Domain Structural Transition and Structural Heterogeneity in GeO$_2$ Glass Under Densification

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1. INTRODUCTION

The microstructure of GeO$_2$ glass at elevated pressure is of interest due to its use in scientific glasses and its significant geophysical and geochemical implications. Therefore, GeO$_2$ glass has been intensively studied for a long time. As we know, GeO$_2$ glass is a typical network-forming glass whose structure consists of basic structural units GeO$_4$, GeO$_5$, and GeO$_6$. Most of the basic structural units at ambient pressure are GeO$_4$, forming a GeO$_4$ tetrahedral network. Under densification, there is a progressively structural transition from GeO$_4$ tetrahedra to GeO$_5$ pentahedra and eventually to GeO$_6$ octahedra, i.e., at elevated pressure, most of the basic structural units are GeO$_6$ forming an octahedral network. Experimental and simulation data in previous studies have shown that the Ge–O coordination number and the Ge–O bond length increase upon increase of pressure. For instance, at 0 and 13 GPa, the number of 4-fold coordinated Ge atoms is dominant, while the average Ge–O bond length is 1.74 and 1.82 Å, respectively. As pressure increases, the Ge–O coordination number increases progressively to 6-fold. At elevated pressure, the number of 6-fold coordinated Ge atoms is dominant, forming an octahedral network. Salmon et al. and Duong et al. indicated that an accomplished octahedral network arises at a pressure greater than 15 GPa. At less than 5 GPa, GeO$_4$ and some GeO$_5$ units are mainly linked via corner-sharing bonds. At elevated pressure, GeO$_5$ and GeO$_6$ units are linked via edge-sharing bonds or face-sharing bonds. They found that the Ge–Ge length is in the range from 2.75 to 2.85 Å, depending on the connection between them. Hong et al. indicated that, at elevated pressure, the Ge–Ge length has two values of 2.79 and 3.20 Å. They suggested that octahedral GeO$_2$ glass is viewed as an analogue of the rutile-structured GeO$_2$. Kono et al. reported that the curve for Ge–Ge length appears as a double-peak characteristic and that the position of the peaks slightly shifts with increasing pressure. It is interesting that the double peak combines into a single peak at a pressure greater than 72.5 GPa. This is interpreted as at pressure greater than 70 GPa, the Ge atoms are linked with six O atoms, but the structure of GeO$_2$ glass is similar to that of pyrite-type GeO$_2$. Shanavas et al. and Zhu et al. found that under densification, the first peak of pair radial distribution functions (PRDFs) $g_{\text{Ge-Ge}}(r)$ splits into subpeaks. However, the structure feature in boundary regions between GeO$_5$ units (midrange order) is not well defined in their studies. Consequently, many aspects of densification in GeO$_2$ glass remain unclear.

As we know, SH as well as dynamical heterogeneity (DH) are mainly related to the number of defective units and the distribution of these defective units. For instance, Weeks et al. and Glotzer indicated that the DH is viewed as a separate aggregation of the most mobile and the least mobile...
Simulation and experiment. At ambient pressure, GeO\textsubscript{2} glass (OE) potential is close to the structural obtained from mechanism and SH are clarified from this analysis. As seen, the OE peak of PRDF exhibits a network of GeO\textsubscript{4} mainly linked via one bridge-oxygen atoms. Our simulation reproduces well the experimental\textsuperscript{28} and simulation data.\textsuperscript{29,30} This indicates that the GeO\textsubscript{3} ions in the structure and density function theory (DFT) methods. As a result, the density of mobile/immobile atoms grows or shrinks as atoms leave their cages and move to other cages or are hop-trapped again. As temperature decreases, the size of the immobile clusters decreases, and, in contrast, the size of the mobile clusters increases. Hence, the dynamics is spatially heterogeneous at intermediate time scales and the determination length of the particle flow direction is significantly less than that in fragile liquids. However, the dynamics of boundary regions between clusters of mobile and immobile atoms is poorly described in these studies.

Therefore, in the present study, a set of models for GeO\textsubscript{2} glass at 300 K and in the range from 0 to 100 GPa is studied to clarify the structure and densification mechanism in GeO\textsubscript{2} glass. That is, we focus on the analysis of basic structural units, types of bonding, and the link-cluster function. As a result, the densification mechanism and SH are clarified from this analysis.

