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Original Article

Structure Analysis of Amorphous and Liquid Magnesium Silicate

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Abstract: We use the Oganov potentials and period boundary condition to perform molecular dynamics simulation of amorphous and liquid Mg2SiO4 systems under pressures 0 GPa and 40 GPa. We clarify structure of amorphous Mg2SiO4 at 0 and 40 GPa and compared with the one of Mg2SiO4 at liquid state. Especially, the origin of sub-peaks in radial distribution function of O-O, Si-Si and Mg-Mg pairs is explained clearly. The change of radial distribution functions, coordination number and the number of all types of bonds including the corner-, edge- and face-sharing bonds is also discussed in detail in this paper.

Keywords: Molecular dynamics simulation, magnesium silicate, structure.

1. Introduction

Magnesium silicate (Mg_2SiO_4) is one of the most abundant materials of the Earth's upper mantle [1, 2]. It is also an important component in many high technology applications [3]. Mg_2SiO_4 system has been extensively investigated for a long time by both experiment (X-ray diffraction, nuclear magnetic resonance, Raman spectroscopy technology) [4-6] and simulation (Molecular Dynamics, Monte Carlo) [1-3, 7-11]. Knowledge of structure of Mg_2SiO_4 system in both solid and liquid states at different temperature and pressure conditions is necessary for understanding about thermal change of the Earth as well as application in the process of new material fabrication technology. The X-ray diffraction and Neutron scattering experimental results showed that [8] Si atoms in Mg_2SiO_4 glass has mainly 4 coordinated oxygens and the mean bond length of Si-O is about 1.60 Å. Meanwhile the Mg atoms are surrounded 5 oxygens and the Mg-O bond length is about 2.0 Å. Using nuclear magnetic resonance [4,

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5] authors indicated that the coordination number of Mg is 5 and 6. The simulation results [2, 10, 11] also showed that structure Mg_2SiO_4 comprise basic structural unit TO_n (T= Si, Mg; *n* is the number of oxygens that surrounded T atoms). There is change of the coordination number of Si and Mg atoms and intermediate range order structure in magnesium silicate melts under compression [2]. Molecular dynamics simulation of $MgSiO_3$ liquid [12, 13] clarified structural organization, network topology as well as the degree of polymerization under compression. In this work, we clarify structure of amorphous Mg_2SiO_4 at 0 and 40 GPa and compared with the one of liquid Mg_2SiO_4. Especially, the origin of sub-peaks in radial distribution function of O-O, Si-Si and Mg-Mg pairs also explain via analysis the TO_n units as well as the corner-, edge- and face-sharing bonds between adjacent structural units TO_n.

2. Calculation Method

Molecular dynamics simulations are used to construct Mg_2SiO_4 models containing several thousand atoms. Simulation method is recognized as a numerical empirical method and plays a close link between

