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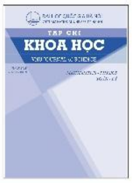

Original Article

Investigation of Pressure Effect on the Structure of $3Al_2O_3.2SiO_2$ System

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Abstract: This paper studies the structure of the Mullite system ($3Al_2O_3.2SiO_2$) by Molecular Dynamics simulation (MDs) using the Born–Mayer–Huggins pair interaction and periodic boundary conditions. The simulation was performed with model of 5250 atoms at different pressure and at 3500 K temperature. The structural properties of the system were clarified through analysis of the pair radial distribution function, the distribution of coordination number, the bond angle and the link between adjacent TO_x units.

Keywords: Molecular dynamics simulation, Mullite, structure, Al_2O_3-SiO_2 system.

1. Introduction

In recent years, oxide systems (Al_2O_3, SiO_2, Al_2O_3-SiO_2) have received a lot of research attention of scientists. Al_2O_3-SiO_2 system with the Al_2O_3 content at 60 mol % (Mullite-$3Al_2O_3.2SiO_2$) has been studied by both experiments [1-3] and computer simulations [4-6] because it is a potential material for both traditional and advanced ceramics [7-9]. Further, thanks to its high-temperature mechanical strength, high creep and thermal-shock resistance, low thermal expansion and dielectric constants and good transmission in the mid-infrared range, $3Al_2O_3.2SiO_2$ is used widely in electronics, optical applications [10]. Therefore, the studying of structure of $3Al_2O_3.2SiO_2$ at different temperature and pressure conditions is necessary. The experiment studies [1] showed that the mean T-O distance (T is Al, Si) for Al_2O_3-SiO_2 glasses increases from 1.61 to 1.79 Å with increasing Al_2O_3 content. The mean coordination number for pair T-O is 4.0 ± 0.1 for Al_2O_3 content less 40 mole %. Some studies showed

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presence of oxygen tri-clusters (O-Al_3, O-Si_3, Al_2-O-Si, Al-O-Si_2 linkages) in structure of Al_2O_3-SiO_2 melt and glass [11, 12]. Recently, simulation studies [4, 5, 13, 14] have been focused on studying the spatial distribution of basic structural units TO_x as well as the determine the proportion of bridging oxygen (BO) and non-bridging oxygen (NBO) in Al_2O_3-SiO_2 system. These give useful insights into their structure. In this work, we use MD simulation to study of $3Al_2O_3.2SiO_2$ system at different pressures. The aim of this work is to serve the basics knowledge about structure of $3Al_2O_3.2SiO_2$ system under compression at atomic level. By analyzing of the partial radial distribution function, the coordinate number, the O-T-O and T-O-T bond angles distribution and the links between adjacent TO_x units, the microstructure properties of $3Al_2O_3.2SiO_2$ system will be clarified.

2. Computational procedure

The MD simulation of liquid $3Al_2O_3.2SiO_2$ is carried out in a 5250-atom system (500 Si atoms, 3250 atoms O and 1500 Al atoms) with periodic boundary conditions using Born – Mayer – Huggins potential. The detail about this potential can be found reference [4]. To integrate the Newton's equation of motion, Verlet algorithm is with the MD step of 0.48 fs. The first configuration is created by randomly placing 5250 atoms in a simulation box. This model is heated to 6000K to remove possible memory effect. Then the model is cooled down 3500K at ambient pressure (model M1). At this condition, a long relaxation (10^6-10^7 MD steps) has been done to get equilibrium state of model M1 (using NPT ensemble). Next, the model M1 is compressed to different pressures (see table 1). Six models at different pressures and at 3500 K are relaxed for a long time to reach the equilibrium. The structural data of considered models is determined by averaging over 2000 configurations during the last 20000 MD steps.

Table 1. MD models for $3Al_2O_3.2SiO_2$ system at 3500K and different pressures.

