Original Article

Structure of GeO$_2$ Glass under Compression Using Molecular Dynamics Simulation

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Abstract: We have investigated the behavior of GeO2 at the temperature of 300 K and the pressure from 0 to 100GPa by using the molecular dynamics simulation (the model with 5499 atoms). The results show that the Ge-Ge, Ge-O bond distance increase but O-O bond distance decreases when increasing the pressure. We find that the peak splitting of Ge-Ge at high pressure corresponds with the Ge-O-Ge and O-Ge-O bond angles. We also find that O-Ge-O bond angle decreases, and Ge-O-Ge bond angle increases with pressure. The core-sharing-bond is major at ambient pressure, but fractions of edge and face-sharing-bonds increase with pressure.

Keywords: GeO2, High pressure, Microstructure, Radial distribution functions (RDFs), Molecular Dynamics simulation, clusters.

1. Introduction

Germanium dioxide (GeO$_2$) is a compound formed as a passivation layer on pure germanium in contact with atmospheric oxygen. In different temperatures and pressures, GeO$_2$ exists in α -quartz trigonal structure, rutile-like structure with tetragonal structure and an amorphous [1]. An amorphous form of GeO$_2$ is similar to fused silica. The α-quartz-type structure has been studied by using both experiment [2- 4], simulation [5-7] and theory [8, 9]. The calculations of the geometric structure and the physical properties of rutile-type GeO2 phase are also investigated in many studies [10]. The amorphous form of GeO$_2$ is researched in [2, 11].

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Because of its importance in industry, GeO₂ glass has been extensively studied both experimentally and theoretically. In ref.[2], Dong et.al investigate the pressure-induced structural changes and polyamorphism of GeO₂ glasses by using X-ray and Neutron diffraction. Extended X-Ray Absorption Fine Structure (EXAFS) experiment reveals that structural transformation in GeO₂ glass occurs in a wide pressure range up to 54 GPa. At low pressure (< 5 GPa) the Ge-O bond distance is almost unchanged with pressure. The degree of structural disorder increases with pressure. In 5-16 GPa pressure range, it shows the increase of Ge-O bond distance and bond disorder to maximum. In 16 -23 GPa pressure range, the Ge-O bond distance decreases significantly; increases slightly from 22,6 to 32,7GPa; decreases as pressure increase from 32,4 to 41,4 GPa and slightly increases up to 54 GPa.

At ultra-high pressure, GeO₂ glass has the polyamorphism with Coordination Number (CN) more than 6. In the work [3], Kono et. al reveal that CN is6 between 22,6 to 37,9 GPa. At higher pressures, CN increases rapidly and reaches 7,4 at 91,7 GPa.

The investigation shows that Radial Distribution Function (RDF) of Ge-Ge has double peak, so Ge-Ge bond length comprises two value: 2.82 and Å at 22.6 GPa; 2,79 and 3.24 Å at 37.9 GPa; 2.73 and 3.15Å at 49.4 GPa; 2.73 and 3.13 Å at 61.4 GPa. The double peak tends to merge into a single peak as pressure increases (>72.5 Gpa). In ref.[5], the authors also study the first peak splitting of Ge-Ge pair RDF. They investigate short range order (SRO) and intermediate range order (IRO) of GeO₂ at 3500 K using molecular dynamics (MD), in pressure from 0 to 100 GPa.

They found that GeO₄ tetrahedra link to each other to form a tetrahedral network. As pressure increases, tetrahedral network transits to octahedral network (GeO₆) via GeO₅ polyhedra. At a middle pressure, GeO₂ exists in three forms GeO₄, GeO₅, GeO₆. GeO₅-cluster reaches the maximum at 15-20 GPa. The authors found that it exists as an immediate configuration in structural transition process. Investigation shows that at low pressure, GeOₓ (x=4,5,6) link to each other by one common oxygen (corner-sharing bond, see figure 11) and at high pressure, by a corner-sharing bond, edge-sharing bond (two common oxygenssee figure 11), and face-sharing bond (three common oxygens, see figure 11). At high pressure, the GeO₅, GeO₆ polyhedra are dominant and tend to link each other by edge-sharing and face-sharing bonds, which become edge-sharing and face-sharing clusters. In ref.[12], the structure of GeO₂ glass is investigated at pressures up to 17.5(5) GPa using insitu time-of-flight neutron diffraction with a Paris–Edinburgh press employing sintered diamond anvils. At low pressure (5 GPa), it exists mainly in GeO₄ units. In 5 to 10 GPa GeO₄ units are replaced predominantly by GeO₅ ones. At pressure beyond 10 GPa, GeO₆ units begin to form.

