The Structure of Liquid PbSiO$_3$: Insight from Analysis and Visualization of Molecular Dynamics Data

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Abstract: The structural characteristics of liquid PbSiO$_3$ have been investigated by means of the molecular dynamics simulation. The simulations were done in a microcanonical ensemble, using pair potentials. Models consisting of 5000 atoms (1000 Pb, 1000 Si and 3000 O) were constructed at different pressures and at temperatures 3200 K. The local structure and network topology were analyzed through radial distribution function, bond angle distributions and coordination number distribution. The local environment around Pb atoms and continuity of silica and lead oxide sub-networks as well as their change under compression are also discussed in detail, moreover, we have used visualization techniques illustrated network structure.

Keywords: Structural phase, liquid, triclusters, simulation, pressure.

1. Introduction

Lead-silicate glass is an important material in many high technology application [1]. They are used as special materials in electronics and optoelectronics (in the production of image plate amplifiers and scintillators [2]). The structural chemistry of glass systems of PbO-SiO$_2$ have been studied for a long time. Because, they exhibit many properties (such as thermal, optical, and mechanical properties) very different than other silicate glasses. Specially, the PbO-SiO$_2$ form a thermally and chemically stable glass over a wide composition range. The atomic structure of lead-silicate glasses has been extensively investigated by using various experimental techniques, including IR spectroscopy [3], Raman spectroscopy [3–5], NMR [4, 6, 7], XPS [8], X-ray [9,10], neutron diffraction methods [11,12], and EXAFS [7,13]. Computer simulations of the structure have also been performed [13]. It is well known that most glasses, depending on the method of preparation, can have various densities with the same composition. In this respect, silica is probably the most studied material (e.g. [14–24]). Studies on

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low- and high-density forms of many binary silica glasses have also been performed. However, the structure and dynamics of rarefied [25] and densified silicate glasses containing heavy-metal oxides, as far as the authors know are still in debate.

The present contribution is a molecular dynamics (MD) [26] study of the structure of rarefied and densified lead-silicate glass of the PbSiO3 composition. In order to see more clearly the structural characteristics of low-and high-density states, we have performed our simulations in a wide range of densities, from 5.9 g/cm^3 to 8.7 g/cm^3. The number of issues need to be clarified such as microstructure, microphase separation, polymorphism and diffusion properties.

2. Calculation method

Molecular dynamic (MD) simulation is carried out for lead silicates systems (5000 atoms) at temperatures of 3200 K and pressure range from 0 to 35GPa. The Born-Mayer potential is used in this simulation. Detail about this potential can be found in Refs. [27, 28] the software used in our calculation, analysis and visualization was written by ourselves. It was written in C language and run on Linux operating system. We use the Verlet algorithm to integrate the equations of motion with MD step of 1.6 fs. This value assures the requirement to accurately integrate the Newtonian equations of motion in order to track atomic trajectories and the computational cost is reasonable. Initial configuration is obtained by randomly placing all atoms in a simulation box. This sample is equilibrated at temperature of 6000 K for a long time (about 10^5 MD steps) and then it is compressed to different pressure (from 0 to 35GPa) and relaxed for about 10^6 MD step. After that the models at different pressure is cooled down to the temperature of 3200 K with the rate of about 10^{13} MD K/s. A consequent long relaxation (about 10^7 MD steps) has been done in the NPT ensemble (constant temperature and pressure) to obtain equilibrium state. In order to improve the statistics the measured quantities such as the coordination number, partial radial distribution function are computed by averaging over 1000 configurations separated by 10 MD steps.
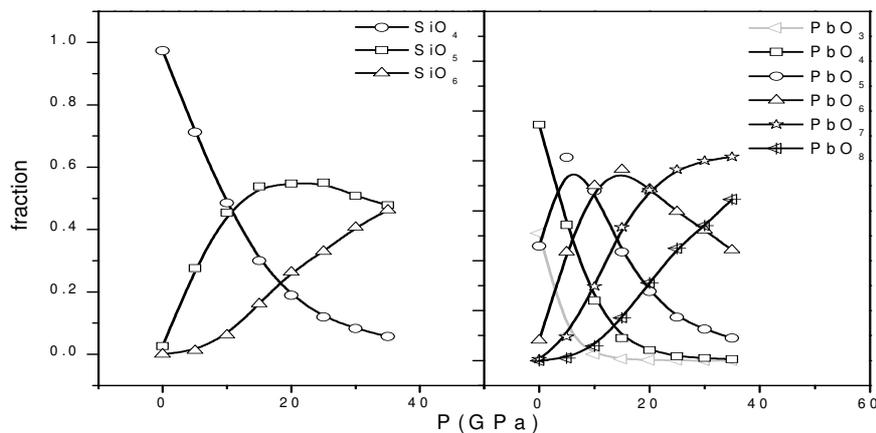
3. Results and discussions

Fig. 1. Distribution of coordination units SiO$_x$(left) and PbO$_x$(right) as a function of pressure.

