# LOCAL STRUCTURE AND DYNAMICS PROPERTY OF LIQUID Li<sub>2</sub>O.xSiO<sub>2</sub> CÂU TRÚC ĐỊA PHƯƠNG VÀ ĐẶC TRƯNG ĐỘNG LỰC CỦA HỆ Li<sub>2</sub>O.xSiO<sub>2</sub> Ở TRẠNG THÁI LỎNG

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## ABSTRACT

The  $Li_2O$ -SiO<sub>2</sub> system composing of 3000 atoms has been constructed by molecular dynamics simulation. Three models with different density and concentration are prepared and analyzed in terms of radial distribution function, coordination number, distance and bond angle. The simulation reveals that despite the significant difference in density and chemical composition, the basic structural units of considered models including SiO<sub>4</sub>,  $LiO_4$ ,  $LiO_5$ , and  $LiO_6$  are identical. The network structure is combined two separated phases silicon oxide and complex lithium oxide. When increasing  $Li_2O$  concentration, Lithium atoms tend to diffuse into free volume which located in tetrahedral SiO<sub>4</sub>. The diffusion coefficient of Lithium increases nonlinearly with increasing concentration at the temperature of 3000 K.

#### TÓM TẮT

Hệ Li<sub>2</sub>O-SiO<sub>2</sub> ôxít gồm 3000 nguyên tử được xây dựng bằng phương pháp mô phỏng động lực học phân tử. Ba mô hình với mật độ và nồng độ khác nhau được xây dựng và phân tích qua hàm phân bố xuyên tâm, phân bố số phối trí, phân bố khoảng cách và phân bố góc. Kết quả mô phỏng chỉ ra rằng mặc dù với mật độ và nồng độ khác nhau nhưng các đơn vị cấu trúc của các mô hình bao gồm SiO<sub>4</sub>, LiO<sub>5</sub> và LiO<sub>6</sub> là không thay đổi. Cấu trúc mạng là sự tổ hợp của hai pha: ôxit silic và ôxit liti. Khi tăng nồng độ Li<sub>2</sub>O, các nguyên tử Li có xu hướng khuếch tán vào vùng thể tích tự do trong tứ diện SiO<sub>4</sub>. Hệ số khuếch tán của Li tăng không tuyến tính với nồng độ khảo sát ở nhiệt độ 3000K

#### **I. INTRODUCTION**

The ion dynamics of Li in liquid lithium silicate has been devoted interesting research [1,2] and to be continued studies from number of reports in glass state [2]. The Li diffusion depends on some factors as the thickness of amorphous thin film, concentration Li<sub>2</sub>O, temperature, pressure, and local structural order. Shin-ichi Furusawa et al. studied the ionic conductivity of amorphous Li<sub>2</sub>O-SiO<sub>2</sub> thin film at range temperatures 500-700 K and showed that the ionic conductivity in thin film is higher than that in polycrystalline about 1 to 2 times. The thickness dependence of the ionic conductivity shows a local maximum at around the thickness 0.15 µm [3]. Another study involves influence concentration Li<sub>2</sub>O on structural and dynamics characteristics in melt  $(Li_2O)_x$ . $(SiO_2)_{1-x}$  system were analyzed [1]. The diffusion coefficient of Li increases with increasing Li concentration in system. The diffusion coefficient of Li is larger that of Oxy. Due to the high binding energy in SiO<sub>4</sub> tetrahedron (rigid network), with increasing

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Li<sub>2</sub>O concentration, the network becomes softer and result leads to diffusion coefficient increase. As an analog to lithium silicate glasses (LiAlSi), sodium silicate glasses (NaAlSi) show enhanced Na diffusion as a function of alumina concentration [2]. The mechanism of Li<sup>+</sup> ion motion in LiAlSi is substantially altered by the disorder present in the glass. The disorder in network structure strongly reduces correlation effects on ionic motion in the glass and results in small activation energy for ionic diffusion [4]. A number of other experimental studies of Li diffusion in glasses have been presented and received similar results for activation energy of Li in oxide glasses [2]. Recently, Andreas Heuer et al. showed complex ion dynamics in oxide glasses  $Li_2O.SiO_2$ by computer simulation method [5]. The complex of the ion dynamics is due to the simultaneous action of the time-dependent Coulomb interaction with the other mobile ions and time dependent interaction with the spatially disorder and basically immobile network. At low temperatures the dynamics can be separated

into local vibration dynamics and hopping events between adjacent lithium sites. Fleurov and Trakhtenberg also studied theoretical by combining the phonon-tunnel model and structural defect concept to explain the kinetic properties of glasses at low and high temperatures [6]. The local structure in lithium silicate (Li<sub>2</sub>O.SiO<sub>2</sub>), one of factors effect to Li+ ion dynamics characteristics, has not been investigated in detail yet. In this paper, three models with different chemical concentrations are prepared and analyzed in terms of radial distribution function, coordination number, distance and angle distribution. The coefficient of individual atoms is also calculated and analyzed in here.