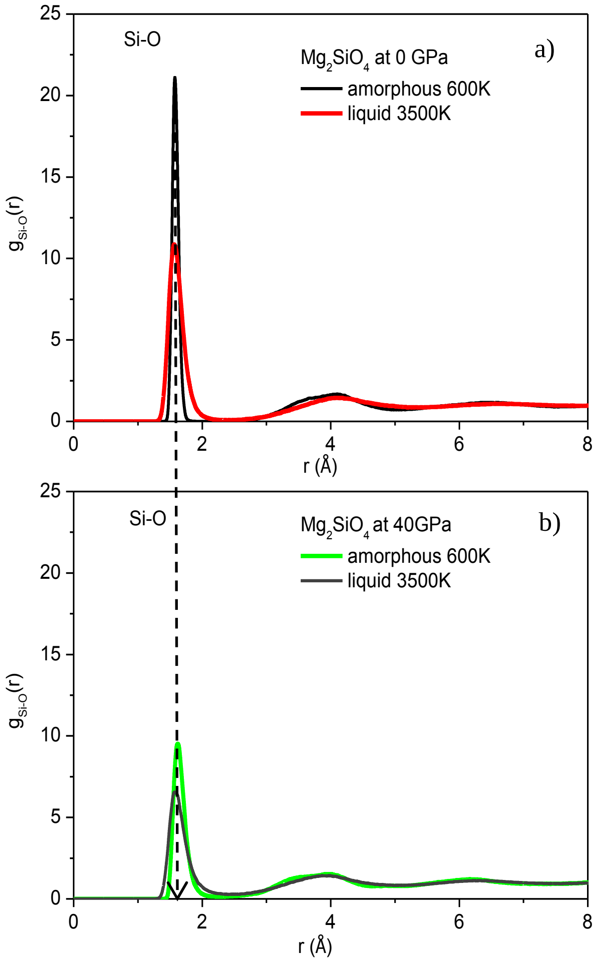

Figure 1. The radial distribution function of Si-O pair at both states at 0 GPa (a) and 40 GPa (b)

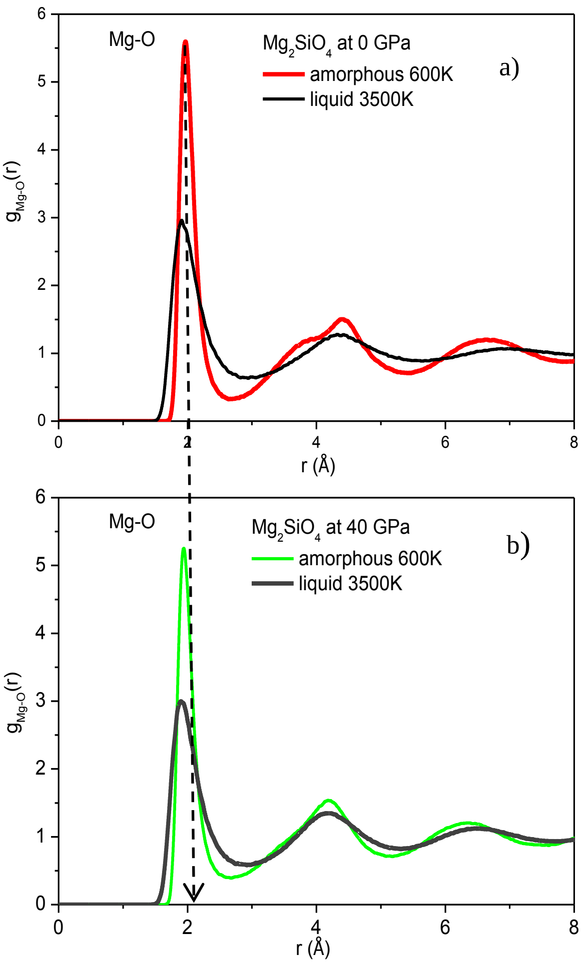

Figure 2. The radial distribution function of Mg-O pair at both states and at 0 GPa (a) and 40 GPa (b)

two theoretical and empirical methods. The initial configuration of the sample is built by randomly placing 4998 Si, Mg and O atoms in a simulation box with the condition that no two atoms are too close together. The motion of atoms in the model follows the Newton's equation of motion. We used the Verlet algorithm to integrate the equation of motion, the Ewald-Hansen approximation technique applied to significantly reduce the time taken to calculate the Coulomb interaction at a distance. The Oganov potentials are used to construct Mg_2SiO_4 models [11, 12]. Under the influence of the interaction force, the atoms will shift to the equilibrium position. The equilibrium state of the model is determined when the energy of the model is stable. Hence, the structural characteristics and properties of the models are determined. Detail about the process of constructing models of magnesium silicate system can be refer in our recent studies [12]