The structural organization in liquid $PbSiO_3$ were investigated through pair radial distribution function, coordination distribution, bond length and bond angle distribution. Intermediate range order is clarified by visual tool.

Firstly, figure 1 shows that, the distribution of coordination units TO_x (T is Si or Pb). With SiO_x units(left), it can been that, at low pressure(density), most of Si atoms has coordination number of 4 (about 97.5%). Meanwhile, the distribution of coordination SiO_5 units is very small (about 2.5 %) and non-existence of the SO_6 units. When increasing pressure, the significant change of SiO_x units. The fraction of SiO_4 units is decreases while the fraction of SiO_5 and SiO_6 increases. The fraction of SiO_5 get maximum at pressure 25 GPa with the fraction 54.98%. At pressure 35 GPa, the fraction SiO_4 units is small and the fraction units of SiO_x mainly consists of the fraction units SiO_5 and SiO_6. This result is in good agreement with calculated results in the works [29, 30], this has been visualization in figure 5. With units PbO_x(right), it can seen that, at ambient pressure, most of coordination units are PbO_3, PbO_4, PbO_5 with the fraction 25.49%, 47.24%, 22.89% respectively. When pressure increases, PbO_x (x=3,4) decreases, whereas the units PbO_x(x=5,6,7 and 8) increases, the fraction PbO_5 and PbO_6 get maximum at about 10GPa, 15GPa respectively. At high pressure, most of coordination units are PbO_6, PbO_7, PbO_8. Of which, the fraction of PbO_7 units is largest (about 40.83%).
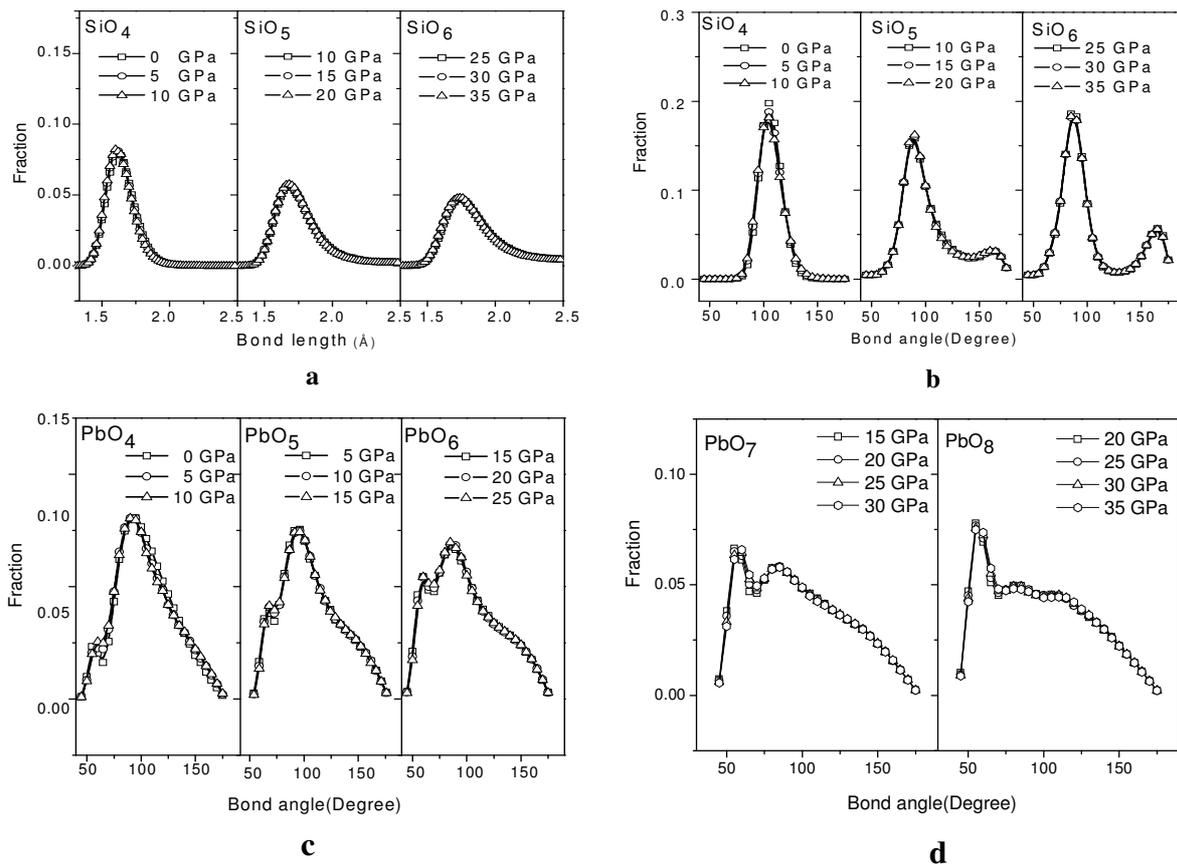