### 2. RESULTS AND DISCUSSION

Table 1 shows the properties of the GeO\textsubscript{2} models and other simulation and experimental data. As seen, the Oelfen–Elliot (OE) potential is close to the structural obtained from simulation and experiment. At ambient pressure, GeO\textsubscript{2} glass exhibits a network of GeO\textsubscript{4} mainly linked via one bridge-oxygen atom and consists of the defective (about 2% of total available units) GeO\textsubscript{4} and GeO\textsubscript{2} units. Most GeO\textsubscript{4} units are connected by corner-sharing bonds and about 1.1% of GeO\textsubscript{4} units are linked by two and three bridge-oxygen atoms. Our simulation reproduces well the experimental\textsuperscript{17,21} and simulation data.\textsuperscript{29,30}

**Figure 1.** Pair radial distribution function of GeO\textsubscript{2} glass at different pressures.

### Table 1. Structural Characteristics of Constructed Models at Dissimilar Pressures and Experimental and Simulation Data\textsuperscript{28}

| models | T (K) | \(r_{\text{Ge-Ge}}\) (Å) | \(r_{\text{Ge-Ge}}\) (Å) | \(r_{\text{O-O}}\) (Å) | \(Z_{\text{Ge-Ge}}\) | \(Z_{\text{Ge-O}}\) | \(Z_{\text{O-O}}\) |
|--------|------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 0 GPa  | 300  | 3.16            | 1.74            | 2.80            | 4.40            | 4.20            | 2.12            |
| 3 GPa  | 300  | 3.20            | 1.74            | 2.80            | 4.60            | 4.26            | 2.13            |
| 6 GPa  | 300  | 3.20            | 1.74            | 2.80            | 4.98            | 4.40            | 2.20            |
| 9 GPa  | 300  | 3.24            | 1.74            | 2.70            | 5.38            | 4.71            | 2.35            |
| 12 GPa | 300  | 3.32            | 1.76            | 2.64            | 5.68            | 4.80            | 2.42            |
| 15 GPa | 300  | 3.38            | 1.78            | 2.62            | 5.90            | 4.99            | 2.49            |
| 20 GPa | 300  | 3.68            | 1.80            | 2.64            | 6.21            | 5.19            | 2.59            |
| 30 GPa | 300  | 3.68            | 1.80            | 2.60            | 6.72            | 5.42            | 2.71            |
| 40 GPa | 300  | 3.68            | 1.80            | 2.58            | 7.08            | 5.52            | 2.78            |
| 60 GPa | 300  | 3.68            | 1.80            | 2.54            | 7.47            | 5.65            | 2.83            |
| 80 GPa | 300  | 3.34            | 1.78            | 2.54            | 7.96            | 5.72            | 2.84            |
| 100 GPa| 300  | 3.32            | 1.78            | 2.50            | 8.07            | 5.77            | 2.88            |

Where T is the temperature (K); \(r_{\text{Ge-Ge}}\), \(r_{\text{Ge-Ge}}\), and \(r_{\text{O-O}}\) (Å) are the interatomic distances for Ge–Ge, Ge–O, and O–O pairs, respectively; \(Z_{\text{Ge-Ge}}\), \(Z_{\text{Ge-O}}\), \(Z_{\text{O-O}}\), and \(Z_{\text{O-O}}\) are the average coordination numbers for Ge–Ge, Ge–O, O–Ge, and O–O pairs, respectively. The bold values show that the structure of GeO\textsubscript{3} glass in the present work is close to the structure obtained from the experiment and other simulations.

(immobile) atoms. During the observation time, the clustering of mobile/immobile atoms grows or shrinks as atoms leave their cages and move to other cages or are hop-trapped again. As temperature decreases, the size of the immobile clusters decreases, and, in contrast, the size of the mobile clusters increases. Hence, the dynamics is spatially heterogeneous at intermediate time scales and the determination length of the particle flow direction is significantly less than that in fragile liquids. However, the dynamics of boundary regions between clusters of mobile and immobile atoms is poorly described in these studies.

Therefore, in the present study, a set of models for GeO\textsubscript{2} glass at 300 K and in the range from 0 to 100 GPa is studied to clarify the structure and densification mechanism in GeO\textsubscript{2} glass. That is, we focus on the analysis of basic structural units, types of specific atoms, GeO subnet and domain D, VP statistics, and the link-cluster function. As a result, the densification mechanism and SH are clarified from this analysis.