Shanavas et.al investigated GeO₂ at the high-pressure and temperature using molecular dynamics simulations [6]. They found that GeO₂ system has a stable phase at ambient conditions of rutile type, in which the Ge-O are octahedrally coordinated. The rutile phase transforms to the tetrahedrally coordinated α-quartz phase as the temperature increases up to around 1280 K. Heating α-quartz, it transforms to β-quartz at above 1020 K and melts at 1378 K to form a network-structure liquid. At 9 GPa, α-GeO₂ transforms to a monoclinic phase. Their simulations on vitreous GeO₂ displays a smoth variation of mixed coordinated state of 4, 5, 6 coordination in pressure between 6 to 10 GPa, as being reported by Guthrie et.al. The research also showed that at high pressures, liquid GeO₂ transitions to a six-coordinated amorphous solid-like phase. Shanavas et.al [6] shows that Ge-O-Ge peak at 135° in the α-phase (at 300 K) and at 145° in β-phase (at 1100 K). The intertetrahedral Ge-O-Ge angle bond increases with temperature in 300 – 900 K temperature range. At higher temperature (900-1000 K) it increases strongly. However, it almost changes from 1000 K to 1500 K, decreases suddenlly from 1500 K to around 1600K and decrease to 1900K. When increasing the temperature, O-Ge-O angle does not change, but from 1500 to 1900K, it increases a little. At pressure from 0 to 20 GPa, O-Ge-O angle has

a peak at 90° and another small peak at 170°. At pressure from 0 to 20 GPa at 300 K and 1650 K, the interpolyhedral Ge-O-Ge angle has a small peak at 85° ascribable to edge-shared tetrahedra. Increasing the pressure, another peak appears around 90°, due to edge-shared octahedra.

The study [7] using MD simulation (in the micro-canonical ensemble, with systems at densities ranged from 3.16 to 6.79 g/cm3, using a pairwise potential) shows that at around 3–7 GPa the main structural changes in amorphous GeO_2 occur, changing from a network composed basically of GeO_4 tetrahedra to the one composed of GeO_6 octahedra.

In the study of Mei and Shen et.al [4], GeO_2 is investigated by using X-ray in pressure up to 15.7 GPa, the results show monotonic increase of the average coordination number of oxygen atoms around Ge with pressure from 4.2 at 5.1 GPa to 5.5 at 15.7 GPa. This reveals the structural transsition of silica glass under compression. However, the detail about the structural transformation is still not clarified.

In this paper, we investigate the GeO_2 model at different pressures, at 300K to find the change of RDFs, CN, angles of bonds and the connect of angles, distances and kinds of sharing bonds. We explain the peak splitting of Ge-Ge at high pressure, O-Ge-O bond angle decreases, and Ge-O-Ge bond angle increases with pressure.

2. Calculation Method

We construct the models of germania glass with the two-body potential developed by Oeffner–Elliott (OE). The detail parameters of the potential are given in ref. [13]. The OE potential has been used in many works for a long time and is known to reproduce the main structural and mechanical properties of GeO_2, see refs. [2, 6, 14-18]. In particular under pressure, the OE potential is known to reproduce the model with structure properties in good agreement with experiment [1-3, 12]. The glass models considered here contain 5499 atoms in cubic periodic simulation cells. They were obtained from a melt equilibrated at 6000 K. After that the model is cooled to 3500 K and compressed to different pressures in 0-100 GPa range. Next, the models are cooled to 300 K at cooling rate of 2.5 K/ps. Next, the models at different pressures are relaxed for a long time (10^6 time steps) to get equilibrated state. The structural properties are calculated by averaging over 1000 configurations during the last 5×10^4 time steps.

