The microstructure of liquid Lead Silicate under PbO content

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Abstract. The structural characteristics of liquid lead silicate xPbO(1-x)SiO2 are performed by means of molecular dynamics simulation at ambient pressure using the Born-Mayer pairwise potentials. The simulations have been performed on the systems which include different samples with a large range of PbO content (0.05 ≤ x ≤ 0.75). The short and intermediate range order in liquid xPbO(1-x)SiO2 have been analysed via pair radial distribution function (PRDFs), coordination distribution, angular distribution and bond length distribution. Calculations show that most of the basic structural units in liquid lead silicate network are SiO4, PbO2 and PbO3 at low ratio of PbO and SiO4, PbO3 and PbO4 at high ratio of PbO. The distribution of O-T-O bond angle and T-O bond length (T is Si or Pb) in SiO4, PbO4 and PbO3 basic structural units are slightly changed when PbO content increase. In intermediate range order, the topology structure of OTy linkages (y=2,3,4) is also investigated in detail.

Keywords: Microstructure, silicate materials, molecular dynamics, Short-range order, Intermediate range order

1. Introduction

Silicate minerals including quartz, feldspar, amphibole, pyroxene and mica are the most popular minerals on Earth. In there, the lead silicate glasses are one of the most important materials for diverse applications including optical elements like holey fibers, electronic equipment and radiation shield because they have the high index of refraction, the great resistance to destruction and the good absorption for X-rays [1-2].

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The research results showed that there was the connection of SiO₄ units forming continuous random tetrahedron network in three dimensions. [3]. In there, the connection between two Si atoms through an O atom is called bridging oxygen (BO) [4]. When another oxide is added to the silica, the network bonds between the Si and O atoms are broken, which results in the creation of new forms of oxygen including non-bridging oxygen (NBO) and free oxygen (FO). The ratio of NBO and FO is increased with increasing network modifier ion, while decreasing the BO number [5]. For PbSiO₄ glass, the results of these studies of the fraction BO, NBO, and FO are different in [6–7] with the amount small. The BO rate is 36.6%, the NBO is 60.0% and the FO is 3.4%, this fraction in [7] is 36%, 62.0% and 2.0%. However, the fraction of BO using X-ray is 42%, reported in [8]. Moreover, the change of this fraction also depends on the concentration of PbO content. The result of X-ray diffraction of Smets with his coworker [9] confirmed that there is an increase in the BO number (from 0.19 to 0.66) with the decrease of PbO content (70 to 30). In addition, when the PbO ratio is greater than 0.4, the silicon atoms are combined in metasilicate units consisting of a tetrahedron of SiO₄ and two atoms of NBO. At lower of PbO content, the part of the silicon atoms is incorporated in disilicate units: a SiO₂ tetrahedron with one NBO atom. This clearly shows that the PbO content has a significant effect on the Si-O- network-former and the degree of polymerization (DOP) of the network featured by the ratio of non-bridging oxygen (NBO). To more details about the property of the thermodynamic of lead silicates, the binding energy of BO and NBO was calculated by Wang and Zhang [10] using the same technique. The binding energy of both BO and NBO decrease corresponding to the PbO content increasing from 0 to 40%. With PbO content increasing above 40%, the binding energies of BO degrade gracefully, while the binding energies of the NBO decrease initially, then remain constant while the content of PbO increases.

A controversial issue resulted from the research of the structural function of lead in glass of lead silicate. In there, the role of lead in lead silicate glasses is the network-forming or network-modifying, there exists the PbO₃ trigonal pyramids or PbO₄ pyramids, the effect of the PbO ratio addition on the structure of glasses was investigated for lead silicates. This issue has been clarified in the works [10–12]. By using different spectroscopic techniques in [10–11] at low concentrations with PbO ratios less than 40%, there is similarity in lead silicate structure and glass structure of alkali-silicate where lead acts as a network modifier. That means the glass network of SiO₂ plays a major role. When the PbO content is large, the three-dimensional network formed by the SiO₄ tetrahedra is strongly destroyed, the PbO₄ molecular chains link to the SiO₄ tetrahedra to form the skeleton glass structure network. At high lead concentrations, when PbO is above 60 mol%, lead plays the role of a network former with polymeric chains of PbO₆ (n = 3, 4). Besides, PbO, when its rate is 40 to 60%, changes its role to become the network former presented in [12–14]. With an increase in the fraction PbO, the PbO₄ polyhedra appears either the pyramid edge-shared PbO₃ trigonal pyramids or the broad distribution of PbO₄ polyhedral with x = 3–5 [14–15]. The analysis above shows that lead oxide can act both as a network-former and a modifier. Distribution of Qⁿ (n is the number of BO) type for lead silicate systems with the change of PbO contents has been investigated by authors in works [11, 13, 16]. The results show that fraction Qⁿ decreases rapidly along the slope as increasing PbO content. The fraction of Qⁿ increase and decrease then, it gets the maximum value at 30% of PbO content. Meanwhile, the peaks of Q² and Q¹ are reached at 50% and 70% of PbO content, respectively. The peak positions reported in works [11, 13, 16] are similar but the height of peaks is discrepant.