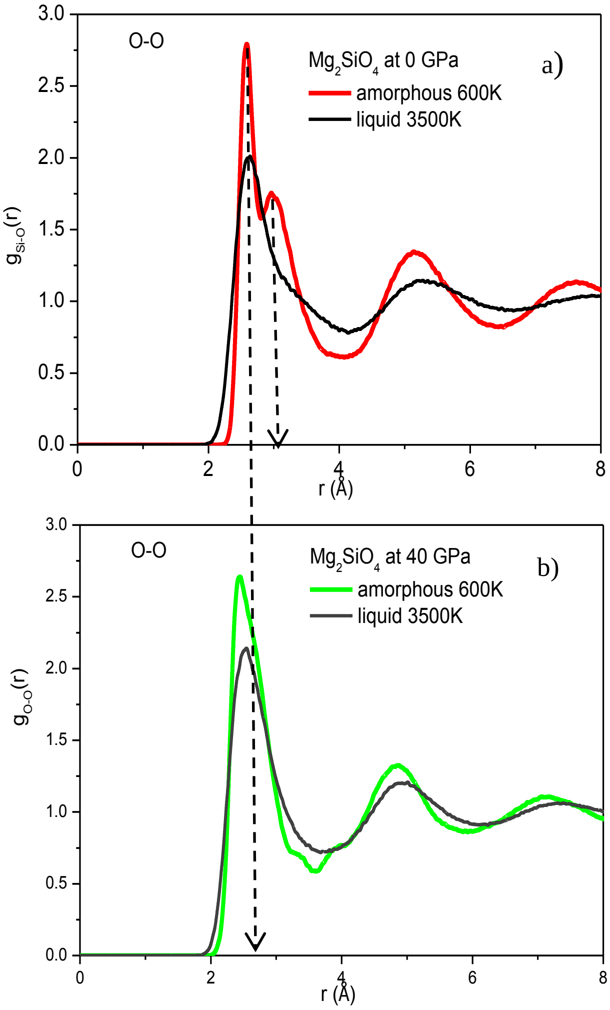

Figure 3. The radial distribution function of O-O pair at both states at 0 GPa (a) and 40 GPa (b).

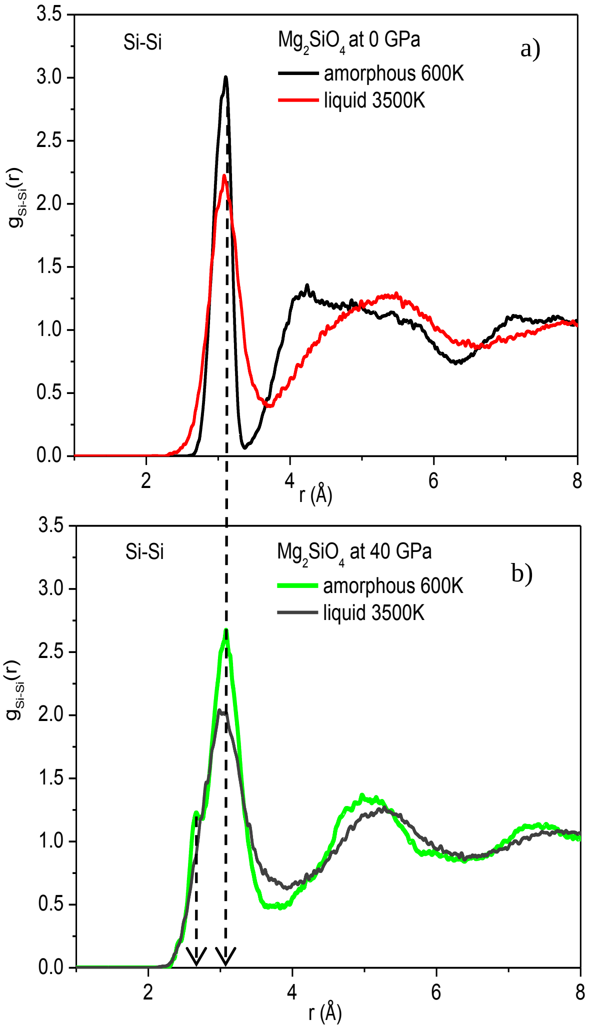

Figure 4. The radial distribution function of Si-Si pair at both states at 0 GPa (a) and 40 GPa (b).