3. Results and Discussion

In the present paper, we analyze the results of molecular dynamic simulation for amorphous GeO_2 in 0-100 GPa pressure range, at 300 K. The structure of GeO_2 glass under compression will be clarified.

Coordination units: Figure 1 shows the pressure dependence of concentration of GeO_x (x=4, 5, 6) and OGe_x (x=2, 3, 4). At 0 GPa, most of the Ge atoms have four-fold coordination (93.24%). The concentration of GeO_4 decreases monotonously with the increase of pressure. At 100 GPa, its concentration is about 0.17%. At pressure of 0 GPa, the concentration of GeO_5 is 5.9%, then increases to maximum value (50.6%), then decreases gradually to 23.8% at 100GPa. With increasing the pressure, the fraction of GeO_6 monotonously increases from 0.86% at 0 GPa to 77.03% at 100 GPa. At high pressure (p>=60 GPa) , most of the Ge atoms have five-fold and six-fold coordination.

The concentration of OGe_x (x=2, 3, 4) also depends on the pressure. At the pressure from 0 to 100 GPa, the fraction of OGe_4 is small, it monotonously increases from 0% at 0GPa to 9.66% at 100 GPa. The fraction of OGe_3 increases with pressure from 8.82% at 0GPa to 69.48% at 100GPa. The fraction of OGe_2 monotonously decreases from 91.18% to 20.88% at pressure of 0-100GPa.
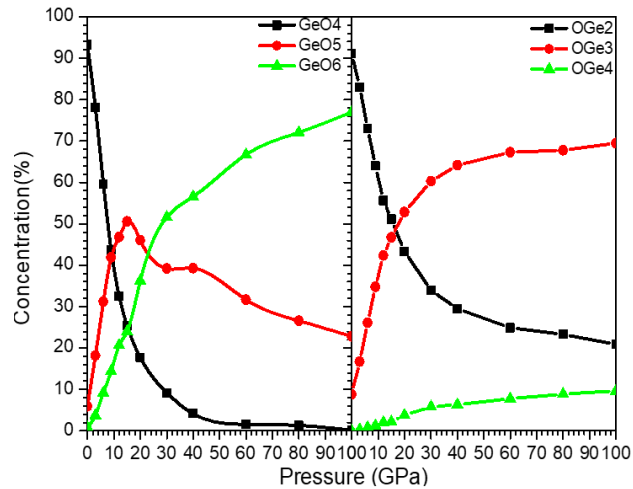
Figure 1. Concentration of GeO$_x$ (x=4, 5, 6) and Oge$_x$ (x=2, 3, 4) as a function.

Bond angle distribution (BAD): The O-Ge-O bond angle distribution (see Figure 2) in GeO$_4$ (in 0-40 GPa range) decreases from 105° to 100° with increasing pressure. The O-Ge-O bond angle distribution in GeO$_5$ in 0-100 GPa range has a main peak at around 85°-90° and a small peak at 165°-170°. Investigation of O-Ge-O bond angle distribution in GeO$_6$ at 3-100GPa shows the same results as GeO$_5$.
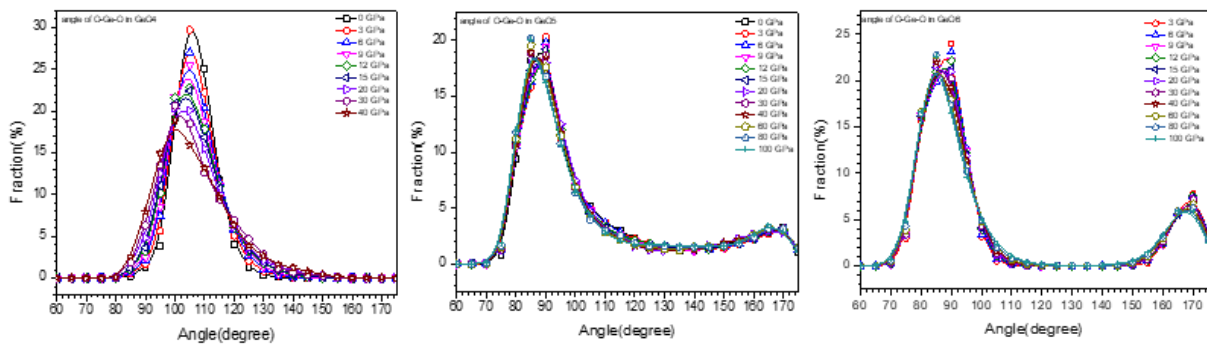
Figure 2. Fraction of angle of O-Ge-O in GeO$_x$ (x= 4, 5, 6).

