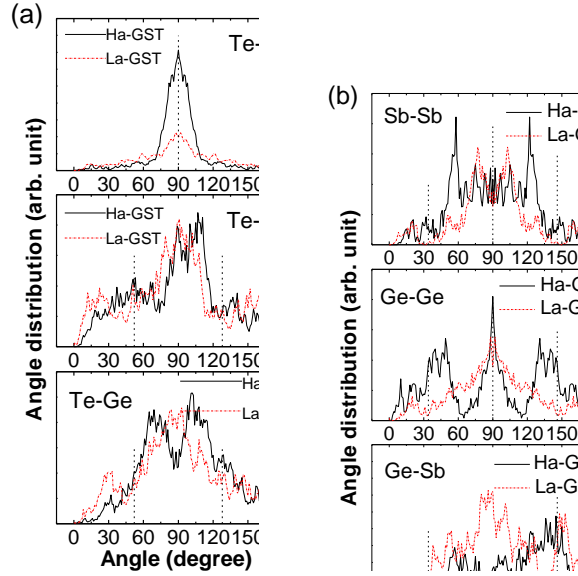


Fig. 4 Bond angle distributions for various pairs of bonds with respect to the $[111]$ direction. Herein the cut off distance to calculate bond angles is 3.5 \AA , the dash vertical lines show the corresponding angle positions in cubic GST.

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Biographies

Zhimei Sun received her Master and Ph. D degree in Materials Science from Institute of Metal Research, Chinese Academy of Sciences, in 1999 and 2002, respectively. Then she worked as a full position researcher at Materials Chemistry of RWTH (Aachen University), Germany, from September 2002 to June 2005, and as a senior researcher at the Department of Physics, Uppsala University, Sweden, from July 2005 to June 2007. Dr. Zhimei Sun joined the faculty of Xiamen University in June 2007. She is currently a professor at the Department of Materials Science and Engineering, Xiamen University. She has been working in the research field of carbides, nitrides and semiconductors, with experience on both experiments and computer simulations. She has published roughly 60 peer reviewed papers in prestigious journals so far.