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Pressure induced short-range structural changes in supercooled liquid Ge₂Sb₂Te₅

Abstract

Phase-change material such as Ge₂Sb₂Te₅ is usually utilized to store data due to the pronounced contrast in optical and electrical properties between crystalline and amorphous phases. As the density differs in the two phases, it is necessary to explore the influence of pressure on the structures of Ge₂Sb₂Te₅, especially for the supercooled liquid which is an inevitable state in the formation of the two phases. The short-range structures in supercooled liquid Ge₂Sb₂Te₅ under compression have been investigated by using ab initio molecular dynamics simulation. The supercooled liquid eventually changes to a solid with an increase in pressure. During the process, tetrahedrons decrease slightly, revealing that tetrahedral structures are insensitive to the pressure. Octahedrons increase as the pressure is less than 3.7 GPa and then decrease, suggesting that a moderate pressure can promote the formation of octahedrons. The body-centered-cubic, face-centered-cubic and hexagonal closed-packed structures are observed at 9.9 GPa and then increase gradually. Additionally, it is noticed that Sb- and Te-centered clusters prefer Ge-centered clusters to forming the high-coordinated short-range structures during the compression process. Our research make us aware of the effects of pressure on short-range structures in supercooled liquid, which is of great importance in the application of phase-change materials.

Keywords

Phase-change materials, Pressure, Short-range order, Molecular dynamics

Disciplines

Engineering Physics | Materials Science and Engineering

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Pressure induced short-range structural changes in supercooled

liquid Ge₂Sb₂Te₅

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Abstract

Phase-change material such as Ge₂Sb₂Te₅ is usually utilized to store data due to the pronounced contrast in optical and electrical properties between crystalline and amorphous phases. **As the density differs in the two phases**, it is necessary to explore the influence of pressure on the structures of Ge₂Sb₂Te₅, especially for the supercooled liquid which is an inevitable state in the formation of the two phases. The short-range structures in supercooled liquid Ge₂Sb₂Te₅ under compression have been investigated by using *ab initio* molecular dynamics simulation. The supercooled liquid eventually changes to a solid with an increase in pressure. During the process, tetrahedrons decrease slightly, revealing that tetrahedral structures are insensitive to the pressure. Octahedrons increase as the pressure is less than 3.7 GPa and then decrease, suggesting that a moderate pressure can promote the formation of octahedrons. The body-centered-cubic, face-centered-cubic and hexagonal closed-packed structures are observed at 9.9 GPa and then increase gradually. Additionally, it is noticed that Sb- and Te-centered clusters prefer Ge-centered clusters to forming the high-coordinated short-range structures during the compression

process. Our research make us aware of the effects of pressure on short-range structures in supercooled liquid, which is of great importance in the application of phase-change materials.

Keyword: phase-change materials, pressure, short-range order, molecular dynamics

Introduction

Chalcogenide alloys, as the typical phase-change materials (PCMs), present sharp contrast in optical and electronic properties between the crystalline and amorphous phases.[1-3] Due to the fast and reversible transition between the two phases, they are widely used to act as the non-volatile memory materials.[4-6] Among the chalcogenide compounds, $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) is a very good choice for the superior performance upon transformation speed and the stability in amorphous state.

During the memory process, GST is fast cooled from liquid to supercooled liquid and then to the amorphous state to storage the data, while amorphous GST is heated to supercooled liquid and then relaxed to the crystalline phase to erase the information. Liquid and supercooled liquid GST, yet with salient difference, is proved to have a high similar short-range order (SRO) to the amorphous phase composed of tetrahedral- and octahedral motifs.[7-10] Crystalline GST presents a NaCl structure with Te occupying the sites of Cl atoms while Ge/Sb/vancies randomly occupying the other sites.[11, 12] Due to the structural differences between the two phases, stress is inevitable in the phase-change process. Therefore, the effect of stress on GST has attracted a lot of attentions and interests. Some researchers studied the local structural changes in the amorphization process of crystalline GST induced by pressure, trying to find the phase-change mechanism between the crystal and amorphous phases.[13-15] And they found a body-centered-cubic (BCC) polymorph under a large pressure.[16, 17] Interestingly, the BCC structure is also observed in the crystallization process of amorphous GST induced by high pressure.[18] As pressurized amorphous GST exhibits better conduction and thermal stability than that formed under stress-free conditions[19, 20] and can fast transform to crystalline phase with lower laser power,[21] some researches are made to explore the influence of pressure on the amorphous GST. Sun et al reported that pressure can lead to amorphous–amorphous transition in GST,[22] while Xu et al. found that pressure can change the electrical resistivity of amorphous GST.[23] Although pressure plays a

significant role in the whole phase-change process, the supercooled liquid as an essential state during the phase-change memory, seems to be ignored in the pressure investigations.