Densification, which means that the short-range order of GeO\textsubscript{2} glass is not sensitive to densification. Under densification, the position of the first peak of PRDF \(g_{\text{Ge-O}}(r)\) has the tendency to shift to the left, i.e., at 0 and 100 GPa, the position of the first peak of PRDF \(g_{\text{Ge-O}}(r)\) is located at 2.80 and 2.50 Å, respectively. This indicates that with increasing pressure, the O–O bond length decreases and the Ge–O coordination number increases. At pressure greater than 6 GPa, the PRDF \(g_{\text{Ge-O}}(r)\) resembles a small peak located at around 3.60 Å, which is related to the appearance of the main peak at 160° for O–Ge–O bond angle distribution.\textsuperscript{20,30} Hence, we can conclude that the short-range order is not sensitive to densification, and, on the contrary, the midrange order significantly depends on pressure.

The fraction of basic units upon pressure is shown in Figure 2. As seen, this fraction strongly depends on pressure. The fraction of GeO\textsubscript{3} decreases strongly with increasing pressure, and the fraction of GeO\textsubscript{4} monotonously increases. Unlike in the case of GeO\textsubscript{4} or GeO\textsubscript{6}, the fraction of GeO\textsubscript{3} increases drastically and reaches a maximum of 0.48 at around 15 GPa and then gradually decreases. The evidence of the GeO\textsubscript{6} units and the existence of a
peak in the range of 9−18 GPa were found by inelastic X-ray scattering and first-principles molecular dynamics (MD) simulations, as can be seen in refs 22, 30, 31, in which the authors suggested that GeO₅ creation occurs immediately before that of GeO₆ octahedra. Therefore, the network undergoes slow structural reorganizations rather than the abrupt first-order-like structural change. Similar to our simulation data, between 9 and 18 GPa, we also observe structures with a significant number of GeO₅ units (~40−48%) and a peak for the curve of GeO₅ at around 15 GPa, indicating an unstable metastable state (an intermediate form of the glass), which may be caused by the spatial symmetry of GeO₅ unit. The existence of the metastable intermediate states (5-fold coordination states) was also proposed by Hong et al., Wu et al., and Guthrie et al. This means that under densification, GeO₂ glass is transformed from a tetrahedral (GeO₄) to an octahedral (GeO₆) structure. This trend, the transformation of the fraction of domain D₄ to domain D₆, is similar to the fraction of basic units (see Figure 3, upper panel). It is suggested that the change Oₓₓ → Oₓᵧ atoms occurs along with splitting of big domain Dx into small ones. Meanwhile, the change Oₓₓ → Oᵧᵧ atoms has the tendency to merge small domain Dx into big ones. According to the upper panel of Figure 3, the fraction of DB atoms increases rapidly up to 49% and then decreases gradually, which shows the intensive splitting of domain D₄ in the range from 0 to 15 GPa. Above 15 GPA, the splitting of domain D₅ and the merging of domain D₆ appear together and the fraction of DB atoms significantly varies. The curves for the fraction of DB atoms and the domain D₅ atoms display a peak near 15 GPa, showing that the number of domains strongly increases at lower pressures and then slowly decreases at higher pressures. This tendency is also obeyed in Table 2. As seen, the domains that consist of fewer atoms rapidly increase and then decrease under densification. Most models consist of one domain possessing a size bigger than 200 atoms. Similar to the graph for the fraction of GeO₅ units, the curve of domain D₅ intersects the curves of domains D₄ and D₆ at around 9 and 18 GPa, respectively.

As shown in the lower panel of Figure 3, the number of O atoms in domain D₄ decreases significantly, in contrast to domain D₆, which indicates that the number of O atoms increases. This is because, at low pressure, the size of domain D₄ is significantly bigger than that of domain D₆. Meanwhile, domains D₆ and D₄ have big and small sizes at high pressures, respectively. In the range of 9−18 GPa, domain D₅ has a large size. Clearly, the number of O atoms in domain Dx is correlated with the size of the domain. It is noted that the curve for the number of O atoms of domain D₅ also intersects the curves of domains D₄ and D₆ at around 9 and 18 GPa, respectively.