3. Results and Discussion

First, we calculate radial distribution function of T-O, O-O and T-T pairs at both states and at 0 GPa and 40 GPa. Regarding to Si-O pair, figure 1a shows that at 0 GPa, the position of the first peak at amorphous and liquid states is about 1.62 Å. It means that Si-O bond length is almost not dependent on temperature. At 40 GPa, the position of the first peak at liquid state tends to shift slightly to the left compare to the one at amorphous state and at 0 GPa. The Si-O bond length at 40 GPa is smaller than the one at 0 GPa (see figure 1b). Besides at the same pressure, the height of the first peak in liquid state is smaller than the one in amorphous states. The full width at half maximum of the first peak in liquid state is larger than the one in amorphous states. It means that the degree of structural order in Mg_2SiO_4 at amorphous is higher than the one in liquid state. The degree of structural order in Mg_2SiO_4 at 40 GPa is higher than the one at 0 GPa. Regarding to Mg-O, figure 2a indicates that the Mg-O bond length in amorphous is about 1.94 Å and the Mg-O bond length is longer than the one in liquid state. Under compression, the first peaks in both states shift to the left, it means that the Mg-O length decreases as pressure increases. For O-O pair, it can be seen that there are two peaks in the O-O radial distribution

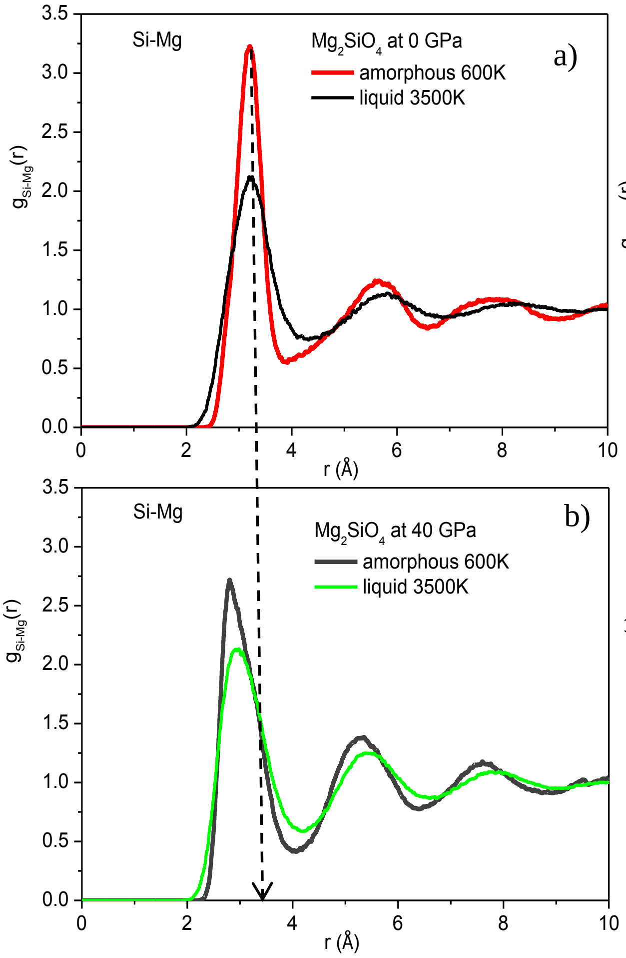

Figure 5. The radial distribution function of Si-Mg pair at both states at 0 GPa (a) and 40 GPa (b).