### **II. COMPUTATIONAL PROCEDURE**

Molecular dynamic (MD) simulation has been carried out for the system  $Li_2O.xSiO_2$ (x=3.1, 4.3, and 6.0) consisting of 3000 atoms at temperature 3000 K. The BKS potential is used in which the potential parameters have been directly taken from ref. [8]. The initial configuration was generated by random placing all atoms in the simulation cell under the constraint that the distance between any two pairs of atoms is greater than a specified value. The densities of this initial configuration are 2.287, 2.268, and 2.254 g/cm<sup>3</sup>, which were determined by experiment [7]. Then, different samples were relaxed at 3000 K and hold at fixed temperature and at zero pressure for over 150 000 steps without any disturbance. After that, the positional characteristics were determined through partial radial distribution function (PRDFs). То calculate the coordination number we used the cut-off radius, which were taken as the positions of minimum after the first peak in PRDF. In order to improve statistics. all the positional characteristics was calculated by performing average over last 1000 configurations separated by 10 MD steps. For diffusion analysis, three liquid models would be signification relaxation through 30000 steps. The diffusion coefficient of the individual species was determined via the mean square displacement.

### **III. RESULTS AND DISCUSSION**

The fig. 1 presents the partial correlation distribution function  $g_{ij}(r)$  for models  $Li_2O.xSiO_2$  with x=3.1, 4.3, and 6.0. It can be that the function gij(r) for all pairs are almost unchanged for three models. The nearest neighbor distance for pair Si-O and Li-O derived from gij(r) are 1.6 and 1.96 Å, respectively. It is agreed in good with experiment data in ref. [9, 10] (Si-O is 1.61 Å, Li-O is 1.98 Å), indicating the stable in network under variation of chemical composition x.



Fig.1 The partial correlation function of Li<sub>2</sub>O-xSiO<sub>2</sub> system at temperature 3000K



Fig.2 The coordination number distribution of Li<sub>2</sub>O-xSiO<sub>2</sub> system at temperature 3000K



Fig.3 The distance distribution in SiO<sub>4</sub>,  $LiO_4$ ,  $LiO_5$ , and  $LiO_6$  units of  $Li_2O$ - $xSiO_2$  system at temperature 3000K

In comparison with pure SiO<sub>2</sub> network and Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub> liquid, the distance of Si-O pair is the same (about  $1.6\pm0.2$ Å). The network structure of SiO<sub>2</sub> in Li<sub>2</sub>O.SiO<sub>2</sub> is tetrahedral units SiO<sub>4</sub> (about 95% for three concentration of x) connected together by oxygen-bridge and Si-O bond is very strong. The lithium atoms are loosely held by single bond with oxygen atoms and located in cavities in the SiO<sub>2</sub> network. The bond strength of the Li-O bond is about one third that of the Si-O bond [8]. The distribution of these lithium atoms is analyzed in detail by position of nearest neighbors. To calculate coordination number distribution, we determine the cut-off distance by the first minimum of

 $g_{ii}(r)$ . Its distribution is displayed in the fig. 2. We easily realize that the fraction of coordination number distribution of pairs Si-O, Li-O, and O-O is slightly changed with chemical component x. The coordination number of Li atoms is wide in the range 3-7 oxygen atoms and dominated at fivecoordinated about 35.5%, addition sixcoordinated is 26%, and four-coordinated is 20%. The three- and seven-coordinated are only several percents. The height of peak only creases slightly about 1.4% when creasing Li<sub>2</sub>O concentration from 14.35% mol to 24.50% mol. Thus, basic network of system is composed of units  $SiO_4$ ,  $LiO_4$ ,  $LiO_5$ , and  $LiO_6$ .