Figure 4 displays the number of domain Dx at different pressures. As seen, the curve of domain D₄ appears as a
pronounced maximum. This means that the splitting and variation of GeO₄ → GeO₅/GeO₆ result from an increase and then a decrease of domain D₄ in the range of 0−15 and 15−100 GPa, respectively. Obviously, at low pressures, the increasing and then decreasing number of domain D₆ is due to the variation of GeO₆ → GeO₅/GeO₄ and merging at larger pressures. For domain D₅, in the range from 0 to 6 GPa, the number of domain D₅ significantly increases due to the transformation of GeO₄ → GeO₅. Then, merging is realized in the range from 6 to 15 GPa, and splitting appears at pressures higher than 15 GPa. According to the right panel of Figure 4, the total number of domains appears as a pronounced maximum at 18 GPa. This means that the merging and splitting occur intensively in the range of 0−15 and 20−100 GPa, respectively.

The fraction of different oxygen (O₅s) is listed in Table 3. We denote O₄₄ and O₄₄₄, O₅₅ and O₅₅₅, and O₆₆ and O₆₆₆ as atoms in Table 2.

### Table 2. Size of Domains at Different Pressures

| size range | 0  | 3  | 6  | 9  | 12 | 15 | 20 | 30 | 40 | 60 | 80 | 100 |
|------------|----|----|----|----|----|----|----|----|----|----|----|----|
| 1−4        | 95 | 216| 404| 509| 614| 612| 546| 441| 372| 284| 233| 160 |
| 5−19       | 5  | 24 | 56 | 74 | 83 | 97 | 63 | 37 | 26 | 11 | 4  | 2  |
| 20−49      | 0  | 5  | 9  | 14 | 12 | 12 | 1  | 0  | 0  | 0  | 0  | 0  |
| 50−99      | 0  | 0  | 1  | 3  | 7  | 2  | 2  | 0  | 0  | 0  | 0  | 0  |
| 100−199    | 0  | 0  | 0  | 4  | 1  | 0  | 0  | 0  | 0  | 0  | 0  | 0  |
| >200       | 1  | 1  | 1  | 2  | 1  | 1  | 2  | 1  | 1  | 1  | 1  | 1  |

The bold values are the number of domains having the size bigger than 200 atoms.

### Figure 4. Number of domains D₄, D₅, and D₆ (left panel) and the total number of domains (right panel) as a function of pressure.