Fig. 2 The bond length distribution and The bond angle distribution in coordination units TO_x (T=Si, Al; x= 4, 5, 6, 7 and 8).

Fig 2 show that, the bond length and bond angle distributions in basic structural units at different pressures. The bond angle can be used to describe the statistical average of angles formed with neighboring atoms(Angular Distribution Function). The peaks of bond-length distributions TO_x(T is Si or Pb) in SiO_4, SiO_5 and SiO_6 units are 1.60, 1.65 and 1.70 Å respectively(fig 2a). The peaks of bond-angle distributions TO_x(T is Si or Pb) in SiO_4, SiO_5, SiO_6 units are 100^0-105^0, 85^0-90^0, 85^0-90^0 respectively(fig 2b). The PbO_4, PbO_5 and PbO_6 units are 85^0-95^0, 85^0-90^0, 80^0-85^0 respectively(fig2c). This values are in good agreement with the experiment [31] and MD simulation [13, 32]. Results show that, the T-O bond length and O-T-O bond angle distribution of TO_x units are undependent minor in pressure. It means that, the topology TO_x (T is Si, x=4, 5, 6 and Pb, x=4, 5, 6, 7 and 8) at different pressure is identical. The fig.2 has a main peak except the bond-angle O–T–O distribution for fig.2c and fig.2d, The appearance of two peaks in the case of PbO_x (x= 4, 5 ,6,7 and 8).
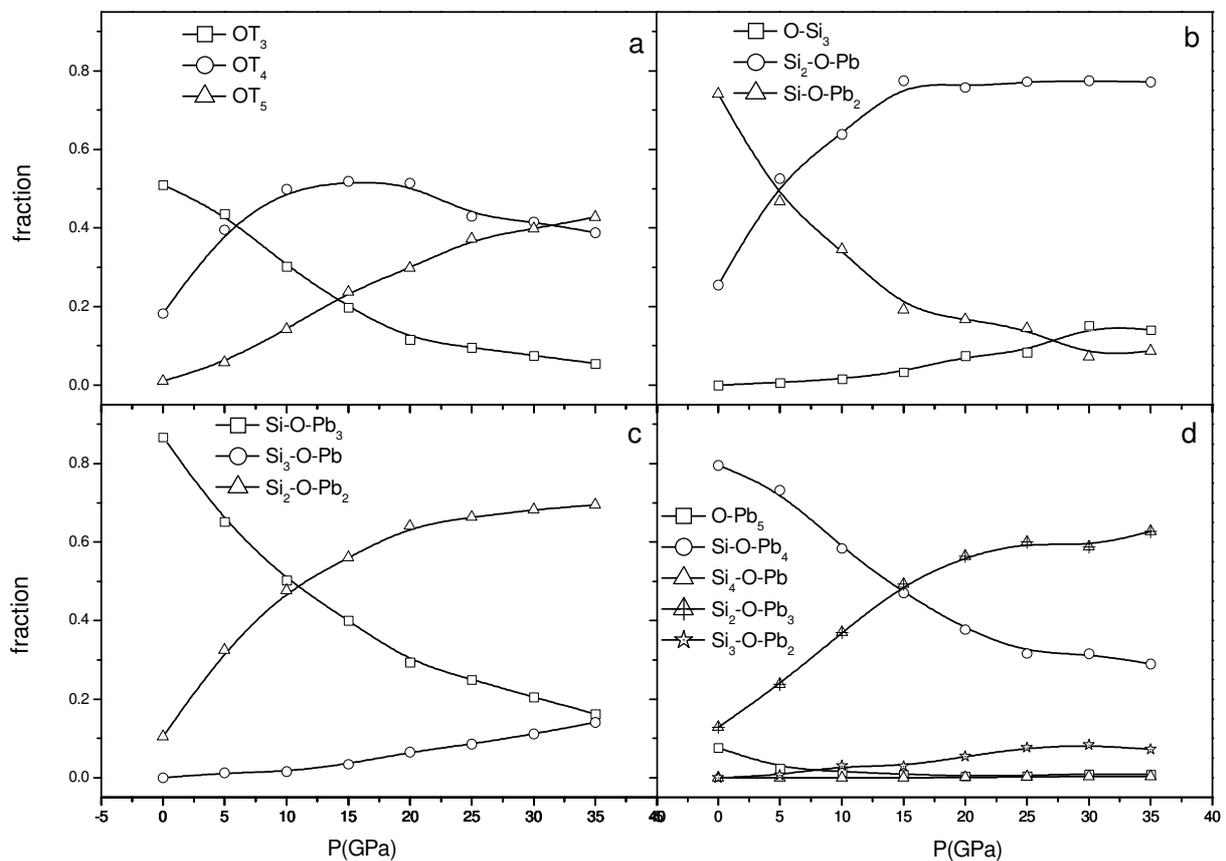