Models	M1	M2	M3	M4	M5	M6
Pressure (GPa)	0.14	4.62	7.28	13.31	21.36	31.34
Length of simulation box (Å)	41.76	39.67	36.54	36.26	36.01	35.55

3. Results and discussion

The structural characteristics of $3Al_2O_3.2SiO_2$ system is considered through the calculation of the partial radial distribution function as shown in figure 1 and table 2. The results show that as the pressure increases, the first maximum peak position of Si - O and O - Al pairs tend to shift to right. Namely, at 0.14 GPa, r_{Si-O} = 1.58 and r_{Al-O} = 1.66 Å, but at 31.34 GPa, r_{Si-O} = 1.66 and r_{Al-O} = 1.74 Å. This means that the average distance of Si - O and O - Al pair increases with pressure. In contrast, for the Si-Si, Si - Al, O - O and Al - Al pairs, under compression, the first maximum peak position of the above pairs decreases. At low pressure, the first maximum peak positions of Si-Si, Si - Al, O - O and Al - Al pairs are 3.18, 3.16, 2.66 and 3.14Å, respectively. At high pressure, their positions are 3.16, 3.12, 2.52 and 3.08 Å, respectively. It means that the average distance of Si-Si, Si - Al, O - O and Al - Al pairs decreases with pressure. Moreover, the height of the first maximum peak of all pairs of atoms decreases and the width becomes wider when the pressure increases. This means that the degree of short-range order decreases as the pressure increases. For Si-Si, Si-Al, Al-Al and O-O pairs there is a significant change in the peaks after the first maximum peak of the radial distribution function in the pressure range from 7.28 GPa to 31.34 GPa. This means that the degree of intermediate-range order tends to become more orderly in the 7.28 – 31.34 GPa range.