In order to compensate the knowledge of pressure upon supercooled liquid GST, in our work, we have explored the structural changes in supercooled liquid GST at 600 K under compression by using *ab initio* molecular dynamics (AIMD) simulations. With the volume of simulation cell decreases gradually, the external pressure increases, and the supercooled liquid GST changes to a solid eventually. Pair correlation function (PCF), coordination numbers (CN), bond-angle distribution function (BDF) and atomistic cluster alignment (ACA) method[24] are used to characterize the short-range orders in the compression process. **Apart from octahedron and tetrahedron, BCC, face-centered-cubic (FCC) and hexagonal closed-packed (HCP) structures are also observed in the solid GST.** The research results can improve the understanding of pressure on the short-range structures in supercooled liquid GST, which contribute to the full application of GST.

Methods

By using the Vienna *ab initio* simulation package (VASP) based on density functional theory,[25, 26] the AIMD simulations were carried out to explore the influence of pressure on the short-range structures in supercooled liquid GST, with the projector-augmented wave (PAW) method and the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA-PBE).[27-29] The simulation box composed of 42 Ge, 42 Sb and 105 Te was obtained from our previous study,[8] which was cooled from 2000 K to 600 K quickly with a rate of 33.3K/ps. The initial simulation cell was adjusted to ensure that the internal pressure was close to zero. The time step was 3 fs and only Γ point was sampled in the Brillouin zone. Each edge length of cubic cell was compressed by 2% and then the cell was relaxed for 6000 time steps every time, until the cell was compressed by 20%. The Nose-Hoover thermostat is utilized to keep a stable temperature and the canonical ensemble was

used to control the simulation cell for each relaxation.[30, 31] With an ACA method which is widely used to explore the SROs of liquids and glasses,[32-34] we have studied the evolutions of the short-range structures in supercooled liquid GST in the compression process.

Results and Discussion

Figure 1(a) shows the pressure-strain curves of GST under compression, the pressure increases slowly when the strain is less than 10% and then increases notably as the strain is beyond this range. Figure 1(b) presents the total pair correlation functions (PCF) of GST under different pressures. As the pressure increases, the first peak becomes sharper notably and shifts to the left slightly, the second peak becomes smaller and disappears gradually, while the third peak becomes prominent and moves to the left to form a new second peak, revealing that the SRO in GST becomes more well-defined with the increasing pressure. It may be that the atoms in the second neighboring shell move to the first neighboring shell make atoms more compact. As the cutoff distance of 3.5 Å (the dashed line in Figure 1(b)) can include most of atoms in the first shell during the compression process, it can effectively reflect the changes in SROs for GST, thus it can be utilized for further structural analysis.

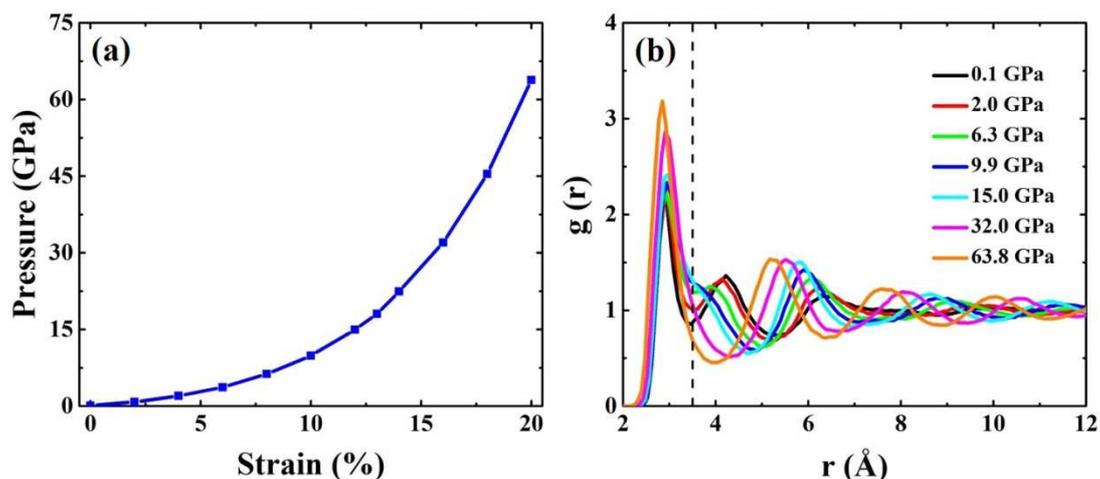


Figure 1. (a) Pressure-strain curve under compression. (b) Total PCF of GST with different pressures.