The Ge-O-Ge bond angle distribution in OGe$_4$ has one peak and two subpeaks in the left and right (see figure 3). The position of corresponding peaks are at 75°, 90° and around 125-130°. Investigating OGe$_3$ in 0-100GPa, we find that from 0 to 3 GPa, Ge-O-Ge BAD has two peaks are around 85°-90° and 115°-120° but from 6 to 100 GPa, the results show the same as OGe$_4$ at pressure from 30 to 100GPa. Investigating OGe$_2$ in 0-100GPa range, we find that from 0 to 6 GPa, Ge-O-Ge BAD has two peaks at around 85°-90° and 125°-130° but in 9-100 GPa range, the Ge-O-Ge BAD of OGe$_2$ has one peak and two smaller peaks in the left and right at around 75°-80°, 90°-95° and 125°-130°.

Corner-, edge- and face-sharing bonds: Figure 4 shows that at low pressure (0 GPa), corner-sharing-bonds are dominant (94.94%), edge-sharing bond is 4.75% and face-sharing bond is 0.31%. At 6 GPa, It exists corner- and edge-sharing bond. The concentration of corner-sharing-bonds is about 83.34%, edge-sharing bonds are about 14.25% and face-sharing-bonds are about 2.41%. In high pressure

(100GPa), It exists three types: corner-sharing-bond with concentration of 68.82%, edge-sharing-bond concentration of 24.69% and face-sharing-bond concentration of 6.49%. We find that concentration of corner-sharing-bond decreases, fraction of face-sharing-bond increases.

Figure 3. The Ge-O-Ge bond angle distribution in GeO_x (x=2, 3, 4).

Figure 4. Fraction of core-, edge-, face-sharing bond in pressure range.

The size distribution of clusters: Table 1 shows that size of clusters decreases with increasing pressure, GeO_4 units link to each other into the largest cluster at ambient pressure. At higher pressure, size of clusters is smaller, it means that the number of GeO_4 decreases with pressure and they split into many smaller cluster. We also find that at high pressure (>40 GPa), the number of GeO_4 clusters and the number of atoms in each cluster decrease. At 100 GPa, it has one cluster with 5 atoms.

Table 1. The cluster of GeO_4 (Na is the number of atoms of the clusters, Nc is the number of clusters having Na correspondly).

0GPa		6GPa		12GPa		20GPa		40GPa		60GPa		80GPa		100GPa	
Nc	Na	Nc	Na	Nc	Na	Nc	Na	Nc	Na	Nc	Na	Nc	Na	Nc	Na
2	5	24	5	145	5-20	186	5-20	48	5	22	5	14	5	1	5
1	5304	5	9	8	21-40	6	21-40	4	9			2	9		
		1	3857	2	41-80	1	40-45	1	13						
				1	80-160			1	17						
				3	160-430										

Table 2 shows that in 12-40 GPa range, the GeO_5 units forms clusters with size of 2000 to over 3000 atoms. At low pressure (0GPa), the number of clusters as well as their size are small. The size of GeO_5 clusters increases and gets maximum at 20 GPa, then decreases with pressure.