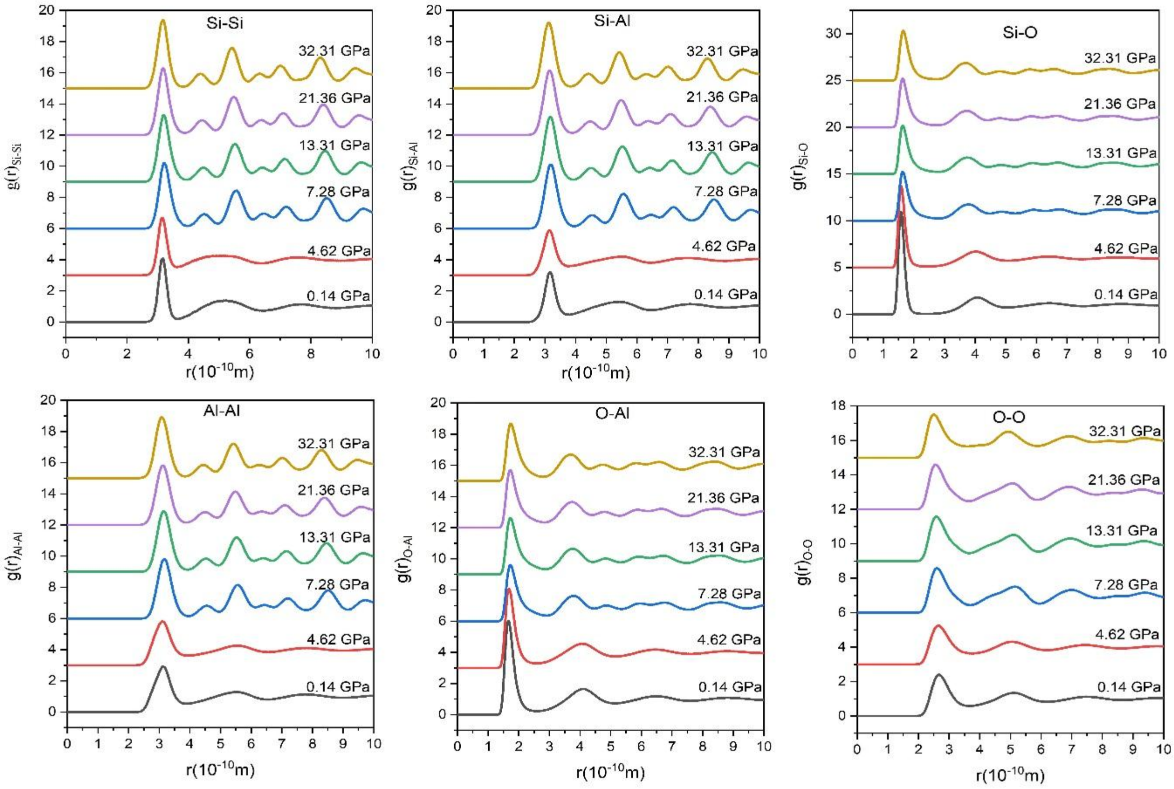


Figure 1. The T-T, T-O and O-O pairs radial distribution functions for $3Al_2O_3.2SiO_2$ system at different pressures (T is Al, Si).

Table 2. The position of the first maximum peaks of the pair radial distribution functions at different pressures

P(GPa)	r_{Si-Si}(Å)	r_{Si-O}(Å)	r_{Si-Al}(Å)	r_{O-O}(Å)	r_{O-Al}(Å)	r_{Al-Al}(Å)
0.14	3.16	1.58	3.16	2.66	1.66	3.14
4.62	3.16	1.58	3.14	2.66	1.68	3.10
7.28	3.22	1.64	3.20	2.60	1.72	3.16
13.31	3.20	1.64	3.18	2.60	1.72	3.14
21.36	3.18	1.64	3.16	2.56	1.72	3.14
31.34	3.16	1.66	3.12	2.52	1.74	3.08

Table 3 shows the change of the percentage fraction of structural units SiO_x and AlO_y as a function of pressure. It can be seen that, at low pressure, most of Si atoms is surrounded by 4 O atoms forming SiO_4 (92.99%) structural unit. And most of Al atoms is surrounded by 4 and 5 O atoms forming AlO_4 (66.91%) and AlO_5 (21.31%) structural unit, respectively. The fraction of the other structural units is negligible. It means that the structure of $3Al_2O_3.2SiO_2$ system is build by mainly SiO_4, AlO_4 and AlO_5 structural units at low pressure.

Table 3. The percentage fraction of structural units SiO_x (x=4÷7) and AlO_y (y=3÷7) in $3Al_2O_3.2SiO_2$ system.

Pressure (GPa)	SiO_4	SiO_5	SiO_6	SiO_7	AlO_3	AlO_4	AlO_5	AlO_6	AlO_7
0.14	92.99	6.72	0.18	0.00	10.38	66.91	21.31	1.36	0.03
4.62	72.85	25.30	1.72	0.01	3.26	51.36	38.96	6.20	0.20
7.28	8.32	37.70	52.87	1.09	0.04	5.53	29.52	53.29	10.69
13.31	5.95	34.34	57.98	1.70	0.01	4.03	26.39	55.66	12.71
21.36	6.06	30.71	61.18	2.04	0.08	3.77	22.66	56.62	15.26
31.34	2.92	19.02	72.90	5.06	0.02	2.33	16.78	55.33	22.87

As pressure increases, from 0.14 GPa to 7.28GPa, the fraction of AlO_4 and SiO_4 units decrease sharply, but the fraction of AlO_6, SiO_6 units increase sharply. It means that, the local environment of Si, Al has a significant change under compression. Continue to compression up to 31.34GPa, the result shows that most of Si and Al atoms is surrounded by six O atoms (72.90% SiO_6, 55.33% AlO_6). Besides the fraction of AlO_5, AlO_7 and SiO_5 units are 16.78%, 22.87% and 19.02%, respectively. Therefore, at high pressure, the structure of $3Al_2O_3.2SiO_2$ system comprises mainly of SiO_6 and AlO_6 units (T is Al, Si).