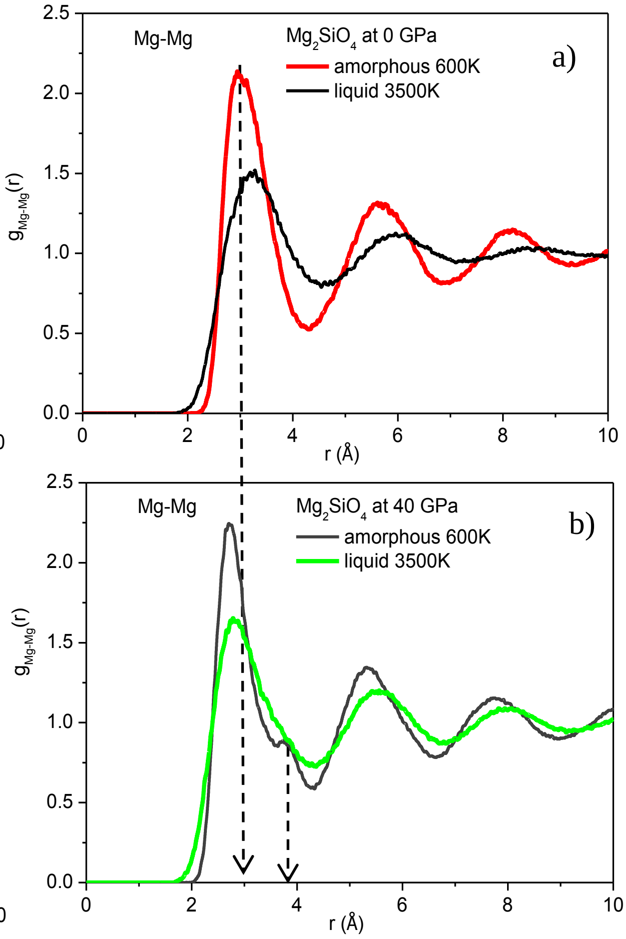

Figure 6. The radial distribution function of Mg-Mg pair at both states at 0 GPa (a) and 40 GPa (b).

function in amorphous state at 0 GPa (see figure 3a). This is not appearance in amorphous state at 40 GPa and in liquid state at 0 and 40 GPa (see figure 3a, b). The main peak is about 2.6 Å and the sub-peak is about 3.02 Å. The position of the first peak of O-O pair shifts to left, thus the O-O bond length decreases when pressure increases from 0 to 40 GPa. Figure 4 indicates the Si-Si radial distribution function at both states. The results show that at 0 GPa and in both states, it has the first peak at location of about 3.10 Å. However, at 40 GPa, the Si-Si radial distribution function in amorphous state appears a shoulder at around 2.82 Å. For Si-Mg pair (see figure 5), the Si-Mg bond distance decreases strongly at both states as pressure increases. At 0 GPa, the Si-Mg bond distance in amorphous and liquid states is about 3.20 Å and 3.40 Å at 0 GPa, respectively. At 40 GPa, these bond distances in amorphous and liquid states is about 2.80 Å and 2.60 Å, respectively. In the Mg-Mg pair radial distribution function, it appears a shoulder at location of 3.80 Å in amorphous state at 40 GPa. Meanwhile, the radial distribution function of Mg-Mg pair in both states at 0 GPa and in liquid state at 40 GPa has only the main first peak at around 2.8 – 3.2 Å. The Mg-Mg bond distances at 0 GPa are larger than the one at 40 GPa. Next, we calculate distribution of the coordination number for simulated Mg_2SiO_4 system at both states and at 0 and 40 GPa, it showed on table 1.