### Figure 5. Fraction of f₄, f₅, f₆ (left), and f₄₅₆ (right) as a function of pressure.

### Table 3. Distribution of the Types of Specific Atoms O₅s and Determination of the Fraction f₅ = mₒ₅s/mₒ

| type O₅s | 0 (GPa) | 3 (GPa) | 6 (GPa) | 9 (GPa) | 12 (GPa) | 15 (GPa) | 20 (GPa) | 30 (GPa) | 40 (GPa) | 60 (GPa) | 80 (GPa) | 100 (GPa) |
|----------|---------|---------|---------|---------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| O₄₄      | 0.767   | 0.5355  | 0.2913  | 0.1538  | 0.0764    | 0.0338    | 0.0136    | 0.0025    | 0.0005    | 0.0000    | 0.0000    | 0.0000    |
| O₄₅      | 0.0717  | 0.1740  | 0.2259  | 0.1959  | 0.1408    | 0.1146    | 0.0540    | 0.0177    | 0.0060    | 0.0000    | 0.0000    | 0.0000    |
| O₄₆      | 0.0113  | 0.0368  | 0.0693  | 0.0734  | 0.0747    | 0.0644    | 0.0516    | 0.0259    | 0.0098    | 0.0022    | 0.0022    | 0.0000    |
| O₅₅      | 0.0090  | 0.2073  | 0.0578  | 0.0895  | 0.0968    | 0.0957    | 0.0636    | 0.0327    | 0.0213    | 0.0104    | 0.0057    | 0.0030    |
| O₅₆      | 0.0030  | 0.0139  | 0.0431  | 0.0720  | 0.0979    | 0.1173    | 0.1282    | 0.1219    | 0.1026    | 0.0709    | 0.0529    | 0.0322    |
| O₆₆      | 0.0005  | 0.0030  | 0.0087  | 0.0180  | 0.0278    | 0.0338    | 0.0687    | 0.0903    | 0.1053    | 0.1252    | 0.1315    | 0.1364    |
| O₄₄₅      | 0.0368  | 0.2564  | 0.0117  | 0.0052  | 0.0033    | 0.0014    | 0.0003    | 0.0003    | 0.0000    | 0.0000    | 0.0000    | 0.0000    |
| O₄₅₆      | 0.0205  | 0.0295  | 0.0276  | 0.0221  | 0.0112    | 0.0071    | 0.0030    | 0.0003    | 0.0003    | 0.0000    | 0.0000    | 0.0000    |
| O₅₅₆      | 0.0074  | 0.0093  | 0.0117  | 0.0134  | 0.0074    | 0.0057    | 0.0044    | 0.0008    | 0.0000    | 0.0000    | 0.0000    | 0.0000    |
| O₅₆₆      | 0.0145  | 0.0404  | 0.0586  | 0.0510  | 0.0353    | 0.0245    | 0.0164    | 0.0044    | 0.0033    | 0.0003    | 0.0000    | 0.0000    |
| O₆₆₆      | 0.0041  | 0.0196  | 0.0450  | 0.0600  | 0.0652    | 0.0625    | 0.0450    | 0.0229    | 0.0098    | 0.0005    | 0.0014    | 0.0000    |
| O₄₅₆₅₅    | 0.0019  | 0.0109  | 0.0226  | 0.0278  | 0.0337    | 0.0396    | 0.0491    | 0.0346    | 0.0158    | 0.0052    | 0.0022    | 0.0000    |
| O₅₆₅₅₅    | 0.0011  | 0.0147  | 0.0300  | 0.0472  | 0.0469    | 0.0559    | 0.0295    | 0.0147    | 0.0101    | 0.0027    | 0.0022    | 0.0000    |
| O₆₆₅₅₅    | 0.0014  | 0.0098  | 0.0390  | 0.0712  | 0.1012    | 0.1195    | 0.1233    | 0.0911    | 0.0810    | 0.0486    | 0.0278    | 0.0117    |
| O₆₆₅₅₅    | 0.0008  | 0.0055  | 0.0202  | 0.0576  | 0.0927    | 0.1230    | 0.1710    | 0.2343    | 0.2499    | 0.2199    | 0.1814    | 0.1386    |
| O₆₆₆₆₆    | 0.0005  | 0.0033  | 0.0038  | 0.0104  | 0.0243    | 0.0420    | 0.1009    | 0.2158    | 0.2853    | 0.3884    | 0.4386    | 0.4962    |

Here, mₒ₅s and mₒ are the total number of O₅s and O atoms, respectively.
domains D4, D5, and D6, respectively. Other types of oxygen belong to DB atoms. As seen, as pressure increases, atoms in domains D4, D5, and D6 transform rapidly into different Os. In addition, according to Figure 5, the graph of $f_5$ intersects with that of $f_4$ at 9 GPa and with that of $f_6$ at 18 GPa, where $f_4$ is the fraction of $O_{44}$ and $O_{444}$, $f_5$ of $O_{55}$ and $O_{555}$, and $f_6$ of $O_{66}$ and $O_{666}$ atoms. The fraction of $O_{456}$, $f_{456}$, shows a maximum at around 15 GPa, and the total number for $O_{456}$ occupies 6.5% of total O atoms. Figure 5 also indicates that the largest $f_4$ at intervals of 0–9, 9–18, and 18–100 GPa corresponds to $f_4$, $f_5$, and $f_6$, respectively. It is suggested that at these intervals, the main domain corresponds to domains D4, D5, and D6, respectively. As seen again, the curve for $f_5$ intersects with that of $f_4$ at around 9 GPa and with that of $f_6$ at around 18 GPa, indicating that the large D4–D5 and D5–D6 coexist. Therefore, we suggest that, at around 9 and 18 GPa, there are two domain-types and other ranges of pressure correspond to one domain.

This means that, under densification, the structure of GeO$_2$ glass goes along with five domain regions: domain D4, domain D4–D5, domain D5, domain D5–D6, and domain D6. The existence of domain D4–D5 and domain D5–D6 shows that a number of separate structural regions coexist in the glass. Clearly, our simulation indicates polymorphism for GeO$_2$ glass at around 9 and 18 GPa.

