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Analysis for characterizing the structure and dynamics in sodium di-silicate liquid

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ABSTRACT

The analysis on dynamics and structure is carried out for sodium di-silicate melt. The simulation shows two moving types: the correlation motion for oxygen, silicon and free motion for sodium. The dynamics heterogeneity (DH) is found for oxygen and silicon. We reveal that the correlation motion type is responsible for DH and positive pressure dependence of diffusivity. The structural heterogeneity of the melt was analyzed by void-simplex, cation-simplex and oxygen-simplex. The densification of the melt is realized by decrease in the radius and change in the number of void-simplex. We show that a number of large interstitial site for oxygen and cation present in the liquid. The large site for oxygen plays a role as the cage capturing the oxygen atom for long time. Furthermore, we found a number of negative-charged and positive-charged clusters which evidence the heterogeneity in chemical composition and local environment. The large positive-charged cluster is found to be a diffusion pathway for sodium.

1. Introduction

Understanding the relationship between structural and dynamics properties of silicate liquid is important for Earth and Material Sciences. The silicate liquid has certain peculiar properties. Namely, silica-rich liquid has negative pressure dependence on shear viscosity although silica-poor liquid has positive pressure dependence [1–4]. The mechanism of negative pressure dependence is thought to be increase in the number of high-coordinated Si [5–6] or decrease in the Si-O-Si angle [7–9]. Further, silicate liquid exhibits DH and dynamical slowdown near the glass transition point [10–14]. The structural heterogeneity of the melt seems to be related to the DH observed.

The molecular dynamics (MD) simulation is appropriate to study the phenomena mentioned above, because it can provide the trajectory of each atom. There are many successful studies to clarify the mechanism of negative pressure dependence of silicate liquid using MD simulation [15–18]. The numerical technique used to study DH is the visualization and cluster analysis. The DH is also clarified on basis of multi-correlation function [19–26]. Recently, many simulations are focused on the organization of TO_x and O^n unit for the 3D network of silicate liquid [27–31]. Here $x = 3, 4, \ldots$; T is the cation (Si, Al, Mg…); $n = 0, 1, 2, \ldots$ is the number of cation that are linked to the given oxygen. However, as far as we know, the structural heterogeneity still remains elusive. This needs more studies to explore both static structure and dynamics.

Sodium silicate is one of simple pseudo-binary silicate consisting of network forming elements (Si, O) and network modifier (Na). More detail, there is a network consisting of corner shared SiO_4 tetrahedron and breaking cation [32]. The pseudo-binary system can be characterized by the basicity, R_2O mol%/SiO_2 mol%. Kushiro [1]) and Scarfe et al. [2] report that high basicity-liquids (>33%) have positive pressure dependence on viscosity at lower pressure and negative pressure dependence at higher pressure, whereas low basicity-liquids show only a negative pressure dependence. MD simulation [33–34] shows that fast sodium dynamics in NS_2 and NS_3 liquid are caused by channels which are reflected by a prepeak around 0.95 $Å^{-1}$ in the static structure factor. Moreover, in the NS_2 a certain number of anomalies appear when the system is compressed to higher density: the diffusivity maxima/minimum is found for network-forming ion (Si, O) which bear some striking similarities with well-known case of water. However, the structural heterogeneity, diffusion mechanism and DH for sodium silicate are still poorly understood yet. Hence, in this study we conduct the analysis on structure and dynamics for sodium di-silicate liquid. In addition we provide the mechanism of positive pressure dependence of diffusivity.

2. Computational method

MD simulation of sodium di-silicate liquid is performed using the MXDORTO code [35]. We use the well relaxed model constructed by Noritake and Kawamura [37]) and composed of 1776 Na, 1776 Si, and 4440 O at 1873 K. The simulation is conducted at two different pressure conditions (0.1 MPa and 8 GPa). The pressure and temperature are maintained constant at a given value using scaling procedure. All

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atoms are moved by applying Verlet algorithm with a time step of 1.0 fs. We applied the potential model consisted of pair and three-body term. The three-body term is proposed by Noritake et al. [36]. The potential model provides semi-quantitative reproduction of structure of various silicate crystals and qualitative reproduction of pressure dependence of transport properties of silicate liquid obtained from experiments.

We have calculated the linkage, simplex and cluster. Two atoms have a linkage, if their distance is less than a defined value r_{lk}. Because the number of oxygen, silicon and sodium in the model is different, hence we use two linkage distance r_{lk} which is equal to 3.66 and 4.65 Å for oxygen and cation, respectively. A cluster is defined as a set of atom where each atom connects to other one through a path consisting of linkages. Fig. 1 a1, a2, a3 represents the cluster and linkage for a set of atom. Here the number of atom in the set is equal to 6. One can see that the cluster with 9 linkages occupies the volume smaller than one with 6 linkages, although both clusters have the same number of atom. Moreover, the set having 3 clusters comprises only 4 linkages. This picture shows that the number of linkage and mean size of cluster can be used to characterizing the clustering of atom from specified set. In present work we calculate the average number of linkage per atom and mean size of cluster. Here the size of cluster is defined as a number of atom in the cluster.