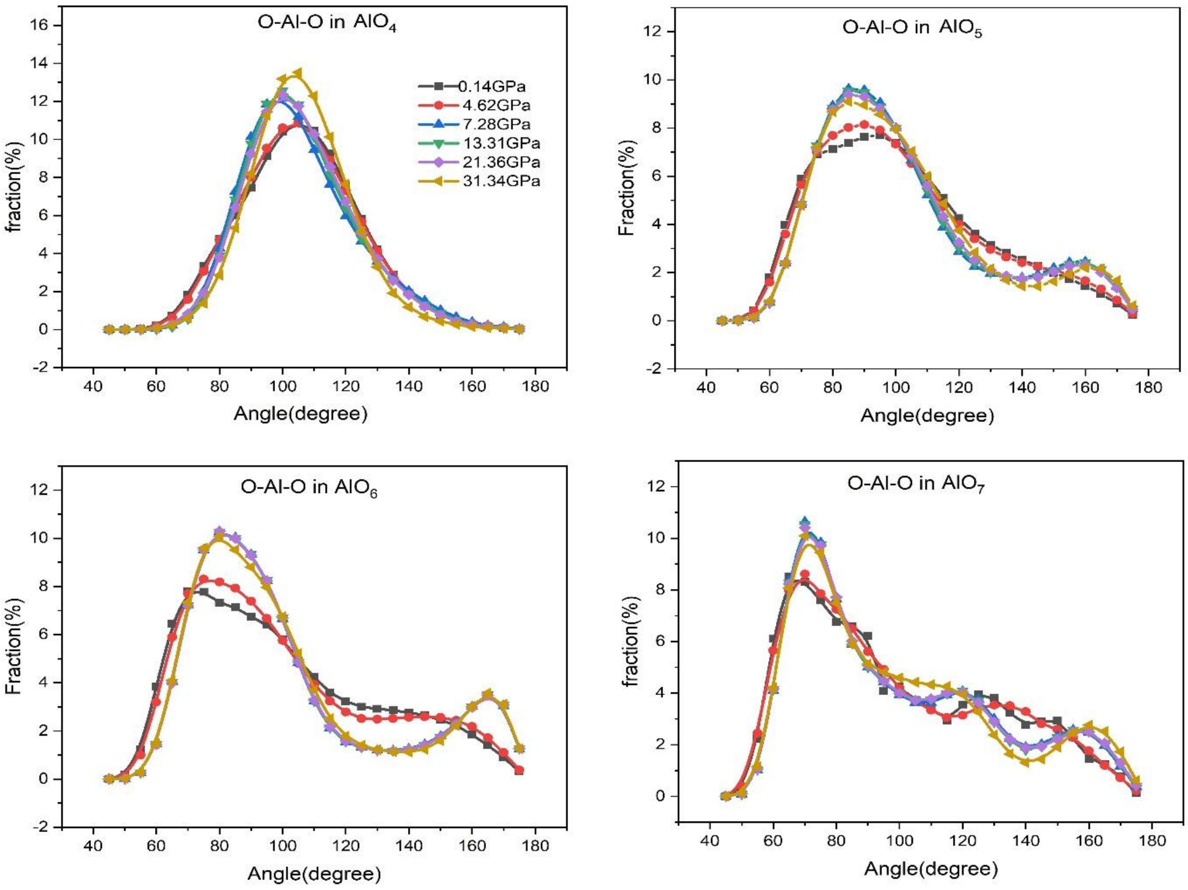


Figure 2. Distribution of O-Al-O bond angle in AlO_x (x=4÷7) structural units at different pressures.