Next, VP volumes for atoms and domain volumes are considered. Figure 6 displays the distribution of VP volumes at various pressures. The graph of O atoms is spread in wider intervals compared to that of Ge atoms. As pressure increases, the pronounced peak of the graphs shifts to the left. This shows that O atoms occupy a bigger volume compared to Ge atoms. The VP volume of atoms monotonously decreases upon...
pressure. Figure 7 indicates the average VP of Ge and O atoms, which is denoted as $\langle V_{\text{Ge}} \rangle$ and $\langle V_{\text{O}} \rangle$, respectively. It can be seen that $\langle V_{\text{Ge}} \rangle$ and $\langle V_{\text{O}} \rangle$ decrease monotonously. In addition, $\langle V_{\text{O}} \rangle$ decreases significantly faster than $\langle V_{\text{Ge}} \rangle$. This again means that the midrange structure varies more than the short-range structure under densification. This implies that upon densification, domain D4 transforms into domain D6 accompanied by the decrease in VP volume. It can be suggested that, under densification, the structure of GeO$_2$ glass has the tendency to decrease the VP volume of atoms and domain D4 transforms into D5 and D5 transforms into D6.

Figure 8 shows the reduced volume of domain Dx and DB atoms at various pressures. As seen, in the range from 0 to 15 GPa, the volume occupied by DB atoms significantly increases, i.e., from 11749 to 33793 Å$^3$, and then slightly decreases to 9590 Å$^3$. Beyond 5 GPa, $V_{\text{DB}}$ is larger than that of domain D4. Moreover, there is about 48% volume of DB atoms per simulation cell volume. $V_{\text{D4}}$ and $V_{\text{D6}}$ monotonously change in opposite directions. In addition, $V_{\text{D5}}$ appears as a maximum at around 15 GPa, at which domain D5 reaches a maximum. As expected, the curve for $V_{\text{D5}}$ intersects that for $V_{\text{D4}}$ at 9 and that for $V_{\text{D6}}$ at 18 GPa. This again demonstrates that GeO$_2$ glass goes along with five pressure regions corresponding to domain D4, domain D4--D5, domain D5, domain D5--D6, and domain D6.

As we know, to describe the local microstructure, many studies have focused on the topology of basic units, which consist of a central atom and coordinated atoms, and on the way these basic units are connected together to form clusters, e.g., Dx.
domain. In addition, these units can be connected to each other by corner-, edge-, or face-sharing bonds. As a result, SH can be inferred from the defective units, distribution of domain Dx, and distribution of corner-, edge-, and face-sharing bonds that are nonuniformly distributed in the simulation space. Here, it is noted that the clusters of face-sharing bonds possess a tree-shaped or chain-shaped form. Therefore, face-sharing bonds are quite stable. Thus, the cluster of face-sharing bonds prefers the rigid cluster embedded in the mixture network of corner- and edge-sharing bonds. Obviously, this distribution is evidence of SH in the GeO2 glass. To clarify the distribution of domains D4, D5, and D6, the domain structure has been visualized in three-dimensional (3D) space.

Figure 9 displays the partial distribution of domain Dx under densification. As seen, domains D4, D5, and D6 are nonuniformly distributed and have the tendency to create clusters of domains D4, D5, and D6. This means that the structure of GeO2 glass is a mixture of regions with different domain Dx. Obviously, the structure of GeO2 glass comprises structural domains D4, D5, and D6, depending strongly on pressure. As seen, at 0 GPa, the domain D4 is linked together forming a big region with the expanse almost covering the whole system. Domain D5 is small and localized at different locations forming separated regions. As pressure increases, the domains D5 and D6 expand and domain D4 shrinks. That is, at 15 GPa, domain D5 expands to the whole model. At 20 and 80 GPa, domains D4 and D5 shrink, and D6 expands almost to the whole model. The snapshots of spatial distribution of domain Dx are given in Figure 10. As seen, at 6 GPa, there is domain D4 and some domain D5 form one-domain type (domain D4). The pressure region at around 9 GPa comprises domains D4, D5, and some D6. The distributions for D4 and D5 are nonuniform, but they tend to create clusters of domains D4 and D5, forming a two-domain type (D4→D5). The pressure region at around 18 GPa comprises two domains D5 and D6 and some domain D4. Also, domains D5 and D6 have the tendency to create clusters of domains D5 and D6, forming a two-domain type (D5→D6).