We consider separately three subsets of oxygen, sodium and silicon. The mobile oxygens are taken from 10% of total number of oxygen which have mean square displacement $<r_t^2>$ larger than one of remaining oxygen atoms. The cluster analysis is performed as follows. Firstly, we find the subset of mobile atoms from their positions in starting configuration and configuration at given time t. Then we find cluster and linkage in the starting configuration. Finally we determine the mean size of cluster $<Z> = N_{at}/N_{cl}$ and average number of linkage $<S> = S/N_{at}$; where $N_{at} = 444$, 178 and 178 for oxygen, sodium and silicon subset, respectively; N_{cl} is the number of cluster; S is the total number of linkage; N_{cl} and S are determined from the starting configuration. We also perform the similar calculation for immobile atoms which have $<r_t^2>$ smaller than one of remaining atoms. To detect the clustering we compare the calculation result for the subset of mobile atom (or immobile atom) with a subset of atom which is randomly taken from the system. For convenience we denote the subset of

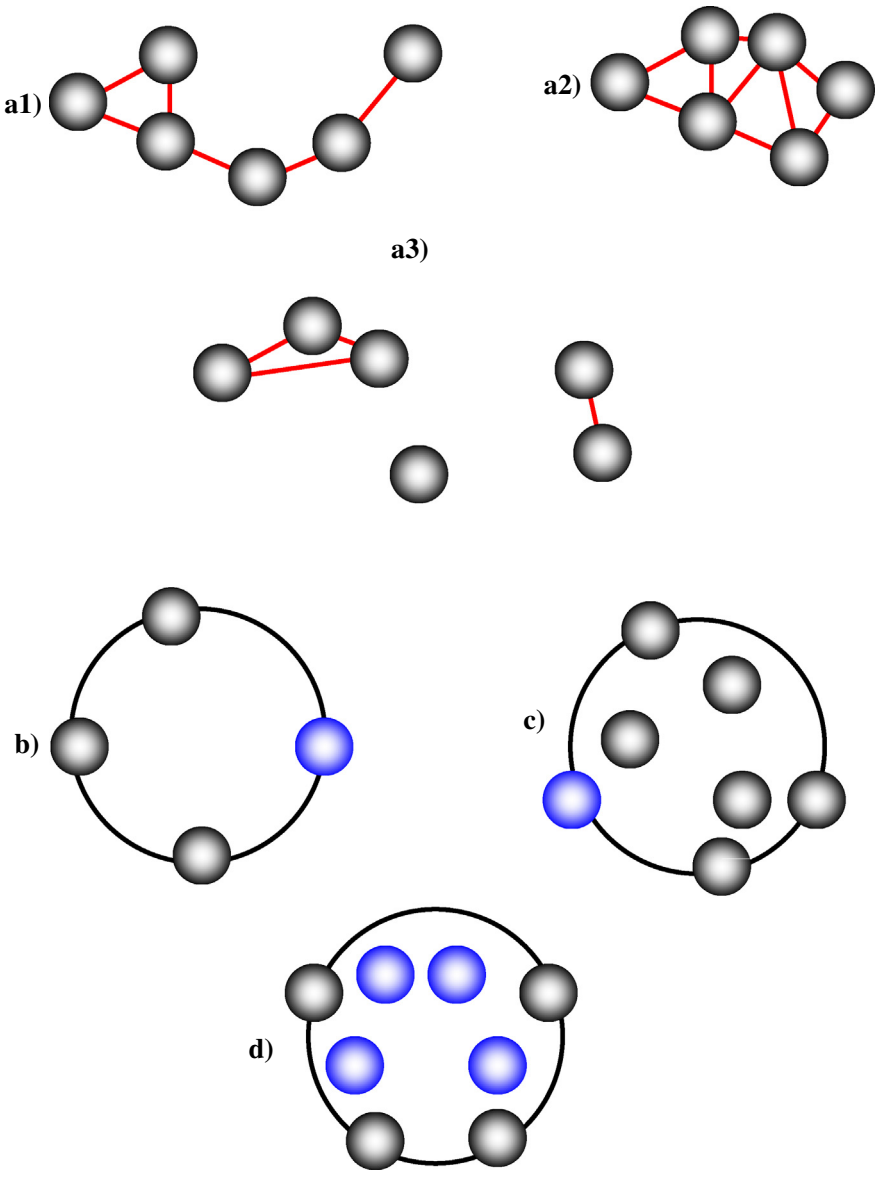

Fig. 1. The schematic illustration of cluster and simplex. A cluster with 6 linkages (a1) and 9 linkages (a2); three clusters with 4 linkages (a3); the void-simplex (b); the oxygen-simplex (c); the cation-simplex (d). The black, blue sphere represents the oxygen and cation, respectively; the red line indicates the linkage; the black circle represents the simplex. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)