Lead silicate systems have been investigated for a long time, however, their structure has not yet clarified at the atomic level. In this article, the study is performed on a silicate system with different PbO content. The microstructure was analyzed through radial distribution functions, bond angle distributions, and coordination number distribution. Moreover, we have used visualization techniques illustrated by the network structure.
2. Computational method

The xPbO (1-x)SiO₂ system consisting of about 5000 atoms has been investigated by molecular dynamics simulation (MD) under the periodic boundary conditions at a temperature of 3000K. The compositions change in the range from 0.05 to 0.75. The interaction of atoms in the system is performed via the interaction potentials of the Born-Mayer type successfully used in Refs. [17, 18] for Lead-silicate glasses. The formula of potentials is followed by Eq. (1)

\[ U_{ij} = \frac{q_i q_j}{r_{ij}} + A_{ij} \exp(-B_{ij} r_{ij}) \]  

with \( i, j = \text{Pb, Si and O} \). Where \( r_{ij} \) refers the distance between an ion of type \( i \) and an ion of type \( j \), \( q_i \) and \( q_j \) are effective charges, \( A_{ij} \) and \( B_{ij} \) are the parameters of potentials of the system. In this works, The Verlet algorithm is used to integrate the equations of motion with a time step of 1.0 fs. Firstly, all atoms are randomly placed in the simulation box to create the initial configuration of the system. In order to have a liquid at 6000K and at zero pressure, simultaneously to avoid the unphysically features of potential at very short distance, the initial configuration is heated up to 6000K and relaxed for over 5.10⁴ time-steps. After having obtained model cooled down to 3000K during 30 ps to reach equilibrium, the model denoted as model M₁ is run for a long time in the NPT ensemble. Following this process, the models by Mₙ (n=2,3,4,5,6,7) are created by changing contents of PbO. Then, these models are relaxed for over a long time to reach the equilibrium. To increase the statistics of the measured quantities consisting of the coordination number, partial radial distribution function, bond-angle distributions, bond-length distributions, etc. We have computed by conducting an average over 1000 configurations separated by 10 MD steps.

3. Results and discussions

3.1. Short-range order

Figure 1 describers the radial distribution function of the atomic pairs as the proportion of PbO component in the model changes. It can be seen that, in the range of 0.2 ≤ x ≤ 0.5, the pairs of Si-O, Pb-O and O-O atoms have positions of the first peaks respectively 1.62 Å, 2.32 Å and 2.64 Å, which slightly decrease when the ratio of PbO ≥ 0.66. These results are in line with the results previously studied by simulation and experiment [17-20]. For the Si-Si and Si-Pb atom pairs, their first peak position is almost unchanged as the ratio of PbO in the sample increases, with values of 3.22 Å and 3.56 Å, respectively. These values are also consistent with the results of Refs. 2, 3 and 5, while the height of the first peaks of the radial distribution functions of Si-Si, Pb-O, Si-O and Si-Pb pairs increases as the value of x increases, while that of the O-O and Pb-Pb pairs are the opposite. In which, the radial distribution functions of Si-O and Pb-O atom pairs characterize the short-range order of the system.

Figure 2a illustrates the coordination numbers function of the Si atom. It can be seen that when the PbO ratio is very small (x = 0.05), the majority of structural units are SiO₄ with more than 90%, and only a small percentage of SiO₃ structural units with about 8.6%. On the other hand, the SiO₄ structural unit ratio increases slightly as the proportion of PbO content in the sample rise, whereas the ratio of SiO₃ structural unit decreases and reaches approximately zero when the value x > 0.66.