Above 20 GPa, most domains are D6. Obviously, domain D6 also creates clusters of domain D6, forming a one-domain type (D6). From the analysis of the characteristics of domain Dx, we can conclude that the structure of GeO2 glass represents structural heterogeneity (SH).

To clearly describe SH, we now consider SH by characteristics of corner-, edge-, and face-sharing link distributions as well as their clustering. To calculate the spatial distribution for the corner-, edge-, and face-sharing links, we consider the following: Ge links with Ge through one bridge-O atom called a corner-sharing link, Ge links with Ge through two bridge-O atoms called an edge-sharing link, and Ge links with Ge through three bridge-O atoms called a face-sharing link. More detailed information can be found elsewhere. Figure 11 shows the spatial distribution of corner-, edge-, and face-sharing links for GeO2 glass. As seen, under densification, the number of face-sharing links increases faster than other types of links. Moreover, the corner-, edge-, and face-sharing links are nonuniformly distributed in the simulation space, and they have a tendency to create clusters of corner-, edge-, and face-sharing links, respectively. Because the face-sharing bonds are quite stable, at elevated pressure, the structure of glass GeO2 prefers the composite structure, which comprises the rigid clusters embedded in the mixture network of corner- and edge-sharing bonds, as seen in Figure 11. It turns out that these clusters represent SH in GeO2 glass. It is noted that the clusters of face-sharing links can form the immobile-atom regions, and, in contrast, the clusters of corner-sharing links correspond to mobile-atom regions in GeO2 glass. Therefore, at higher pressure, the mobility of atoms is much slower than that at lower pressure. The domain structure becomes more compact upon increasing pressure. This demonstrates that the coexistence of separate structures is the origin of spatial SH with microscaled domain separation in GeO2 glass.

Finally, we consider the effect of pressure on SH through sets of selective atoms, which are characterized by the link-cluster function, \( F_{\text{link}}(r) \). More information about the function \( F_{\text{link}}(r) \) can be found elsewhere. The sets of mobile atoms (SMAs), immobile atoms (SIMAs), and random atoms (SRAs) are considered. Each set comprises 1099 atoms (20% of total atoms), where the SRAs are randomly selected from the model and the SMAs are selected so that the mean square displacement (MSD) of these atoms is greater than that of the remaining atoms. In addition, the SIMA has MSD lesser than that of the remaining atoms. The atoms of SMA, SIMA, and SRA are calculated by the position of the atoms in the configuration at 6 × 10^5 time steps. Figure 12 shows the link-cluster function \( F_{\text{link}}(r) \) at 6, 12, 20, and 40 GPa. It can be seen that at 6 and 40 GPa, the \( F_{\text{link}}(r) \) for SMA, SIMA, and SRA is significantly dissimilar. For example, as \( r \) increases from 1.5 to 1.9 Å, \( F_{\text{link}}(r) \) for SIMA, SMA, and SRA drops drastically to 595, 653, and 774 atoms at 6 GPa and 506, 551, and 664 atoms at 40 GPa, respectively. With the further increase of \( r \), a shoulder appears, and then \( F_{\text{link}}(r) \) decreases gradually. The same observations are also obtained at pressures of 0, 3, and 9 GPa and 30, 60, 80, and 100 GPa. In contrast, at 12 GPa, SIMA, SMA, and SRA drastically drop to the identical values of 740, 744, and 767 atoms and 685, 687, and 714 atoms at 20 GPa, respectively (see Figure 12, lower panel). Furthermore, \( F_{\text{link}}(r) \) for SRA differs from that for SIMA, but the difference is less marked compared to the cases of 6 and 40 GPa. This observation is understood as follows. Under 10 and over 20 GPa, GeO2 units as well as domain Dx are nonuniformly distributed in the glass.
contrast, in the range of 10−20 GPa, the spatial distribution of GeO units has a tendency to become more homogeneous, which may be caused by a strong rearrangement of atoms compared to the case of different-pressure regions. This reveals that the GeO2 glass exhibits SH, the degree of which is reduced within the range of 10−20 GPa.