To identify the state of GST in the compression process, we computed the self-part of the time-dependent van Hove correlation function

$$G_s(\mathbf{r}, t) = \frac{1}{N} \langle \sum_{j=1}^N \delta(\mathbf{r} + \mathbf{r}_j(0) - \mathbf{r}_j(t)) \rangle \quad (1)$$

where N is the number of atoms in the system, $\mathbf{r}_j(t)$ is the time-dependent position coordinate of the j^{th} atom. $4\pi r^2 G_s(\mathbf{r}, t) d\mathbf{r}$ is the probability of finding an atom at time t in the vicinity $d\mathbf{r}$ of points at the distance r given that initially the particle was located at the origin. The self-part of the time-dependent van Hove correlation functions $G_s(r; t)$ for GST under different pressures are illustrated in Figure 2. **As the pressure increases from 0.1 GPa to 18.0 GPa (during the strain range from 0% to 13%), $G_s(r; t)$ presents an obvious change with time, revealing that GST is still a supercooled liquid in this stage. When the pressure increases to 22.4 GPa, the peak of $G_s(r; t)$ changes very small with time, indicating that GST changes to a solid. And as pressure continuously increases to 63.8 GPa, $G_s(r; t)$ hardly changes with time, suggesting that pressure can effectively inhibits the motion of atoms.**

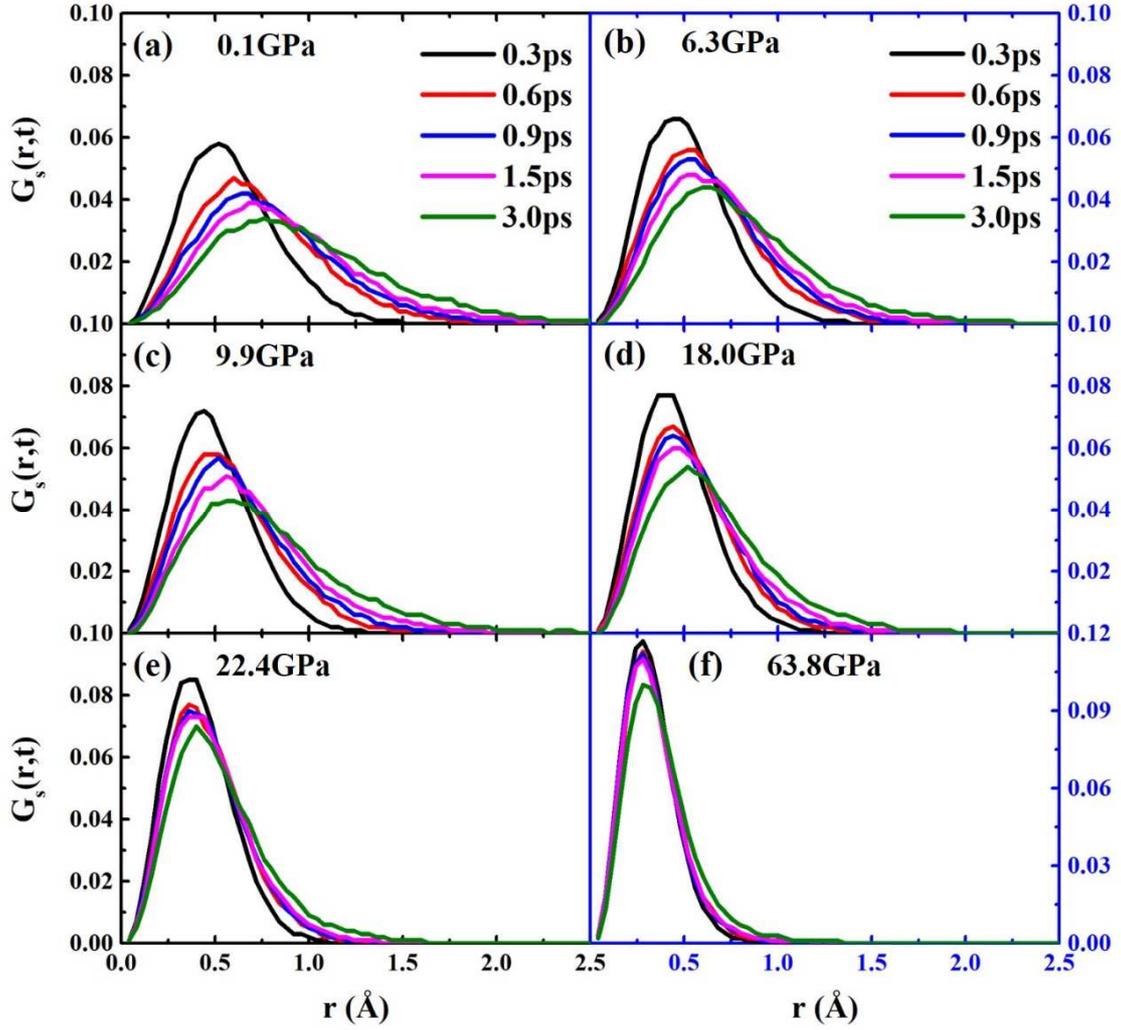


Figure 2. The self-part of the van Hove correlation function $G_s(r,t)$ for GST at 600 K at six different pressures.