Table 2. The clusters of GeO5 (Na is the number of atoms of the clusters, Nc is the number of clusters having Na correspondly)

0GPa		6GPa		12GPa		20GPa		40GPa		60GPa		80GPa		100GPa	
Nc	Na	Nc	Na	Nc	Na	Nc	Na	Nc	Na	Nc	Na	Nc	Na	Nc	Na
47	6-10	58	6-20	25	6-10	17	6	43	6-20	67	6-20	94	6-20	122	6-20
5	11-15	5	21-40	1	11-15	1	11	4	21-40	6	21-40	13	21-40	10	21-40
3	16-20	3	41-60	1	16-20	1	16	1	54	6	41-60	7	41-60	1	41-60
3	21-25	4	61-80	1	21-25	1	33	1	86	2	61-80	6	61-80	1	78
1	26-30	2	81-100	1	3348	1	3379	1	2432	1	81-100			1	156
		4	101-200							5	101-200			1	173
		2	201-400							1	540				

Table 3 shows that GeO_6 forms clusters: At 0 GPa, the number and the size of the clusters are minimun. There are only 12 clusters, each of clusters has 7 to 14 atoms. Increasing pressure from 0 to 9 GPa, the number of clusters also the size of them increase. At 9 GPa, there are 119 clusters and the biggest cluster has 161 atoms. Then, increase the pressure, we find that the size of clusters increase and the number of clusters decreases. At 12 GPa, there are 106 clusters, the biggest cluster has 177 atoms. At pressure > 30 GPa, each cluster has more than 4000 atoms, it is maximum at 100 GPa with 5113 atoms. We find that at pressure > 40 GPa, the atoms convergeinto one cluster. The simulation model has 5499 atoms so the fraction and the concentration of GeO_6 are dominant.

Table 3. The clusters of GeO6 (Na is the number of atoms of the clusters, Nc is the number of clusters having Na correspondly)

0GPa		6GPa		12GPa		20GPa		40GPa		60GPa		80GPa		100GPa	
Nc	Na	Nc	Na	Nc	Na	Nc	Na	Nc	Na	Nc	Na	Nc	Na	Nc	Na
9	7	94	7-20	78	7-20	12	7	1	4456	1	4851	1	4995	1	5113
2	11	4	21-40	16	21-40	1	11								
1	14	1	42	6	41-60	2	13								
		1	45	3	61-100	1	16								
				2	101-200	2	18								
						1	20								
						1	41								
						1	3150								

Radial distribution function (RDF): We find that the Ge-Ge RDF has many peaks at high pressure. From 0 to 3 GPa, the RDFs of Ge-Ge have one peak. The first peak of RDF shows that Ge-Ge bond length is 3.16 Å at 0 GPa. From 6 to 9 GPa, the RDFs of Ge-Ge have one main peak and a small peak on the left. At 6 GPa, Ge-Ge bond length comprises two values of 2.7 Å and 3.2 Å. From 12 to 100 GPa, the RDFs of Ge-Ge have three peaks. At 100 GPa, it consists of three peaks showing that Ge-Ge bond lengths are 2.28, 2.64 or 3.32 Å. The first peaks of RDFs of Ge-O show Ge-O bond length is about 1.74 – 1.78 Å. The first peak positions shifts to the right with increasing pressure. The RDFs of O-O show that O-O bond length is about from 2.5 to 2.8 Å. The first peak shift to the left as pressure increases. At pressure beyond 9 GPa , the O-O RDF has a small peak at around 3.6Å after the first peak.
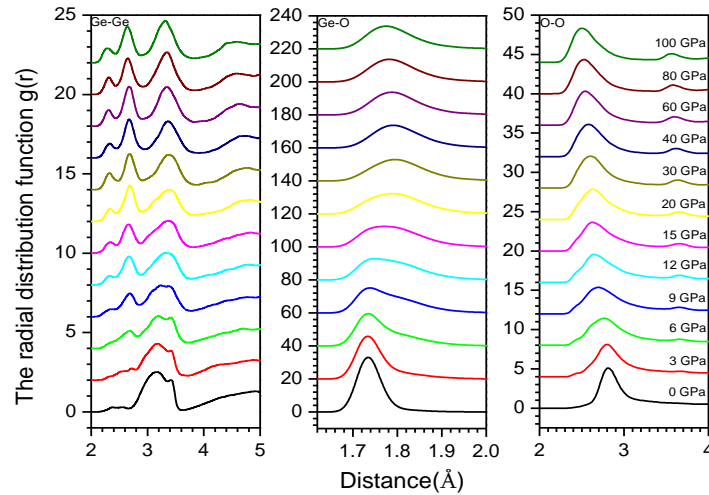
Figure 5. Radial distribution functions of Mg-Mg, Mg-O, and O-O pairs at different pressures.

