



Structural transformations in sodium silicate liquids under pressure: A molecular dynamics study



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ABSTRACT

We present the results of force-field molecular dynamics simulations of the static and dynamic properties of sodium silicate liquids. We studied the relationship between the structure and properties with varying SiO₂ content and pressure. We found that the silicate liquids have at least three types of characteristic structures before the coordination number of Si changes with increasing pressure; these structures are, ionic, network, and coesitic structured liquids. In the ionic liquid like structure, simple diffusion of large silicate anions is dominant in the liquid and their motion is impeded by compression. In contrast, in the network liquid, a small portion of the network of corner-shared SiO₄ tetrahedra diffuses via bond exchange and flow globally. Bond exchange is activated by pressure in the entangled network liquid because of distortion of the corner-shared SiO₄ tetrahedra network and the tetrahedra themselves. The SiO₂ rich liquids soften as a result from of these distortions. The derivative of bulk moduli of the sodium silicate liquids increases significantly at a certain pressure because of changes in densification mechanism. The changes in those densification mechanisms are coherent with the changes in pressure dependence of transport coefficient.

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1. Introduction

Silicate liquids are important materials in geosciences and technology. It is very challenging to understand the relationship between the properties and microscopic structures from a physical perspective. The physical properties of silicate liquids show peculiar behaviors under pressure. The pressure dependence of the shear viscosities of silicate liquids have been investigated since the 1970s. The viscosities of liquids with low basicity decrease with increasing pressure [1,2,3]. Moreover, the self-diffusivity of O and Si atoms in the liquids increases with increasing pressure [4,5]. These characteristics result in softening of silicate liquids under pressure.

The microscopic structure of silicate liquids have been investigated using various spectroscopic methods. According to X-ray diffraction studies, the Si–O distance remains constant up to pressures of several giga-pascals whereas the Si–Si distance decreases [6,7]. These results indicate that the compression of silicate liquids is caused by shrinking of the –Si–O– network as the Si–O–Si angle decreases. NMR studies regarding glass quenched under pressure revealed that pressure-

induced polymerization occurs and higher-coordinated Si species appear above 10 GPa [8,9]. This type of structural change was also revealed by Raman scattering studies [10,11].

Several mechanisms have been proposed by various researchers in order to explain the softening of silicate melts at high pressure. One hypothesis is that the Si–O bond is weakened by bending of the Si–O–Si angle from the ideal angle and distortion of the SiO₄ network during compression [12,13]. An alternate hypothesis is that diffusion of oxygen is likely to occur via highly coordinated Si species, which gradually appear with increasing pressure [5,8,9]. However, these hypotheses have not been verified by spectroscopic methods because these methods can only determine the inter-atomic lengths of near neighbor atoms and amounts of coordination species.

To obtain more precise information on the structures of silicate liquids under high pressure, knowledge of the network conformation and inter-atomic distances is required. In this study, the structure and properties of Na₂O·nSiO₂ liquids under pressure are investigated using force-field (classical) molecular dynamics (MD) simulations in order to elucidate the relationship between the structures and properties of silicate liquids. The MD simulation is a suitable method for investigating liquids because it enables direct access to the atomic coordinates and velocities at the desired ensembles which cannot be obtained in real experiments. The MD simulation studies using density functional theory [14,15] provide important structural and dynamical information of silicate liquids [16,17]. However, the simulation size

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and time are limited because of calculation cost. Force-field MD simulations can handle large simulations which allows us to obtain large scaled dynamic/static properties and better statistical averaged data. They also aid in avoiding the finite-size effect of simulations in acidic silicate liquids [18]. Wang et al. [19] regarding the high-pressure properties of silicate liquids under pressure using MD simulations mentioned that the softening of silicate liquids is caused by an increase in the number of oxygen tri-clusters. However, the simulation size and time in that study was too limited to obtain good statistically averaged data. In addition, they simulated an aluminous system, which is a difficult system to use to elucidate the nature of silicate liquids under pressure because the coordination number of aluminum changes at a lower pressure than that of silicon. Simple system was also investigated. Horbach et al. [20] gives the microscopic insight of sodium di-silicate and tri-silicate at pressure via the force-field MD simulations with sufficient number of atoms. Using the time-dependent bond probability and the self-part of the van Hove function, they concluded that the diffusion of oxygen and sodium take place by activated hopping events. However, they did not discuss about the pressure dependence. Bauchy et al. [21] regarding the pressure dependence of dynamic and static properties of sodium di-silicate liquid via the force field concluded that the softening of silicate liquids cannot be explained by considering only coordination number change of Si. We provide systematic simulation results of the effects of pressure and composition on simple binary liquids in properly sized system and with sufficient simulation time.