Figure 2b shows the proportional change of PbOₓ structure units as the ratio of PbO component changes. As we can see with x = 0.05, the model is mostly PbO₂ and PbO₃ structural units with the same proportion about 40%, and followed by a very small percentage of PbO₄ structural units. Note, when the PbO component increases, the portion of PbO₂ structure units sharply decreases to about 5.8%, while that of the PbO₃ structure unit increases sharply to 54.4% at the value of x = 0.25 and then decreases to 45.3% at x = 0.75. For the PbO₄ structural unit, its proportion increased significantly from 11.5% to 41% when the PbO component ratio increased from 0.05 to 0.75. Thus, when the ratio of PbO components is large, the models are mainly SiO₄, PbO₃ and PbO₄ structural units.
Figure 1. The radial distribution function of different atom pairs in liquid \( x\text{PbO} (1-x)\text{SiO}_2 \) system.

Figure 2. Distribution of coordination numbers of \( \text{SiO}_y \) units \( (y = 4, 5) \) and \( \text{PbO}_y \) units \( (y = 1 \div 5) \) in liquid \( x\text{PbO}(1-x)\text{SiO}_2 \) system as a function of content.

The figure 3 presents the O-T-O bond-angle distribution in TO\(_x\) structure units (T is Pb or Si). It display that the distribution of bond angle of \( \text{SiO}_x \) structural units has the first peak height increases, and its position increases slightly as the ratio of PbO component increases. From the figure 3, the O-Si-O bond angle of the \( \text{SiO}_4 \) structural unit reaches a peak at angle 105\(^0\) and this value is almost constant with different ratios of PbO component. In the case of \( \text{SiO}_5 \) structural units, the first peak position of the O-Si-O bond angle distribution is about 85\(^0\), and this value increases very little when the ratio of the PbO component increases.

In the case of PbO\(_x\) structural units, the first peak height of the angular distribution increases as the ratio of PbO increases. It is obvious that the distribution of the O-Pb-O angle of PbO\(_3\) structural units is not clear when the ratio of PbO in the sample \( x < 0.33 \). When \( x \geq 0.33 \), however, the O-Pb-O angle distribution has the first peak at position 90\(^0\), which is almost unchanged as the PbO component ratio
increases, and the height of the peak increases slightly. For PbO$_4$ structural units, the bond angle distribution appears only clear a peak at $85^\circ$ when the value $x > 0.33$. These results are comparable to the results [17-20].

![Figure 3](image1)

**Figure 3.** Bond angle distributions of SiO$_y$ units ($y = 4, 5$) and PbO$_x$ units ($x = 3, 4$) in liquid $x$PbO($1-x$)SiO$_2$ system.

![Figure 4](image2)

**Figure 4.** Distance distribution of SiO$_y$ units ($y = 4, 5$) and PbO$_x$ units ($y = 3,4$) in liquid $x$PbO($1-x$)SiO$_2$ system as a function of composition.

The distance distribution of TO$_x$ structural units ($T =$ Pb or Si) with different component ratios of PbO is described in detail in Figure 4. In the case of $x = 0.05$, the Si-O distance distribution of SiO$_4$ and SiO$_5$ structural units have the first peak positions respectively at 1.64 Å and 1.72 Å, these values decrease to 1.62 Å and 1.70 Å when the PbO ratio is 0.75. Thus, when the proportion of PbO component increases, the distance distribution of the atoms decreases, while the height of the peak decreases insignificantly. It is obvious that the Pb-O bond distance distributions in PbO$_3$ and PbO$_4$...
structural units have peaks located at around 2.24 Å for PbO$_3$ unit and at around 2.32 Å for PbO$_4$ unit, these position decrease slightly as the proportion of PbO component increases. These results are consistent with those previously studied [18].

3.2 Intermediate-range order

The intermediate range order (IRO) have been investigate in order to understand the link characteristics between the TO$_x$ (T is Pb or Si, x = 2÷4) in the liquid silicate systems.

**Figure 5.** Visualization of the linkages between the TO$_x$ basic structural units: a) SiO$_x$ (in blue) and PbO$_y$ (in black) connect with each other, b) the OT$_y$ linkage (O in red, Si in blue and Pb in black)

Figure 5a presents the OT$_y$ linkages between the basic structural units of TO$_x$ (x=2,3,4) including SiO$_x$ units and PbO$_x$ units in xPbO(1-x)SiO$_2$ systems. It revealed that SiO$_x$ and PbO$_x$ units trend to connect with another in three cases: corner-sharing (one common O atom), edge-sharing (two common O atom) and face-sharing (three common O atom). It also evidence that the IRO is not heterogeneous.