Figure 3 shows the partial PCF of GST with pressure. In the beginning of compression, the first peaks of PCFs for homopolar bonds (Ge-Ge, Sb-Sb, Ge-Sb and Te-Te) are relative small while those for heteropolar bonds (Ge-Te and Sb-Te) are prominent, indicating that GST tend to present an ABAB (A: Ge, Sb and B: Te) arrangement without a large compression.[35, 36] However, the first peaks of PCFs for homopolar bonds strengthen gradually and become notable as the pressure increases, while the first peaks of PCFs for heteropolar bonds only shift to the left slightly with a small change, indicating that the homopolar bonds increase pronounced as the simulation cell is reduced. When the pressure reaches 63.8 GPa, the first peaks of PCF for homopolar bonds become very prominent, illustrating that

homopolar bonds play a significant role in the first shell during the compression process.

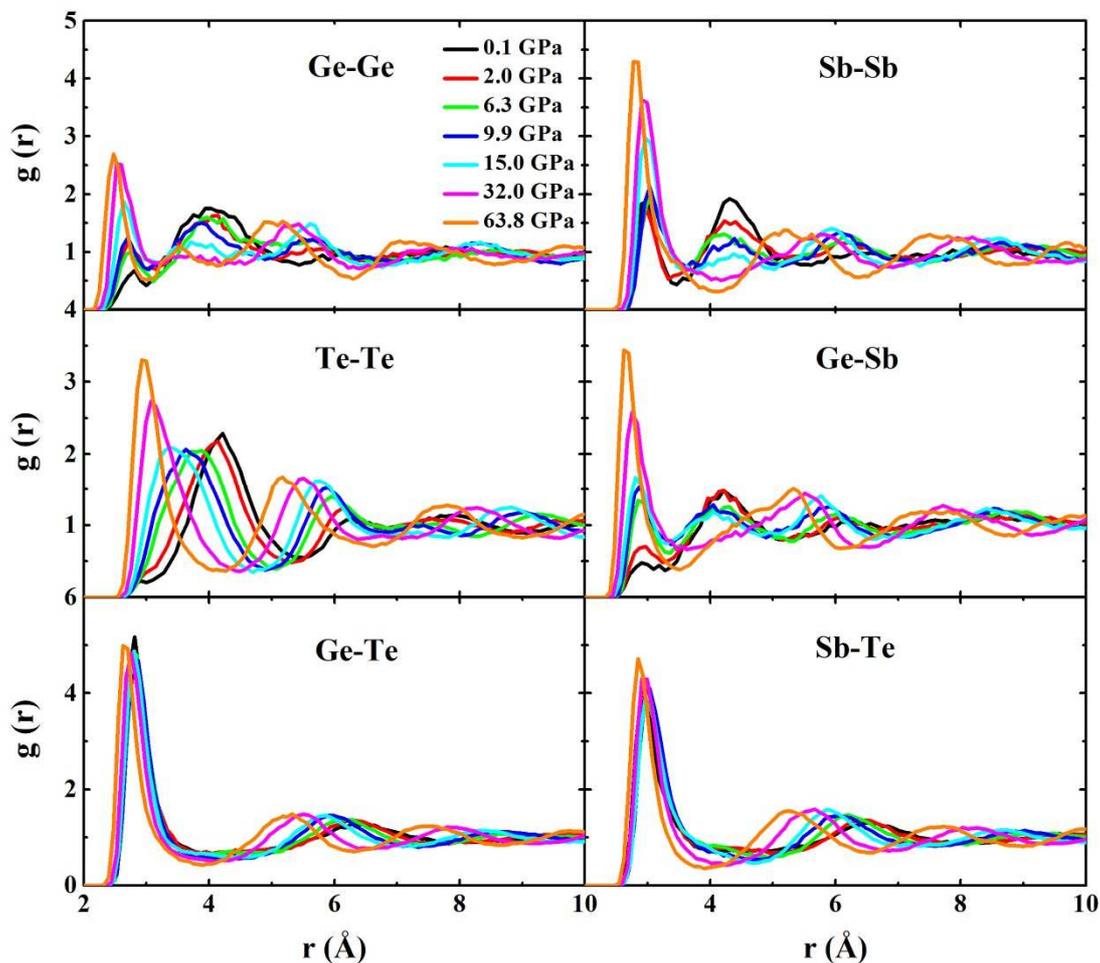


Figure 3. Partial PCF of GST under different pressures.

To further study the local chemical environment of each element under different pressures, we have calculated the coordination numbers (CNs) for GST with a cutoff distance of 3.5 \AA , as shown in Figures 4(a)-(c). As the pressure increases to 63.8 GPa gradually, CNs of Ge, Sb and Te eventually increase to 10.8, 11.7 and 12.2, respectively, which are close to the CNs in FCC and HCP structures. Interestingly, CNs of homopolar bonding atoms are always smaller than those of heteropolar bonding atoms for Ge- and Sb-centered configurations. However, CN of Te-Te increases quickly and becomes larger than those of Te-Ge and Te-Sb for Te-centered configuration at 9.9 GPa, indicating that homopolar bonding atoms have a more important effect on Te-centered configuration. Figures 4(d) and (e) show the CN

distribution of each element when the pressure is 0.1 GPa and 63.8 GPa, respectively. CN of both Ge and Sb atoms concentrate on 4 and 5 while that of Te atoms concentrate on 3 and 4 under 0.1 GPa. As the pressure becomes 63.8 GPa, CN of Ge atoms center on 10 and 11, and that of Sb atoms center on 11 and 12, while that of Te atoms center on 12 and 13. CN of Te atoms show a largest increase in the deformation process, indicating that Te-centered short-range configurations are more sensitive to the pressure.