Table 1. Distribution of the coordination number for simulated Mg_2SiO_4 system at both states and at 0 and 40 GPa; C_x are the fraction of SiO_x units (x=4-6), D_y are the fraction of MgO_y units (y=3-8)

Fraction (%)	amorphous state		liquid state	
	0 GPa	40 GPa	0 GPa	40 GPa
C_4	92.20	9.90	99.20	10.79
C_5	5.60	46.90	0.80	46.61
C_6	0.10	42.30	0.00	42.59
D_3	14.20	0.00	0.45	0.00
D_4	39.90	0.10	32.67	0.01
D_5	32.90	3.50	49.58	2.53
D_6	10.40	24.70	16.87	39.37
D_7	1.20	41.50	0.43	42.40
D_8	0.10	24.30	0.00	15.69

The results show that, at amorphous state there are percentage of SiO4 units is 92.20% at 0 GPa. At 40 GPa, the fraction of SiO_4 decreases strongly while the fraction of SiO_5 and SiO_6 increase sharply. It means that there is structural phase transition from SiO_4 to SiO_5 and SiO_6 units under compression. The fraction of SiO_x units in Mg_2SiO_4 in liquid states is similar to the one in amorphous states and at both pressure 0 and 40 GPa. Relating to MgOy units, it can be seen that there is difference about the percentage of structural units MgOy at amorphous and liquid states as well as at different pressure. Namely, at 0 GPa, the fraction of MgO_3, MgO_4 and MgO_5 units is dominant in amorphous Mg_2SiO_4, meanwhile the fraction of MgO_4, MgO_5 and MgO_6 units is dominant in liquid Mg_2SiO_4. At 40 GPa, percentage of MgO_6, MgO_7 and MgO_8 is dominant in both states. The above analysis illustrates that the structure of amorphous Mg_2SiO_4 is built mainly by the SiO_4, MgO_3, MgO_4 and MgO_5 and a number of small SiO_5 network at 0 GPa. Meanwhile, the structure of liquid Mg_2SiO_4 is built mainly by the SiO_4,

MgO_4, MgO_5 and MgO_6 network. At 40 GPa, the network structure of Mg_2SiO_4 at both states consists of SiO_5, SiO_6, MgO_6, MgO_7 and MgO_8 network. These SiO_x, MgO_y structural units can be link to each other via oxygens to form network structure of Mg_2SiO_4 system that visualized in figure 7 and 8.

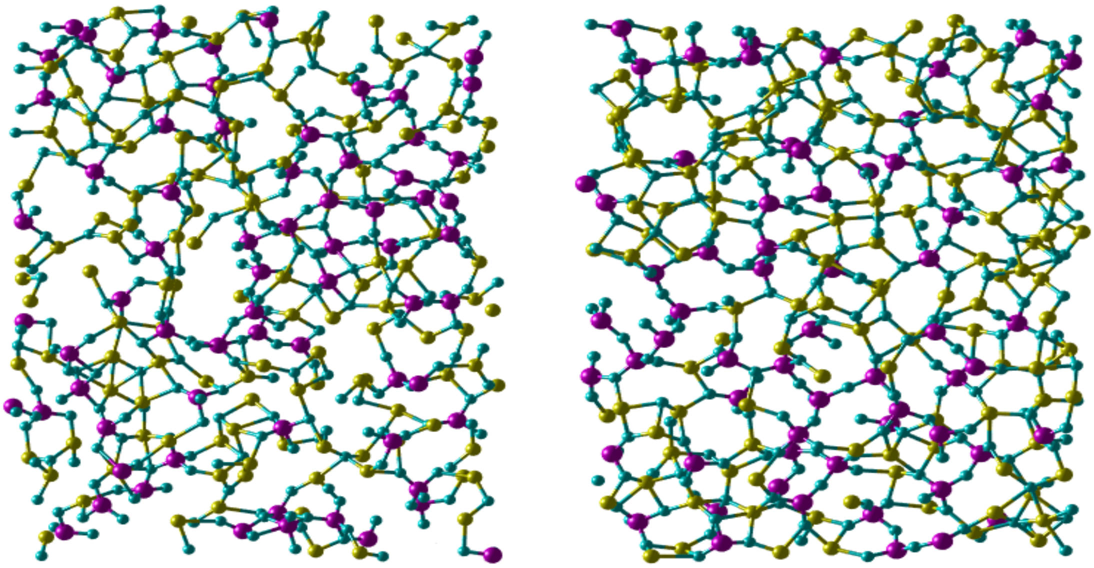

Figure 7. The snapshot of network structure of Mg_2SiO_4 at 0 GPa and at both states: amorphous (left) and liquid (right)