The peaks splitting of Ge-Ge RDF: The Ge-Ge distance depends on the bond type. At high pressure, we find that it has three peaks corresponding to corner-, edge- and face-sharing bonds (see figure 5). The distances of Ge-Ge are different with each sharing bond. The Ge-Ge distance depends on bond type. So, the Ge-Ge RDF has three peaks at high pressure. At low pressure (0GPa), it exists mainly corner-sharing bonds and has one peak.

The distance of Ge-Ge also depends on the Ge-O-Ge bond angle.

$$d_{Ge-Ge} = \sqrt{d_{O-Ge}^2 + d_{O-Ge}^2 + 2 * d_{O-Ge}d_{O-Ge}cos\widehat{Ge-O-Ge}}$$

Figure 6 shows that at high pressure (100 GPa), The Ge-O-Ge BAD has three peaks at 75°, 90° and 130°. So, the Ge-Ge RDF has three peaks corresponding with Ge-Ge bond lengths of 2.28, 2.64 and 3.32 Å. At low pressure (0GPa), It has two peaks (one main peak and a small peak on the left), we find that the RDF has one peaks and a shoulder. We also find that the peaks of Ge-Ge RDF shift to the right with increasing the pressure. Because the distance of Ge-O increases with pressure, the distance of Ge-Ge also increases.

Bond distance: Figure 7 shows that the peaks of Ge-O bond distance distribution in GeO_x (x=4, 5, 6) shifts to the left with increasing the pressure. At pressure in 0-40 GPa range, Ge-O bond length in GeO_4 decreases from 1.74 Å to 1.72 Å. At pressure from 3-100 GPa, Ge-O bond length in GeO_5 decreases from 1.78Å to 1.76Å. At pressure from 3 to 100 GPa, the Ge-O bond length in GeO_6 decreases from 1.88Å to 1.78Å.
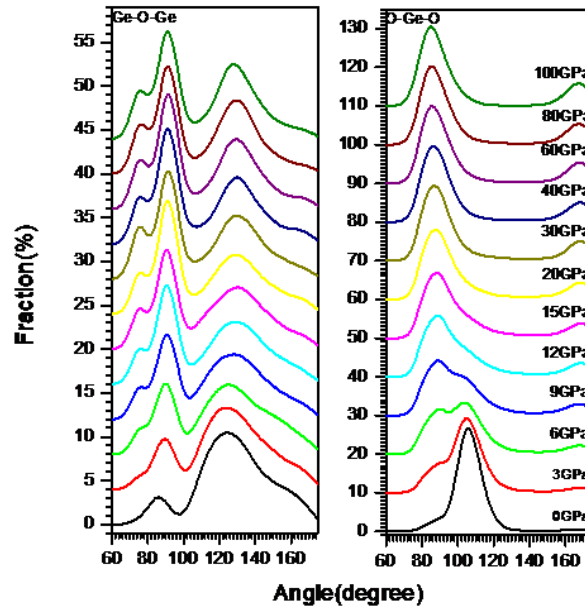
Figure 6. The Ge-O-Ge and O-Ge-O bond angle distribution at different pressures.

Figure 8 shows the distance Ge-O of OGe_x(x=2, 3, 4). Investigating OGe_4 in 20-100 GPa, we find that the Ge-O length bond decreases from 1.84Å to 1.8Å. At pressure of 0-100 GPa, the Ge-O length bond increases from 1.76Å (in 0GPa) to maximum value at 1.8Å (in 60GPa) then decreases to 1.78Å (in 100GPa). The Ge-O bond length increases from 1.74Å (in 0GPa) to maximum value at 1.78Å (in 30-40 GPa range) then decrease to 1.78Å (in 100GPa).