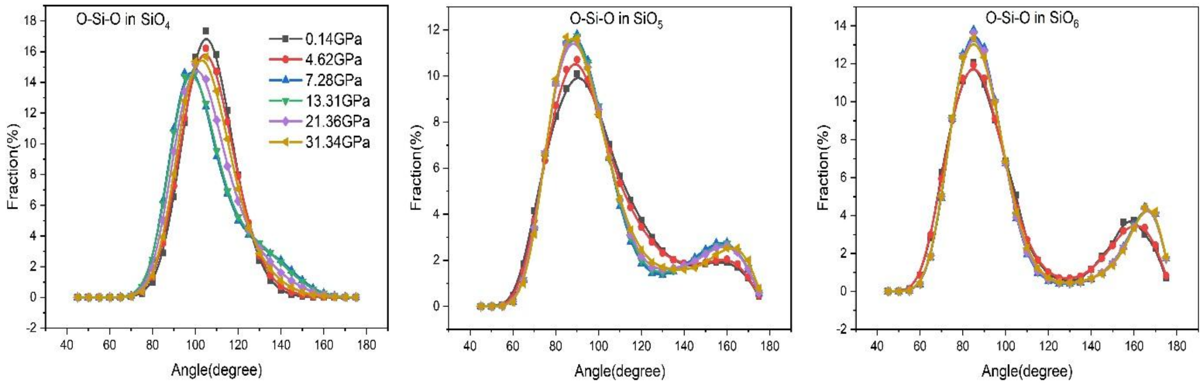


Figure 3. Distribution of O-Si-O angle in SiO_x (x=4÷6) structural units at different pressures.

We have calculated the bond angles in structural units at different pressures. Figure 2 and Figure 3 describe in detail the O-Si-O and O-Al-O bond angle distribution in AlO_x units and SiO_y units, respectively under compression. The results show that at low pressure, the O-Al-O bond angle distribution in AlO_4, AlO_5, AlO_6 and AlO_7 units has a peak at 100, 90, 80 and 70 degrees, respectively. The O-Si-O bond angle distribution in SiO_4, SiO_5, SiO_6 units has a peak at 105, 90 and 90 degrees, respectively. Under compression pressure, the position of peaks is almost not change. However, the form of distribution is slightly changed with pressure. The results also show that the structural units can connect to each other via O atoms to form network structure of $3Al_2O_3.SiO_2$ system. So, to clarify the intermediate-range order structure, we analysis the distribution of T-O-T bond angles in OT_n units at different pressures (n=2÷4) (see figure 4).It can see that at low pressure, the T-O-T bond angle distribution in OT_2 and OT_4 units has a peak at 155 and 90 degrees, respectively. when the pressure increases to 31.34GPa, they have a peak at 165 and 100 degrees, respectively. For T-O-T bond angles in OT_3 unit, T-O-T bond angle decreases from 120 to 105 degree under compression. In order to clarify Mullite's network structure, we visualize the network structure for $3Al_2O_3.2SiO_2$ system at pressures of 1.41 and 21.36GPa (see figure 5). It reveals that under compression, the structure of the $3Al_2O_3.2SiO_2$ system tends to become more order.

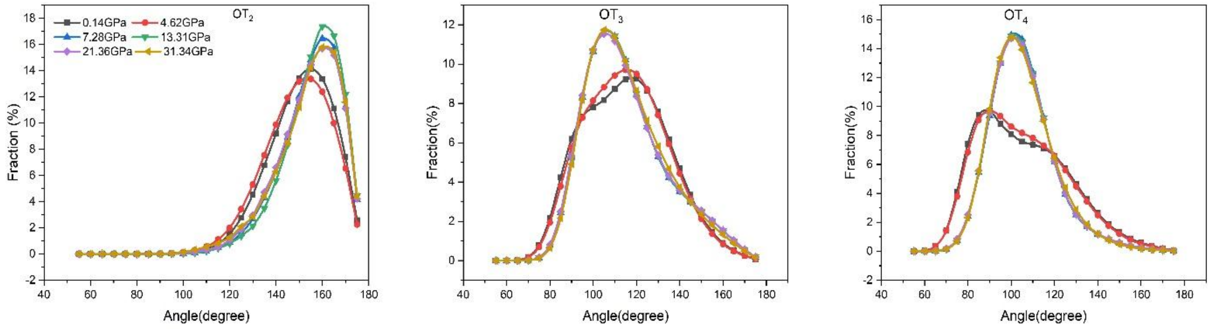
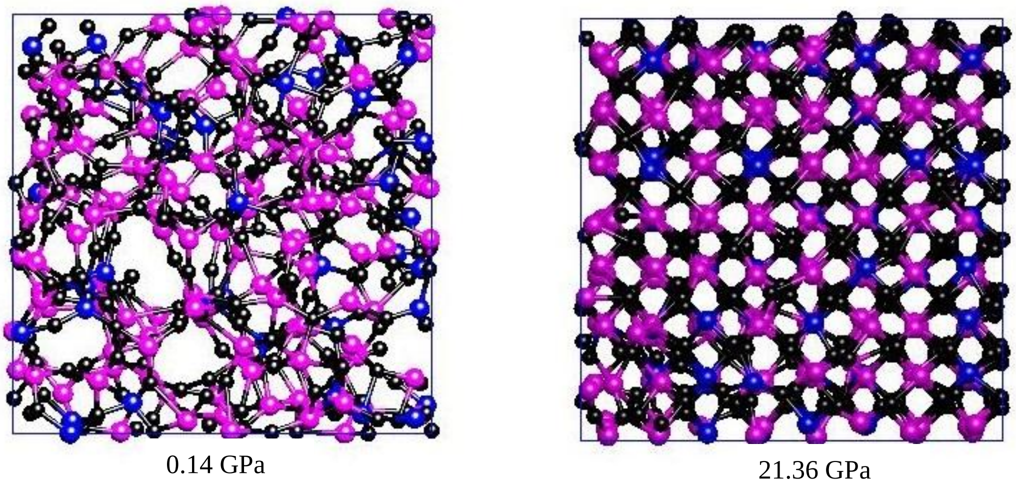