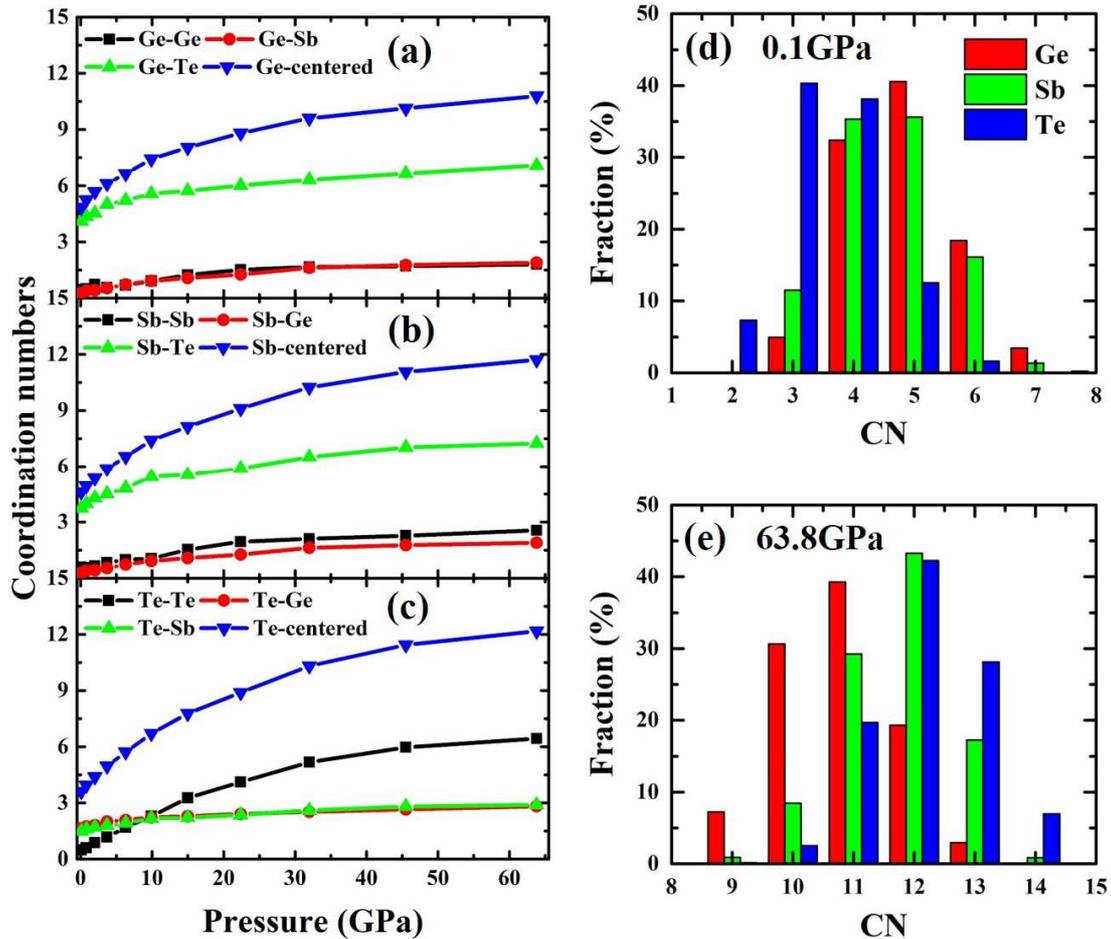


Figure 4. CN and the associated distribution of GST with the pressure under compression.

Figure 5 shows the bond-angle distribution functions (BDFs) of total, Ge-, Sb- and Te-centered atoms under compression, respectively. For the BDF of total atoms, the main peak locates at $\sim 90^\circ$ when the pressure is 0.1 GPa, reminding us of the octahedral structures, and a small shoulder is observed at $\sim 50^\circ$. As the pressure increases to 15.0 GPa gradually, the main peak at $\sim 90^\circ$ maintains while the small

shoulder becomes notable and shifts to $\sim 60^\circ$. With the pressure increases continuously, the peak at $\sim 60^\circ$ changes to the main peak notably while the peak at $\sim 90^\circ$ disappears, in addition, a remarkable peak at $\sim 110^\circ$ is observed, which reminds us of the SROs in distorted FCC and HCP structures. The BDFs of Ge-, Sb- and Te-centered atoms present a similar tendency to that of total atoms during the compression process, indicating that Ge-, Sb- and Te-centered SROs change from octahedral structures to FCC or HCP structures in the compression process. In addition to the similarity, the difference between them should also be noticed, the peak at $\sim 60^\circ$ is more prominent in Te-centered BDF with the increasing pressure, hinting that Te-centered SROs prefer Ge- and Sb-centered SROs to form the well-defined FCC or HCP structures.