Fig. 3. Distribution of all types of coordination units OTy
(T is Si, Pb; y= 3, 4 and 5) in liquid PbSiO3 as a function of pressure.

The fig 3a show that, at ambient pressuse, the fraction of coordination OT_3, OT_4 and OT_5 are about 51.03%, 18.23% and 1.01% respectively. As pressuse increases, the fraction of coor-dination OT_5 units increases. While, the fraction of coordination OT_3 units decreases. The fraction of coordination OT_4 units increases to the maximum value (at pressures about 15 GPa) and then decline with increasing pressure. At high pressure (35 GPa), the fraction of coordination OT_3, TO_4 and TO_5 units are 5.51%, 38.83% and 42.73% respectively. Fig 3b, 3c and 3d show the distribution of all types TO_x. Fig 3b show that, at ambient pressuse, the fraction of coordination Si_2-O-Pb and Si-O-Pb_2 units are 25.45%, 74.08% respectively. As pressure increases, the fraction of Si-O-Pb_2 decreases. While, the fraction of Si_2-O-Pb increases. At high pressure(about 35 Gpa), this fraction is 77.17% and 8.69% respectively. The number of O–Si_3 and O-Pb_3 is very small(about 15%). Fig 3c show that, at ambient pressure, the most coordination units is Si-O-Pb_3. When pressure increases, this fraction decreases. In contrast, the fraction Si_2-O-Pb_2 increases When pressure increases. At high pressure(35GPa), this fraction is 69.51%, the other type is very small. Fig 3d show that, the most coordination OT_5 units are Si-O-Pb_4 and Si_2-O-Pb_3, the other type is very small (total about 10%). At ambient pressure, the most coordination Si-O-Pb_4 units (about 79.4%), while the fraction of Si_2-O-Pb_3 is 12.8%. When increases pressuses, the fraction Si-O-Pb_4 decreases. Whereas, the fraction Si_2-O-Pb_3 increases. At high pressure(about 35 Gpa), the fraction Si-O-Pb_4 about 29% and Si_2-O-Pb_3 63%.