2. Computational method

MD simulations of $\text{Na}_2\text{O} \cdot n\text{SiO}_2$ liquids ($n = 1, 2, 3, \text{ and } 4$) were performed using MXDORTO code [17]. Hereafter we denote $\text{Na}_2\text{O} \cdot \text{SiO}_2$, $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$, $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$, and $\text{Na}_2\text{O} \cdot 4\text{SiO}_2$ liquids as NS1, NS2, NS3, and NS4 liquids, respectively. The simulation conditions are as follows: Systems of approximately 8000 particles at a pressure range of 0.1 MPa to 10 GPa (every 1 GPa) and 1873 K using the potential model which provides semi-quantitative reproduction of the structures of various silicate crystals [22] and qualitative reproduction of the pressure dependence of transport properties obtained by experiments [1,4] (Fig. 1). Note that although there are difference of a half order of magnitude between calculated and experimental dynamic properties, the pressure dependence of dynamic properties are reproduced. We imposed periodic boundary conditions in all directions. Ewald summations were applied to evaluate the long-range Coulombic interactions. The pressure and temperature were kept constant at a given value via scaling procedures. All the atoms were moved by applying the Verlet algorithm at a time interval of 0.5 fs for relaxation runs and 0.25, 0.50, 0.75, and

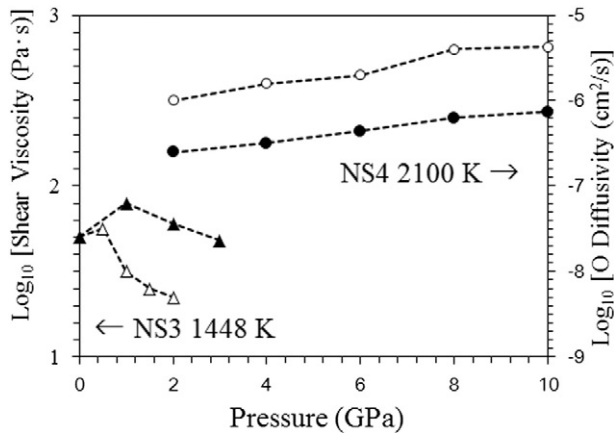


Fig. 1. (Left-axis) A comparison of the calculated viscosity of NS3 liquid at 1448 K (filled triangles) with the experimental data (open triangles) by Kushiro [1]. (Right-axis) A comparison of the calculated oxygen diffusivity of NS4 liquid at 2100 K (filled circle) with the experimental data (open circle) by Rubie et al. [4].

1.00 fs for production runs for n values of 1, 2, 3 and 4, respectively. Starting with a randomly generated structure and randomly generated velocities of the atoms, we first ran calculations through 2.0–8.0 ns (i.e., 4–16 million steps) as relaxation at 0.1 MPa with NPT ensembles. Then, the static and dynamic properties were obtained from 4,000,000 step production runs (1.0–4.0 ns) under a micro-canonical ensemble. Starting from the relaxed structure, relaxation and production runs at 1 GPa higher pressures than the prior runs were performed up to 10 GPa.

The function of the inter-atomic potential model used in this work is as follows [22]:

$$U_{ij} = \frac{1}{4\pi\epsilon_0} \frac{Z_i Z_j e^2}{r_{ij}} + f_0(b_i + b_j) \exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) + \frac{c_i c_j}{r_{ij}^6} + D_{1ij} \exp(-\beta_{1ij} r_{ij}) + D_{2ij} \exp(-\beta_{2ij} r_{ij}) \quad (1)$$

This model explicitly includes the Coulomb potential as the first term, short-range repulsion as the second term, van der Waals force as the third term, and the radial part of the covalent effect as the fourth and fifth terms of Eq. (1). The fourth and fifth terms are only used for interaction between Si–O bonds. In addition to the two-body term, the following three body term for Si–O–Si angle was also used.

$$U_{ijk} = -f [\cos\{2(\theta_{kij} - \theta_0)\} - 1] \sqrt{k_{ij} k_{ik}} \quad (2)$$

$$k_{ij} = \frac{1}{\exp[g_r(r_{ij} - r_m)] - 1} \quad (3)$$

The parameters were taken from Noritake et al. [22].

3. Result

Fig. 2 shows the pressure dependence of the self-diffusion coefficients. The diffusion coefficients of the Na atoms decrease with increasing pressure in every composition. The diffusion coefficients of the network-forming elements show complex behavior, as reported in past studies involving measurements of the shear viscosity and direct measurements of the diffusion coefficients. The diffusion coefficients simply decrease with increasing pressure in the NS1 liquid. However, the inclination of the plot becomes shallower with increasing pressure. The diffusion coefficients of the network-forming elements in the NS2 liquid show two types of pressure dependence: The diffusion coefficients decrease with increasing pressure up to 3 GPa, and then increase with increasing pressure above 3 GPa. Also, the diffusion coefficients have positive pressure dependence in acidic liquids. The decrease around 10 GPa is similar to the results reported by Diefenbacher et al. [23]. The Si–O bond exchange rate, R_{exc} , represents the number of bond exchange events per unit time. Fig. 3 shows the pressure dependence of R_{exc} . The pressure dependence of R_{exc} is similar to that of the diffusion coefficients of the network-forming elements. There are two types of power laws between the self-diffusion coefficients of the network-forming elements and exchange rate of Si–O bonding. Fig. 4 shows the log-log plots of the self-diffusivity of oxygen versus R_{exc} . The relationship between R_{exc} and the self-diffusivity of the network-forming elements, D_{nwf} , of basic liquids at lower pressures is as follows:

$$D_{nwf} = a R_{exc}^n \quad (4)$$

where a is constant and n is 1–2. Meanwhile, the n value of the relationship for acidic liquids at higher pressures is 1/5–1/3.

The shear viscosity, η , can be obtained from an auto-correlation function of off-diagonal stress via the Kubo–Green equation [24,25], as follows:

$$\eta_{xy} = \frac{V}{k_B T} \int_0^\infty \langle \sigma_{xy}(t) \cdot \sigma_{xy}(0) \rangle dt \quad (5)$$

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