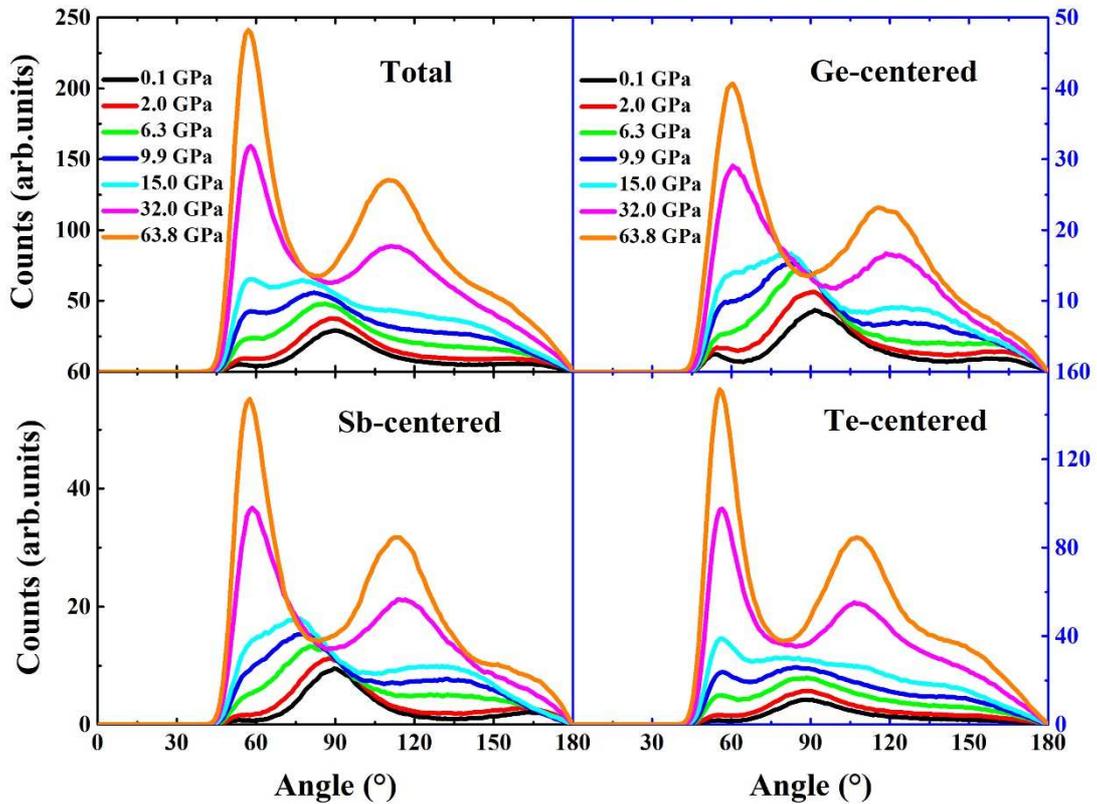


Figure 5. BDFs of GST with different pressures under compression.

To qualitatively identify the short-range structures in GST, the ACA method,[24] which can present the uniform SRO visually, is utilized. 2000 clusters are randomly selected from 6000 trajectories and each cluster is composed of one central atom and twelve neighboring atoms. These clusters are aligned with each other to minimize the

overall mean-square distances by rigid rotation and relative translation. Then we obtain the atomic density contour map for a given iso-surface value, as shown in Figure 6. When the pressure is 0.1 GPa, both Ge- and Sb-centered clusters show the octahedral structures while the uniform SRO of Te-centered clusters is relative disorder. As the pressure becomes to 9.9 GPa, Ge-centered cluster presents a distorted octahedral structure and the contours is nonuniform, Sb-centered cluster shows a distorted structure similar to the defective octahedron, while SRO of Te-centered cluster is still not obvious, suggesting that SROs in GST change with the increasing pressure. As the pressure reaches 63.8 GPa, interestingly, Ge-centered cluster becomes disorder whereas both Sb- and Te-centered clusters present a distorted FCC structure, indicating that the Sb- and Te-centered SROs in GST tend to change to FCC structures when the atoms in the first shell increase with the pressure.