Figure 4. Distribution of T-O-T bond angles in OT_y (y=2÷4) units at different pressure pressures.


0.14 GPa

21.36 GPa

Figure 5. Snapshot of structural models for $3Al_2O_3.2SiO_2$ system (Si, Al and O atoms in blue, purple and black.

Table 4. The everage number of edge sharing bonds (N_e) and face sharing bonds (N_f) per TO_x units. AlO_x-AlO_x are the links between two AlO_x units; AlO_x-SiO_x are the links between AlO_x and SiO_x units

Pressure (GPa)	AlO_x-AlO_x		AlO_x-SiO_x	
	N_e	N_f	N_e	N_f
0.14	0.464	0.016	0.067	0.001
4.62	0.619	0.017	0.150	0.005
7.28	1.484	0.003	0.692	0.001
13.31	1.541	0.003	0.697	0.000
21.36	1.752	0.012	0.792	0.003
31.34	1.967	0.013	0.880	0.001

To clarify the linkage among structural units TO_x, we have investgated the all the bond kind between TO_x. It reveals that most of linkages between TO_x units are the corner sharing bonds. The edge and face sharing bonds only exist between AlO_x units and between AlO_x and SiO_x units. The edge- and face-sharing bonds amongst AlO_x and between AlO_x and SiO_x is significant and increases strongly with pressure (see table 4). At low pressure, each AlO_x unit has only about 0.46 the edge-sharing bond and it increases to around 2 at 31.34 GPa. The number of face sharing bonds is very little, about 0.01 face bond per AlO_x unit. Similarly, each TO_x unit has 0.067 the edge-sharing bond and it increases to 0.880 at 31.34 Gpa. the average number of face sharing bonds per TO_x units is negligible.

4. Conclusion

In this paper, the structural properties of $3Al_2O_3.2SiO_2$ system under compression have been clarified. At low pressure, structure of $3Al_2O_3.2SiO_2$ is mainly formed by AlO_4 and SiO_4 units. At high pressure, it is mainly formed by AlO_6 and SiO_6 units. This shows structural transition from tetrahedral to octahedral network. The average distance of Si-O, O-Al pairs increases with pressure. In contrast, the average distance of Si-Al, O-O, Si-Si and Al-Al pairs decreases. The link between TO_x units via edge-, face-sharing bonds lead to decrease of T-T distance. At low pressure, the adjacent TO_x units are mainly linked to each other via the corner-sharing bonds. However, at higher pressure, they can link to each other via the corner-, edge-, face-sharing bonds. Under compression, the structure of the $3Al_2O_3.2SiO_2$ system tends to become more order.

Acknowledgments

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