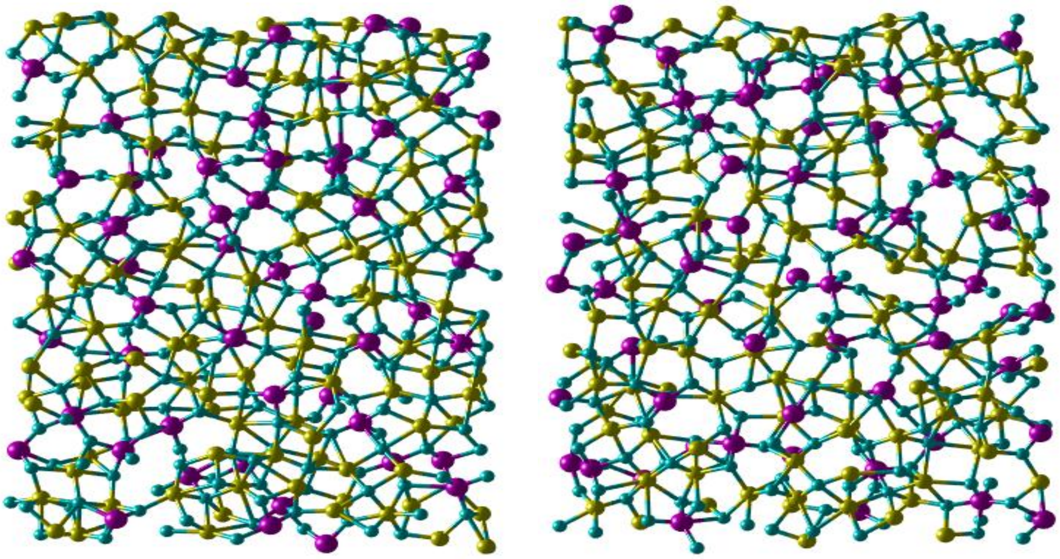

Figure 8. The snapshot of network structure of Mg_2SiO_4 at 40 GPa and at both states: amorphous (left) and liquid (right).

It can be seen that the atoms tend to arrange more orderly at 40 GPa compare to 0 GPa. The O-O bond distance depends on the O-Si-O and O-Mg-O bond angle in the SiO_x and MgO_y units, respectively.

The previous studies [2, 13, 14] indicated that magnesium silicate system at 0 GPa has the O-Si-O and O-Mg-O bond angle are different, around 105-110^0 and 85-90^0 degree, respectively. Meanwhile, at high pressure (40GPa) or in liquid Mg_2SiO_4, the O-Si-O and O-Mg-O bond angle are almost the same. Thus, there are only two O-O bond distances in amorphous Mg_2SiO_4 at 0 GPa. This leads to existence of sub-peak in the O-O radial distribution function in amorphous Mg_2SiO_4 at 0 GPa. Furthermore, in amorphous Mg_2SiO_4 at 40 GPa, MgO_y are mainly MgO_6, MgO_7 and MgO_8 units. The Mg-O-Mg bond angle distribution has a peak at around 80 and a shoulder at around 150 degree [14]. This is original of appearance of sub-peak in the Mg-Mg pair radial distribution function in amorphous Mg_2SiO_4 at 40 GPa. We continue studying all type of links between adjacent SiO_x units, adjacent MgOy units and adjacent SiO_x and MgO_y units in Mg_2SiO_4 system. We found that there are three type of links including the corner-, edge- and face-sharing bonds. The number of the corner-, edge- and face-sharing bonds is showed in Table 2.