3. CONCLUSIONS
We have investigated the structural transition and SH in GeO2 glass consisting of 5499 atoms at 300 K under densification up to 100 GPa. The results indicate that the structure of GeO2 glass comprises separate regions, such as domains D4, D5, or D6. Under densification, the structure of GeO2 glass goes through five domain regions, domains D4, D4−D5, D5, D5−D6, and D6, and Oxy linked with Ge atoms reside in boundaries between domain Dx, i.e., the number of Oxy atoms connected with three Ge atoms increases. This shows that the structural transition occurs along with the Oxy → Oxx atom variation, which possesses both the merging and splitting of domain Dx. The results also demonstrate that, under densification, VP volumes of O atoms decrease faster than those of Ge atoms, indicating that densification leads to the decrease in the VP volume and the transformation of domain D4 to D5 and domain D5 to D6. We find that the coexistence of separate domain regions is the origin of spatial SH in GeO2 glass. It is also found that the GeO2 glass exhibits SH, the degree of which is reduced within the range of 9−18 GPa. We therefore suppose the new insights into the densification mechanism in GeO2 glass through analysis of GeO subnet, domain Dx and VP statistics, and the link-cluster function.

4. COMPUTATIONAL METHOD
Models of GeO2 glass consisting of 1833 Ge and 3666 O atoms at 300 K and in the range of 0−100 GPa are built by MD simulation. We used the OE potentials and the periodic boundary conditions to construct the models of GeO2 glass. The Verlet algorithm is used to integrate the motion equation with a MD step of 0.478 × 10−15 s.20,35 The initial configuration of the model is created by randomly placing all atoms in a simulation cell and heating up to 6000 K to remove the effect of remembering the initial configuration by relaxing the initial configuration within 5 × 105 MD steps. Then, the model is cooled to 4000, 2000, 1000, and 300 K within 8 × 105 MD steps with a cooling rate of 2.5 K/ps. Next, the model is built in the
From this model, the 11 models at 300 K and different pressures (3, 6, 9, 12, 15, 20, 30, 40, 60, 80, 100 GPa) are created by rescaling the simulation cell length and relaxing within $6 \times 10^5$ MD steps to reach equilibrium in the isothermal-isobaric NVE ensemble. To improve the statistics, the measured quantities such as the radial distribution function (RDF) and coordination number are computed by averaging over 1000 configurations separated by 10 MD steps. To calculate the coordination number, we have used the cutoff distance, i.e., $r_{Ge-O} = 2.32 \text{ Å}$.

To study the structural transition of GeO$_2$ glass, we considered the basic units GeO$_x$ and OGe$_y$ types of specific atoms, the Ge−O subnet, and domain Dx. Here, GeO$_x$ and OGe$_y$ units comprise a central atom and coordinated atoms, with $x = 4, 5, 6$ and $y = 2, 3$ are the number of coordination of atoms, respectively. Ge atoms can be assorted into Ge$_4$, Ge$_5$, Ge$_6$, and Geoth, where Ge$_4$, Ge$_5$, Ge$_6$, and Geoth possess the coordination numbers of 4, 5, 6, and other, respectively. Meanwhile, O atoms are denoted as O$_{xx}$ and O$_{yy}$ atoms. O$_{xx}$ atom is linked only with Ge atoms that have the same coordination number. O$_{yy}$ atom is linked with Ge atoms that have different coordination numbers (see Figure 13a). Ge−O subnet includes Ge and O atoms linked with each other by oxygen atoms called bridging atoms (see Figure 13b). Obviously, domain Dx is the Ge−O subnet that only includes Ge and O$_{xx}$ atoms, as seen in Figure 13c. Note that all Ge atoms of domain Dx possess the same coordination number of $x$. We also denoted four groups of atoms as follows: domain D4, domain D5, domain D6, and DB (domain-boundary) atoms. Domain Dx only comprises atoms of GeO$_x$ units, whereas DB includes O$_{yy}$ and Geoth. It is noted that all GeO$_x$ units are either of Ge$_4$, Ge$_5$, or Ge$_6$, therefore, the majority of Ge concerns domain D4, D5, or D6. Meanwhile, DB atoms are only O$_{yy}$ atoms. As a result, the atoms of domain DX are placed in separate regions, but DB atoms are located in the boundary between the separate space regions in GeO$_2$ glass.

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**Notes**

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