

"Mixed Alkali Effect" Revisited

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If one alkali oxide is gradually replaced by another in a series of silicate glasses, some physical properties vary in an extremely non-linear manner (Isard, 1969). For example, addition of calcium oxide to sodium-silicate extremely lowers mobility of modifier cations (Dutta et al., 2008). On the other hand, introduction of another alkali cation lowers glass viscosity (Ingam, 1987). Unlike sodium-silicate, soda-lime silicate glasses are waterproof, so commonly used as windows, bottle, and so on. However, the mechanism of these "mixed alkali effect" is still unknown. Force-field molecular dynamics (FFMD) simulation is a suitable method for investigation of atomistic mechanism of the mixed alkali effect because it enables direct access to the atomic coordinates and velocities at the desired ensembles. Moreover, FFMD simulations can handle nm/ns system which allows us to obtain large scaled dynamic/static properties and better statistical averaged data comparing with BOMD/CPMD. In fact, the mixed alkali effect is well investigated using FFMD (Habasaki et al., 1995; Park & Cormack, 1994). These studies conclude that lowering of mobility of alkali ions in mixed alkali silicates is caused by blocking of diffusion path among different alkali ions. However, this conclusion is mainly based on distinct part of van Hove's function, that is, definition of diffusion path is left obscure. It is believed that some kind of diffusion channel exist in silicate glass/liquid structure as shown in Greaves (1985). Recently, our study clearly defines diffusion pathway in silicate liquid using simplex division regarding oxygen atoms as discrete points (Noritake, 2017; Hung et al., 2017). In this study, I will present results that clarify the mechanism of mixed alkali effect obtained using a newly developed analysis method. A newly developed topology-based Si-O network analysis method also will be introduced in this presentation.

MD simulations of $x\text{CaO} \cdot (3-x)\text{Na}_2\text{O} \cdot 7\text{SiO}_2$ liquids/glass were performed using MXDORTO code. The inter-atomic potential model was taken from Noritake et al. (2012). Systems of approximately 20000 particles in cubic-shaped simulation cell in periodic boundary condition were firstly annealed for 5.0 ns at 1573 K from randomly generated structure. Then the production runs were conducted within micro-canonical ensembles for 5.0 ns. The systems were cooled by the rate of 10^{12} K/s for the calculation at lower temperature condition. Diffusivities of network modifying cation decreased with gradual replacing Na atoms with Ca atoms. Changes in geometry of diffusion pathway and Si-O network will be discussed in this presentation.

Keywords: Silicate Glass, Silicate Liquid, Molecular Dynamics Simulations, Mixed Alkali Effect