Table 2. The number of corner-, edge- and face-sharing bonds (denoted N_{corner}, N_{edge} and N_{face} respectively) between adjacent TO_n units (T=Si,Mg)

Structural units		amorphous state		liquid state	
		0 GPa	40 GPa	0 GPa	40 GPa
SiO_x-SiO_x	N_{corner}	487	983	535	894
	N_{edge}	0	182	0	11
	N_{face}	0	29	0	46
MgO_y-MgO_y	N_{corner}	3574	4483	3222	4609
	N_{edge}	1746	2651	1052	2511
	N_{face}	267	1407	152	1232
SiO_x-MgO_y	N_{corner}	4077	3980	2857	4080
	N_{edge}	367	2402	460	2014
	N_{face}	2	488	15	463

It can be seen that at 0 GPa, links between two adjacent SiO_x units are corner-sharing bonds in amorphous and liquid states. The number of corner-sharing bonds at amorphous and liquid state is 487 and 535, respectively. At 40 GPa, in both states, the adjacent SiO_x units link each other by three types of bonds. The number of corner-sharing bonds is also dominant. Note that, the number of edge-sharing bonds in amorphous Mg_2SiO_4 at 40 GPa is the largest. As above mentioned, the structure of amorphous Mg_2SiO_4 is mainly build by SiO_4 units at 0 GPa and SiO_5, SiO_6 units at 40 GPa. It means that links between two adjacent SiO_4 units are corner-sharing bonds, meanwhile links between two adjacent SiO_5, SiO_6 units are corner-, edge-, and face- sharing. Thus, the appearance of sub-peak in Si-Si radial distribution function at around 2.82 Å at 40 GPa due to existence of the edge-, face-sharing bonds. For the adjacent MgO_y units, they link to each other by all three types. At 0 GPa, the number of corner-, edge-, and face- sharing is 3574, 1746 and 267 in amorphous Mg_2SiO_4 and 3222, 1052 and 152 in liquid Mg_2SiO_4, respectively. As pressure increases, the number of all three types bonds increases. At 40 GPa, the number of corner-, edge-, and face- sharing is 4483, 2651 and 1407 in amorphous Mg_2SiO_4 and 4609, 2511 and 1232 in liquid Mg2SiO4, respectively. Similar to the results for the adjacent MgO_y units, the links between adjacent SiO_x and MgOy units consist of all three types of bonds and the number of all three types bonds increases as increasing pressure.

4. Conclusion

We find that the structure of Mg_2SiO_4 consists of basic structural units TO_n (T=Si, Mg; n=3-8). These TO_n link to each other through oxygen atoms to form network structure. The T-O coordination number increases as pressure increases. The amorphous Mg_2SiO_4 comprises mainly SiO_4, MgO_3, MgO_4 and MgO_5 and a number of small SiO_5 network at 0 GPa. Meanwhile, the structure of liquid Mg_2SiO_4 comprises SiO_4, MgO_4, MgO_5 and MgO_6 network. At 40 GPa, the network structure of Mg_2SiO_4 at both states consists of SiO_5, SiO_6, MgO_6, MgO_7 and MgO_8 network. In amorphous and liquid Mg2SiO4 system, the links between the adjacent SiO_x units are mainly corner- and edge-sharing bonds. Meanwhile the links between the adjacent MgO_y units, the adjacent SiO_x and MgOy units are all types of bonds including corner-, edge-, and face- sharing bonds. The appearance of the sub-peaks in radial distribution function of Si-Si pair due to existence of the number of significantly edge- and face-sharing bonds in amorphous Mg_2SiO_4 at 40 GPa. The existence of the sub-peak in the O-O radial distribution function in amorphous Mg_2SiO_4 at 0 GPa is due to difference of the O-Si-O and O-Mg-O bond angle. The original the sub-peak in the Mg-Mg pair radial distribution function in amorphous Mg_2SiO_4 at 40 GPa relates to existence of two peak in the Mg-O-Mg bond angle distribution in MgO_y units.

Acknowledgments

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