Fig. 4 The angle distribution in SiO<sub>4</sub>,  $LiO_5$ , and  $LiO_6$  units of  $Li_2O$ -xSiO<sub>2</sub> system at temperature 3000K

However, other coordinated distributions are strongly changed with x. The distribution curves of Si-Li and Li-Li clearly shows a shift to larger but the heights of peak decrease with increasing Li<sub>2</sub>O concentration. The coordinated distribution of Li-Si is shift to smaller both value and fraction. Thus, the distribution of Li around cations (Si, Li) is changed with chemical composition x. It is explained that when the concentration of Li<sub>2</sub>O is increasing, lithium ions locate inside free volume which existed in loose silica lead to increase coordination number distribution of Si-Li and Li-O but at the same time it decreases the fraction of Li-Si pair distribution. The showed coordination number distribution Z<sub>O-Li</sub> demonstrates a dependence on increasing concentration of Li<sub>2</sub>O. That is decreased fraction of  $Z_{O-Li}=0$  and increased fraction of  $Z_{O-Li}=0$ Li=2, 3, 4 Li atom (fig.2). Furthermore, information of local structure of lithium silicate is provided by investigating O-T-O bond-angle and T-O bond-length distributions (with T is Si or Li). Fig. 3 and 4 show the distribution for angle and distance in SiO<sub>4</sub>, LiO<sub>5</sub>, and  $LiO_6$  units. We can see that the bond-length and bond-angle distributions are almost identical for all considered models. The angle distribution O-Si-O in SiO<sub>4</sub> and O-Li-O in LiO<sub>4</sub> are dominated at  $105^{\circ}$ , indicating the slightly distorted tetrahedron  $TO_4$  and the tetrahedral

network structure in the liquid lithium silicate. The angle distribution in LiO<sub>5</sub> is separated into two peaks, a peak at  $65^{\circ}$  and one at  $95^{\circ}$ . The angle distribution in LiO<sub>6</sub> has a peak at  $60^{\circ}$ , indicating Li atom locates on center and oxygen atoms at sites of a hexagon. It indicates topology of LiOy (y = 4, 5, 6) is multiform and fairly complex. It is admitted as a phase including two main separated networks SiO<sub>4</sub> and LiOy. The first network is similar to one silica liquid and the second network is complex network LiOy liquid. The dynamics property of the individual species in the system is calculated via mean square displacement. The diffusion coefficient has been determined and listed in the table 1. We see that the diffusion coefficient of silicon and oxygen are small and slightly increased with increasing Li<sub>2</sub>O concentration. Thus, the increasing concentration Li<sub>2</sub>O in system makes SiO<sub>2</sub> network to be "softer". The Li atoms are very mobile in network lithium silicate by weak bonds with oxygen bridges [9].

Table 1. The diffusion coefficient of atoms in Li<sub>2</sub>O.xSiO<sub>2</sub> system

x	$D_{Si}$ (10 <sup>-5</sup> cm <sup>2</sup> .s <sup>-1</sup> )	$\frac{D_{O}}{(10^{-5} cm^{2}.s^{-1})}$	$D_{Li}$ (10 <sup>-5</sup> cm <sup>2</sup> .s <sup>-1</sup> )
6.0	1.203	1.449	7.263
4.3	1.484	1.540	7.431
3.1	1.770	2.002	7.351



Fig.5 The  $Li_2O$ -4.3Si $O_2$  model at temperature 3000 K with size of cubic box 20 x 20 (Å)

Diffusion of the lithium ions occurs as Li bonds are broken and lithium ions hop between atoms in network. The coefficient of Li is about 5 times larger than that of Si and O. It is slightly changed and increased nonlinearly with investigated concentrations. This result is obtained and explained in detail in ref.[1] with temperature above 2500 K. We saw that the lithium ion diffusion coefficient had Arrheniustype temperature dependence [11]. The diffusion coefficient of all atoms in oxide systems is small and about  $\sim 10^{-5}$  cm<sup>2</sup>.s<sup>-1</sup>, thus error between this work and ref. [11] can be accepted and explained by difference from model size.

## **IV. CONCLUSIONS**

In this study we have presented the molecular dynamics simulation of Li<sub>2</sub>O.xSiO<sub>2</sub> liquid with x=3.1, 4.3, and 6.0 and at 3000 K. The simulation reveals that the structure of these liquids consist two separate networks  $SiO_4$  and LiOy (with y = 4, 5, 6). Those basic units are identical for three models, but their proportions depend on the chemical composition x. The concentration increase of Li2O changes the coordination number distribution of lithium around Silicon and Lithium. Lithium atoms are trend to diffuse into free volume which is located in tetrahedral SiO<sub>4</sub>. The silica network in these models is similar that in pure silica. The coefficient of Li+ ion is 5 times larger than that of Si and O and nonlinearly increased with increasing investigated concentration at temperature 3000 K.

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