The distance of Ge-O increases with the pressure: The Ge-O distance increases from 1.74 Å to 1.78 Å with pressure from 0 to 100 GPa. With increasing the pressure, the Ge-O CN increase, the result shows that coulomb repulsions between Ge and Ge, between O and O increase, leading to increasing Ge-O bond length. The Ge-O distances in GeO_x (x=4, 5, 6) decreases with increasing pressure but the Ge-O distances in GeO_6 > the ones in GeO_5 > the ones GeO_4 (see Figure 8). The fraction of GeO_6 increases, the fraction of GeO_4 and GeO_5 decreases with increasing pressure so that the distances of Ge-O increases. Both of the Ge-O distances in OGe_2 and OGe_3 also increases with the pressure. The fraction of OGe_2 and OGe_3 increases with increasing pressure so the Ge-O distance increases.
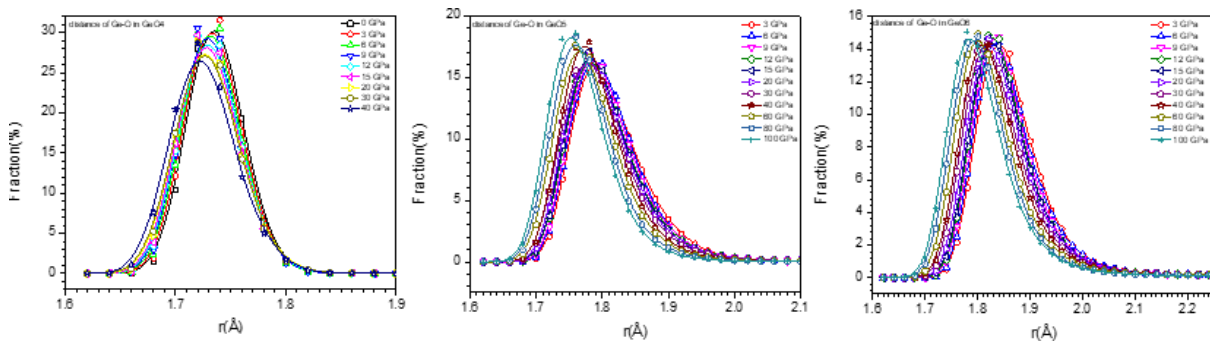
Figure 7. Fraction of distance of Ge-O in GeO_x (x=4, 5, 6).
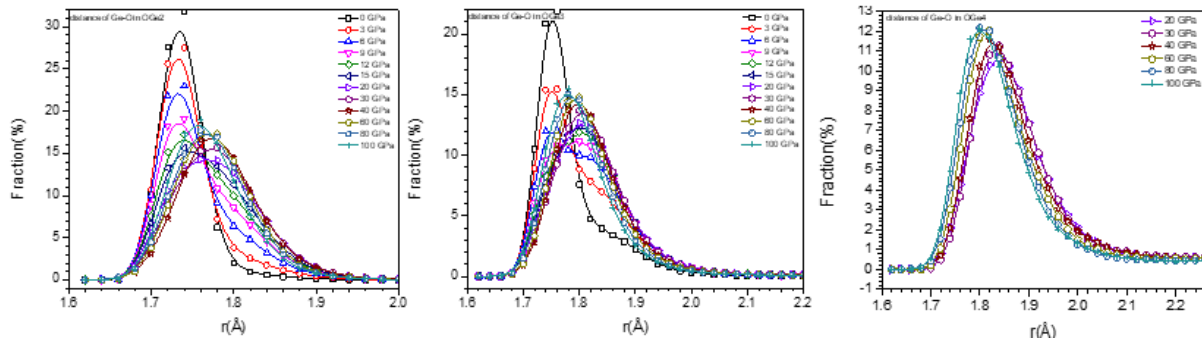
Figure 8. The Ge-O bond distance distribution in GeO$_x$ (x=2, 3, 4).

The distance of O-O decreases when increasing the pressure: With increasing the pressure, the O-Ge-O bond angle decreases from 105° to 85° (see Figure 5) and the distance of O-O decreases from 2.8 to 2.5 Å. O-Ge-O BAD (Figure 5) has one more peak at 170-175° at high pressure so that the RDF of O-O has one peak at 3.6Å. This distance is approximately double the distance of Ge-O.

$$d_{O-O} = \sqrt{d_{O-Ge}^2 + d_{O-Ge}^2 + 2 * d_{O-Ge}d_{O-Ge}cosO - \widehat{Ge} - O}$$