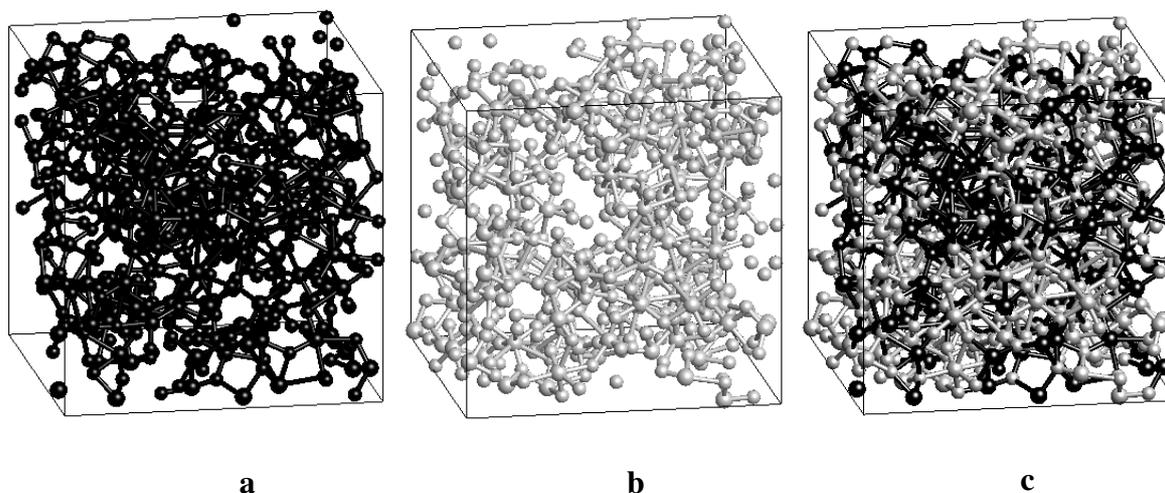**a**   **b**   **c**

Fig. 4. Spatial distribution of (a) units SiOx;(b) units PbOx; and (c) mixture
of units SiOx and PbOx in $PbSiO_3$. Model is constructed at 0 GPa.

Figures 4 show the spatial distribution of SiO_x , PbO_x and mixtures of SiO_x and PbO_x at different pressures. It can be seen that, the distribution of coordination units PbO_x is not uniform, but tend to form clusters of units PbO_x. Similarly, the coordination units SiO_x tend to form clusters of units SiO_x and this is the origin of microphase separation.

Figure 6a shows that, the density as a function of pressure, when the pressure increases, the density increases, the density and pressure is function linearly. The density of Pb is hight compared with other

metals. figure 6b shows that, The number "bridging oxygen bonds". It means that, the SiO_x units link to each other can be symbolized by using Q^n. where n represents the number of SiO_x units link to each other via a bridging oxygen bonds. In which, the value of n range from 0 to 6. It can be seen that, the fraction of Q^0 is very low(4.4%). It means that, the number oxygen are not bridging bonds very small. At ambient pressure , The number bridging

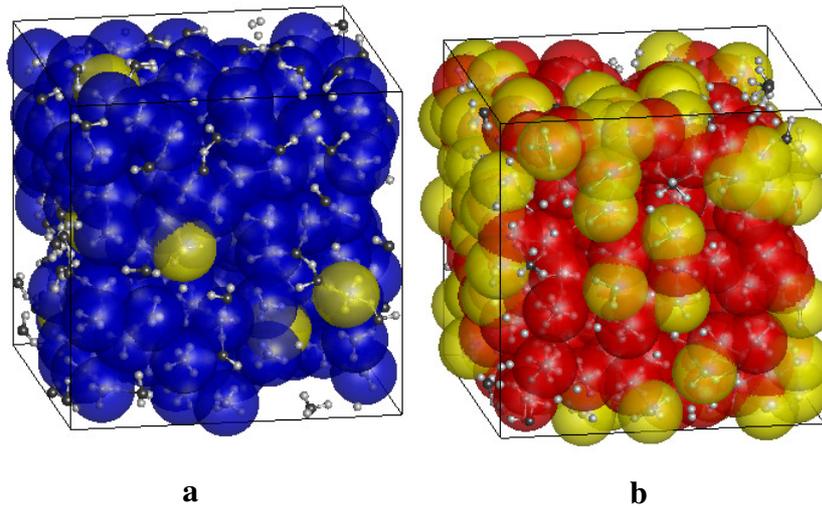**a**   **b**

Fig. 5. Network structure of SiOx that is extracted from $PbSiO_3$ at ambient pressure (a); at 35 GPa(b). Regions with blue color is cluster/chain of SiO_4, red color is cluster/chain of SiO_6, yellow color is cluster/chain of SiO_5 units.
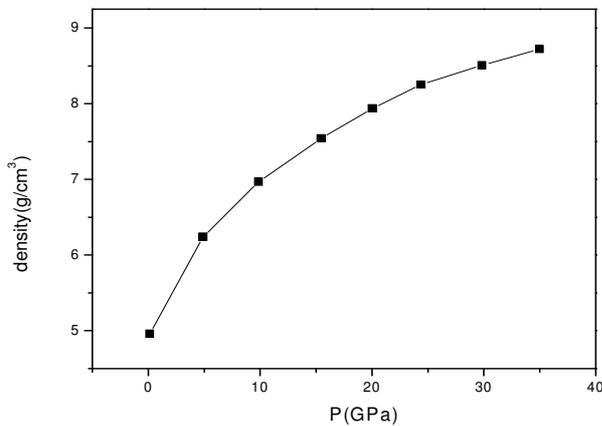