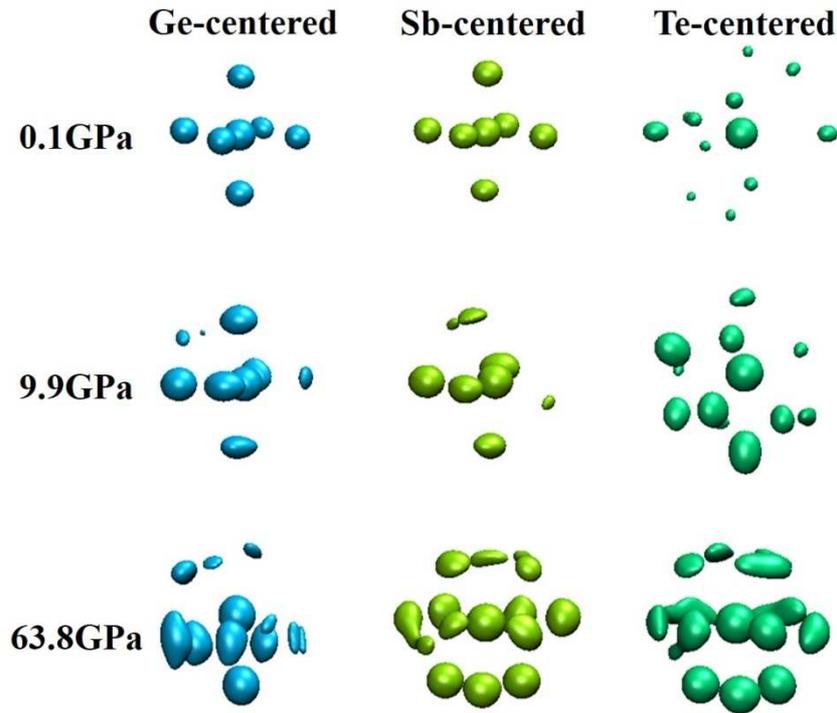


Figure 6. Atomic-density contour plot of GST from the ACA method at selected pressures of 0.1, 9.9 and 63.8 GPa, with the iso-surface value of 0.18, 0.25 and 0.45\AA^{-3} , respectively. Cyan, yellow and green contour plots represent the SROs of Ge-, Sb- and Te-centered clusters, respectively.

To quantitative identify the fractions of SROs in GST under different pressures, the

individual cluster-template alignment analysis from ACA method is applied. Five standard templates (Tetrahedron, octahedron, BCC, FCC and HCP) are built. As a standard template is fixed, the selected cluster with more atoms than template is randomly rotated to minimize the mean-square distance between the template and selected cluster:

$$\Delta r_T^2 = \min_{C=1,\dots,n_C} \Delta r_{C,T}^2 \quad (2)$$

$$f = \min \left(\frac{1}{n_T} \sum_{T=1}^{n_T} \Delta r_T^2 \right) \quad (3)$$

where $\Delta r_{C,T}^2$ is the distance between atom C in cluster and atom T in template. Δr_T^2 is the minimal square distance between atom T in the template and all n_C atoms in the cluster. Structure fitting score f acts as an important parameter to identify the structural similarity between template and selected cluster. When the structure fitting score is smaller than 0.2, the selected cluster is regarded as the similar structure to the template. A larger f means the selected cluster has more deviation from the standard template.

Figure 7 shows the fractions of the five structures in GST during the compression process. For total clusters, only tetrahedrons and octahedrons are observed in the early stage of compression when the pressure is close to zero, as shown in Figure 7(a). As the pressure increases, the fraction of octahedron increases first during the pressure range from 0.0 to 3.7 GPa and then decreases gradually, while that of tetrahedron shows a small decrease. In addition, BCC, FCC and HCP structures are also observed when the pressure reaches 9.9 GPa, and all of them increase with the pressure except a decrease at 63.8 GPa for HCP structure. In our previous study,[8, 10] we find that GST is mainly composed of tetrahedron and octahedral structures (i.e., defective and distorted octahedrons), then it is inferred that some octahedral structures in supercooled liquid GST will change to BCC, FCC and HCP structures as the pressure is larger than 9.9 GPa.

To further understand the role of Ge-, Sb- and Te-centered SROs played in the compression process, we have calculated the fractions of the five SROs centered Ge,

Sb and Te atoms, respectively, as shown in Figures 7(b)-(d). For Ge-centered SROs, tetrahedrons decrease quickly when the pressure is less than 9.9 GPa and then decrease slowly, octahedrons increase first in the pressure range from 0.0 to 6.3 GPa and then decrease when the pressure is beyond the scale. Ge-centered BCC, FCC and HCP structures are first found at 22.4 GPa and then they increase gradually, as seen in Figure 7(b). For Sb-centered SROs, the fraction of tetrahedrons is relative stable with the pressure, the fraction of octahedrons shows an obvious increase from 0.1 to 2.0 GPa and then decreases to zero quickly, BCC, FCC and HCP structures arise at 9.9 GPa and then increase with the increasing pressure, as seen in Figure 7(c). As for Te-centered SROs, tetrahedrons and octahedrons first increase when the pressure is change from 0.1 to 6.3 GPa, and then the fraction of tetrahedrons remains at ~5% whereas octahedrons tends to disappear with the increasing pressure. BCC, FCC and HCP structures are observed at 9.9 GPa and then increase with the increasing pressure, but the fraction of HCP structure presents a drop at 63.8 GPa, as seen in Figure 7(d).