4. Conclusion

The paper reported the microstructure of GeO$_2$ glass by using the molecular dynamic method. It showed that: i/ The fraction of GeO$_x$ (x=4,5,6) and OGe$_x$ (x=2, 3, 4) changes significantly in considered pressure range; ii/ The O-Ge-O bond angle decreases with increasing pressure. The change of Ge-O-Ge BAD under compression resulting in the change of Ge-Ge and O-O distance and formation of edge-, face-sharing-bonds. The fractions of edge-, face-sharing-bonds is increase with pressure and this is the cause of the first peak splitting of Ge-Ge RDF at high pressure; iii/ The glassy network structure of GeO$_2$ changes significantly under compression, the GeO$_4$ units tend to link each other forming GeO$_4$ clutsers. Similar GeO$_5$ and GeO$_6$ also tend to form GeO$_5$ and GeO$_6$ clusters. This shows the polyamorphism in GeO$_2$ glass at high pressure. The O-O distances decreases, meanwhile Ge-O distance increases with pressure.
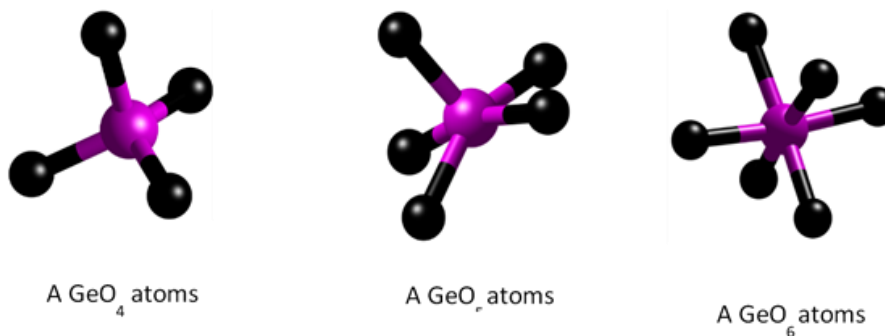

A GeO$_4$ atoms   A GeO$_5$ atoms   A GeO$_6$ atoms

Figure 9. The structure of GeO$_x$ (x=4, 5, 6).

A GeO₄ cluster has 9 atoms   A GeO₅ cluster has 11 atoms   A GeO₆ cluster has 11 atoms
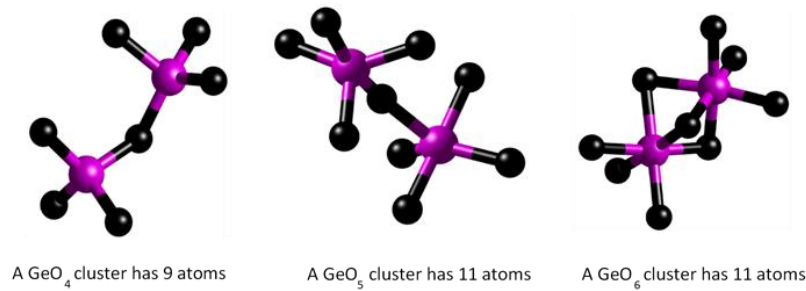
Figure 10. Linkage between GeO$_x$ (x=4, 5, 6) in clusters.

Face-sharing-bond   Core-sharing-bond   Edge-sharing-bond
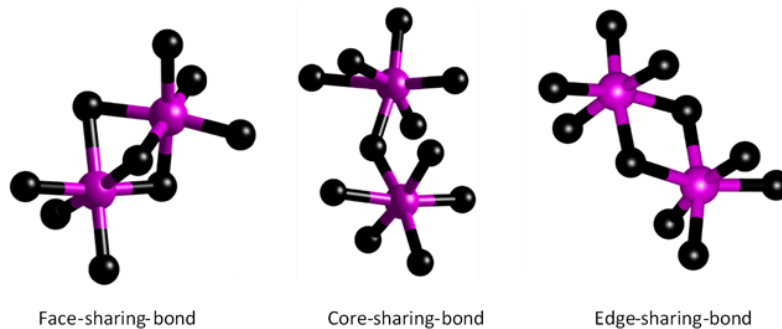
Figure 11. The structure of core-, edge-, face-sharing bonds.

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