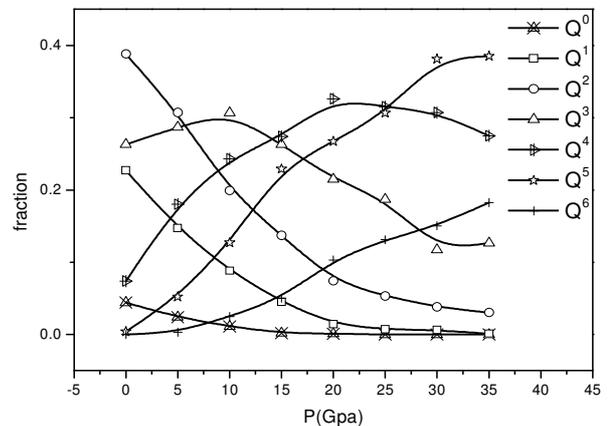Fig.6a. The dependence of density on pressure.   Fig.6b. The number bridging oxygen bonds.

Oxygen bonds mainly are Q^1, Q^2 and Q^3. In which, the fraction Q^2 is largest (about 38.8%). When the pressure increases, Q^1 and Q^2 strongly decreases. At high pressure(about 35GPa), the fraction Q^1 and Q^2 are 0.1% and 3% respectively. Meanwhile, the Q^3 initially increases, the maximum value about 30.7%(10GPa). Then decreases with pressure, at high pressure(about 35GPa) this the fraction is

12.64%. In contrast, the fraction Q^4, Q^5 and Q^6 increases when pressure increases. At ambient pressure, they is very small. when pressure increases, the fraction Q^5 strongly decreases. At high pressure(about 35GPa), this the fraction is 38.5%. Meanwhile, Q^4 and Q^6 are 27.48%, 18.25% respectively. It means that, The number "bridging oxygen bonds" Q^n change when pressure increases. At ambient pressure, the fraction Q^n mainly Q^1, Q^2 and Q^3. At high pressure(about 35GPa), the fraction Q^n mainly Q^4, Q^5 and Q^6. This result is in agreement, when at pressure ambient, the structure units mainly is SiO4. At pressure 35GPa, the structure units mainly is SiO_5 and SiO_6(see that in the fig 5). In which, fig.5a(0 GPa), mainly is the ball color blue(SiO_4). Fig.5b(30 GPa). Mainly is the ball color red and yellow(SiO_5 and SiO_6).

4. Conclusion

The structure of $PbSiO_3$ comprises basic structural units TO_4, TO_5 and TO_6 (T is Si or Pb). at low pressure, most of structural units is TO_4. When increasing pressure, the fraction of units TO_4 decreases, while the fraction of SiO_6 increases. At hight pressure, most of structural units is TO_6. The distribution of units SiO_4, SiO_5 and SiO_6 are not uniform, but tend forming SiO_4, SiO_5 and SiO_6 clusters. and this is the origin of polyamorphism in liquid $PbSiO_3$

The SiOx is connected to each other through common O atoms "bridging oxygen bonds". The fraction Q^n change When increasing pressure. At ambient pressure, the fraction Q^n mainly Q^1, Q^2 and Q^3. At high pressure(about 35GPa), the fraction Q^n mainly Q^4, Q^5 and Q^6. and forming network of SiO_x units that is similar to pure silica network. However, due to the existence of Pb^{+2} incorporates in to silicate network mainly via linkages Si-O-Pb, $Si-O-Pb_2$, $Si-O\_Pb_3$ anh $Si-O-Pb_4$ (mainly at low pressure) and via linkages Si_2-O-Pb, Si_2-O-Pb_3 and Si_2-O-Pb_4(at high pressure).

The distribution of bond length T–O and bond angle O–T–O in units TO_x do not depend on pressure. These results reveal that, the structure of TO_x units does not depend on pressure. It means that, the basic structural units TO_x of different models (different densities) are identical.

Acknowledgments

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