Compare the changes in fractions of Ge-, Sb- and Te-centered SROs, Ge-centered tetrahedrons decrease whereas Te-centered tetrahedrons increase in the pressure range from 0.1 to 6.3 GPa, leading to that the fraction of total tetrahedrons is relative stable in the compression process. As the pressure increases gradually, all of Ge-, Sb- and Te-centered octahedrons increase first and then decrease, indicating that a moderate pressure can promote the formation of octahedrons but a large pressure will destroy the octahedrons. BCC, FCC and HCP structures centered Sb and Te atoms are formed at 9.9 GPa which is earlier than those in Ge-centered clusters, revealing that Sb- and Te-centered clusters prefer to forming the high-coordinated SROs (i.e., BCC, FCC and HCP).

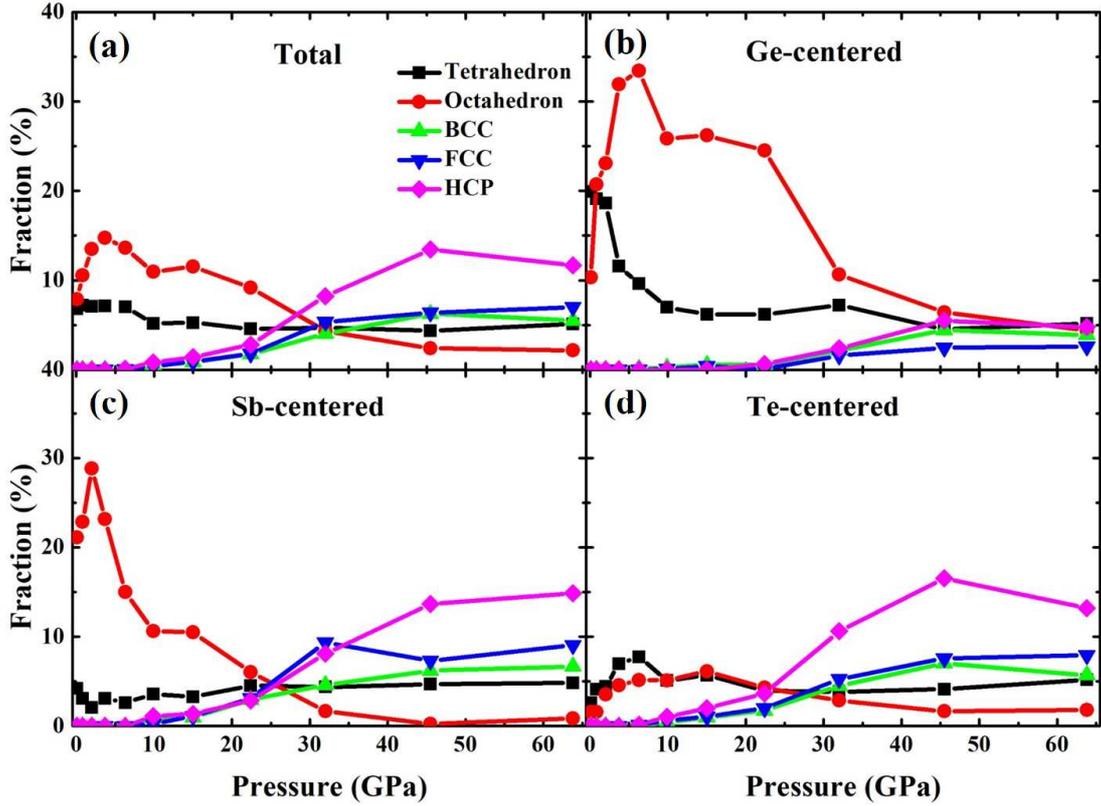


Figure 7. Fractions of diamond, 6-fold octahedron, BCC, FCC and HCP in GST with different pressures.

Conclusions

In summary, we have studied the influence of pressure on the short-range structures in the supercooled liquid GST by using the AIMD simulations and the ACA analysis. The results suggest that the supercooled liquid GST will change to a solid with the increasing pressure. And the SROs in GST also present a notable variation during the process. As the pressure is less than 6.3 GPa, the Ge-centered tetrahedrons show a large decrease with pressure, but Te-centered tetrahedrons present a notable increase, resulting in a little change in total tetrahedrons. Beyond the limitation, Ge-, Sb- and Te-centered tetrahedrons changes little as the pressure increases continuously. As the pressure increases, Ge-, Sb- and Te-centered octahedrons increase at first and then gradually decrease, leading to that the total octahedrons increase as pressure is less than 3.7 GPa and then decrease with the increasing pressure. While BCC, FCC and HCP structures are first found in Sb- and Te-centered clusters at 9.9 GPa and then

they increase gradually. As a whole, total tetrahedrons are insensitive to the pressure, a moderate pressure contributes to the formation of octahedrons but a large pressure will destroy the octahedral structures, and the high-coordinated clusters will be formed as the pressure is larger than 9.9 GPa. Our work renew the importance of pressure on the short-range structure in supercooled liquid GST, which is valuable for the further application of phase-change materials.

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