**Figure 6.** Bond angle and bond length distributions of OT$_y$ units (y =2,3,4) in liquid xPbO(1-x)SiO$_2$ system as a function of composition.

Figure 6 displays the distribution of T-O-T bond angle and bond length O-T in OT$_y$ linkages in liquid xPbO(1-x)SiO$_2$ system at different composition. In OT$_y$ linkages, there is the little reduction of T-O-T bond angle one the PbO content increases. In OT$_2$ linkages, the peak of T-O-T bond angle declines from 155° at x = 0.05 down to 145° at x=0.75 and the fraction of T-O-T also decreases from
14.8% at x=0.05 down to 10.45% at x=0.75. The position of the peak of the distribution of O-T bond length in OT₂ linkages is almost unchanged with the change of composition but its fraction decreases significantly (from 12.60% at x=0.05 down to 8.00% at x=0.75). It is well known that the Coulomb repulsion force between cations (Si or Pb) trend to increase when the T-O-T link angle decreases. This will bring about the increase of the O-T bond length. Because, in this case, the T-O-T bond angle in OT₂ linkages reduces a little bit, the O-T bond length is just about unaltered with composition.

From Figure 6, the peak of T-O-T bond angle of OT₃ and OT₄ linkages is slightly relying on PbO content. The T-O-T bond angle distribution of OT₃ and OT₄ have the peaks at around 110° and 90°, respectively. Similarly, the fraction of O-T bond length of OT₃ and OT₄ linkages is just about unaltered under composition. The O-T bond length distribution of OT₃ linkages has the first peak at around 1.7Å (x=0.05) and 1.6 Å (x ≥ 0.02) and the second peak at around 2.24 Å. The O-T bond length distribution of OT₄ linkages has the first peak at around 1.64 Å and the second peak at around 2.26 Å. It is evident that the topology structure of OT₃ and OT₄ linkages is slightly deformed with increasing PbO content. The OT₃ is presented visually by Figure 5b where one O atom connects with three T atoms (two Pb and one O).

**Figure 7.** The distributions of bond angle and length of OSi₂ and OPb₂ linkages in liquid xPbO(1-x)SiO₂ system as a function of composition.

Figure 7 display the distribution of T-O-T bond angle and T-O bond length of OSi₂ and OPb₂ linkages at different PbO content. In general, the OSi₂ and OPb₂ linkages are almost unchanged under composition. In OSi₂ linkages, the Si-O-Si bond angle has the position of the peak around 155° (from x=0.05 to 0.75) and the O-Si bond length is 1.64 Å (at from x=0.05 to 0.75). In the case of OPb₂ linkages, the peak of the Pb-O-Pb bond angle is around 90° (at from x=0.05 to 0.75) and the O-Pb bond length is around 2.32 Å (at from x=0.05 to 0.75). These results show that the topology structure of OSi₂ and OPb₂ linkages is slightly dependent on composition.

4. Conclusion

The Lead-silicate system consisting of the structure parameters, good accordant with the experimental data, is constructed by molecular dynamics simulation. The structure of system includes the basic structural units of SiOₓ (x=4,5) and PbOᵧ (y=2,3,4). At low ratio of PbO, the basic structural units of SiOₓ, PbO₂ and PbO₃ are dominant. At high ratio of PbO, most of the basic structural units are SiOₓ, PbO₂ and PbO₃. Under the influence of the ratio of PbO, the structural unit of SiOₓ changed marginally as ratio of PbO increases, while the the structural unit of SiO₃ is almost unchaned with ratio of PbO. The structural units of PbO₂ and PbO₃ decrease slightly in the bond length in the whole considered content range of PbO. Our simulations also show that the shape of OT₂ linkage is moderately distorted, while the aspect of OT₃ and OT₄ linkages are just about stabilized as the ratio of...
PbO increases. The size of $OT_3^-$ linkage is considerably fallen as the ratio of PbO rises from $x=0.05$ to $x=0.2$, and the one is almost unchanged in the 0.2-0.75 ratio range, the $OT_2^-$ and $OT_4^-$ linkages is stayed in the size as the ratio of PbO increase. The shape and size of $OSi_2^-$ and $OPb_2^-$ linkage are practically unchanged in the whole considered PbO content range.

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