

# MOLECULAR DYNAMICS OF SILICATE GLASS STRUCTURE

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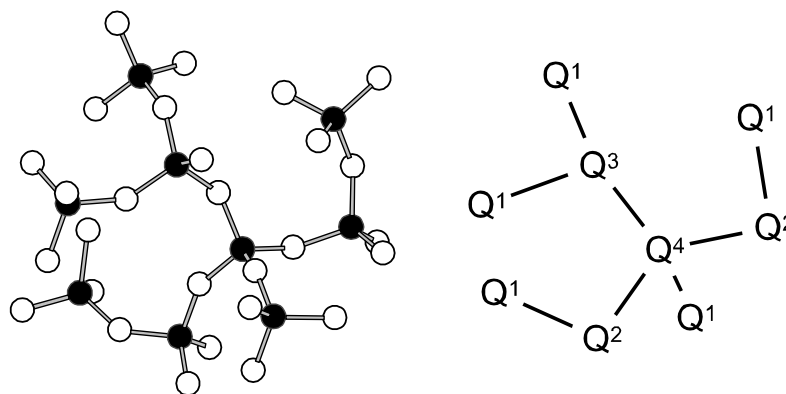
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**ABSTRACT:** This work studies the structure of silicate glasses by means of molecular dynamics simulation (MD). The structure of simulated alkali-silicate glasses was investigated using Q-species ( $Q^n$ ) distribution where “Q” denotes  $\text{SiO}_4$  tetrahedra and  $n$  is number of bridging oxygen atoms. The structure of MD glass at room temperature shows much lower fraction of  $Q^3$  units than the structure of real glass. Nevertheless, it was confirmed that small alkali cations produce more extensive decrease of the  $Q^3$  amount if compared with larger alkali cations and that it is caused by their effort to surround themselves with NBO atoms. Silicate network defects  $\{\text{Si}\}^5$  present in MD glasses were discussed with respect to alkali concentration and cationic field strength of alkali modifiers.

**KEY WORDS:** MD, simulation, silicate, glass, Q-species

## 1 INTRODUCTION

Alkali silicate glass belongs to the most explored non-crystalline materials of all. Nevertheless, the structure of glass is still in a shroud of secrecy. No experimental method is able to obtain as complete picture of glass as X-ray or neutron scattering allow in crystals.  $^{29}\text{Si}$  MAS-NMR (solid state NMR) is a method sensitive to bonding differences of silicon atoms. The method identifies so called  $Q^n$  units (or Q-species) where  $n$  is number of bridging oxygen atoms (BO) bonded to a certain tetrahedrally coordinated silicon atom (Fig. 1).



**Fig. 1:** Two graphic representations of silicate framework. First figure: ball-and-stick model, silicon - black; oxygen - white. Second figure: the same structure using  $Q^n$  notation. The lines represent BO atoms.

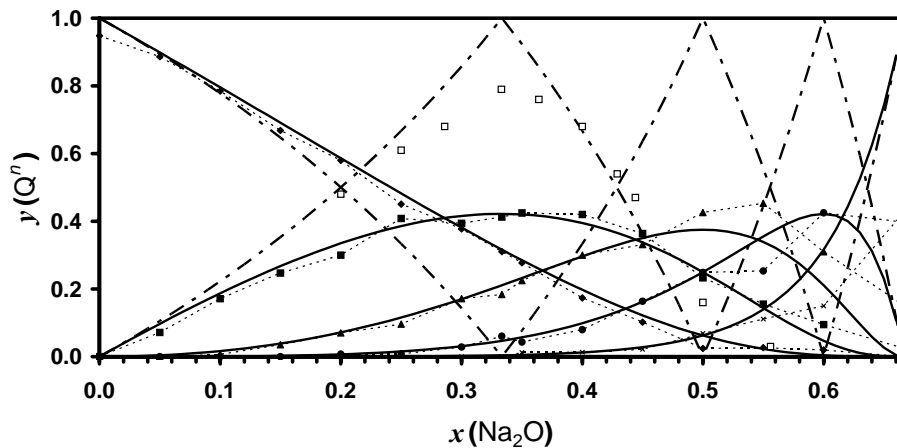
$^{29}\text{Si}$  MAS-NMR measurements have found that fraction of  $Q^n$  units in binary alkali-silicate glass does not correspond exactly to the theoretical value based on stoichiometric considerations. The decrease of  $Q^3$  units was compensating by the equimolar increase of  $Q^2$  and  $Q^4$  which can be described by relation:  $2Q^3 = Q^2 + Q^4$  [2]. Such disproportionation (or speciation) was observed largest in lithium glass and decreasing towards caesium glass [4].

$^{29}\text{Si}$  MAS-NMR also showed that the silicate network contains a small amount of structural defect  $\{\text{Si}\}^5$  (a silicon bonded to 5 BO atoms). Such defects were detected in both glasses prepared under high pressure and rapid quenched glasses under normal pressure [7]. More  $\{\text{Si}\}^5$  units occur in tetrasilicate glasses and, among them, in potassium glasses. It was suggested that the  $\{\text{Si}\}^5$  unit plays a role in migration of oxygen atoms in a silicate melt [1].

An analysis of  $Q^n$  units in glass reveals a lot about the silicate structure; nevertheless some extra information from other methods is always needed. In last decades, it was many times demonstrated that MD simulation (molecular dynamics) contributes substantially to better understanding of the glassy state [3, 5]. The aim of this study is to simulate binary alkali-silicate glasses and compare results of the simulations with available experimental data and discuss discovered similarities or contradictions from the atomic point of view.

## 2 COMPUTATIONAL DETAILS

The MD simulations of  $x\text{Na}_2\text{O}\cdot(1-x)\text{SiO}_2$  glasses ( $x = 0, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.33, 0.35, 0.4, 0.45, 0.5, 0.55, 0.6, 0.66$ ) and  $\text{M}_2\text{O}\cdot 2\text{SiO}_2$  glasses (M stands for Li, Na, K, Rb, Cs) were performed by DL\_POLY software [6]. Interatomic interactions were described by Buckingham short-range potential and Coulomb long-range potential. BKS parameterization [9] was used; the potential parameters for Si-O, O-O can be found in [9], for Na-Na, Na-O in [5] and the other in [8]. A short-range cut-off was set to 7.6 Å and the Coulomb part of the potential was summed using classic Ewald scheme. A cubic computational box with periodic boundary conditions was used. Newton equations of motion were numerically integrated by the leap-frog algorithm with time step of 2 fs (1fs in case of the Li system). MD simulations were performed with a constant pressure 1kbar for  $x\text{Na}_2\text{O}\cdot(1-x)\text{SiO}_2$  systems and a constant volume (experimental density) for  $\text{M}_2\text{O}\cdot 2\text{SiO}_2$  systems. The cooling regime comprised a step-by-step temperature decrease (temperature step set to 100 K). The simulation started from a random configuration of particles at 5000 K. Each temperature step consisted of the numeric control of the reached temperature and pressure (for 2500 time steps) followed by equilibration (constant total energy, for 7500 time steps). The cooling procedure was stopped at 300 K where the system can be taken as completely frozen. Non-bridging (NBO) and bridging oxygen (BO) atoms were identified by the following way. All oxygen atoms coordinated by one silicon atom within radius 2.46 Å were considered to be NBO. Oxygen atoms with more than one silicon within this radius were identified as BO. The value 2.46 Å corresponds to the first local minimum of the RDF Si-O.



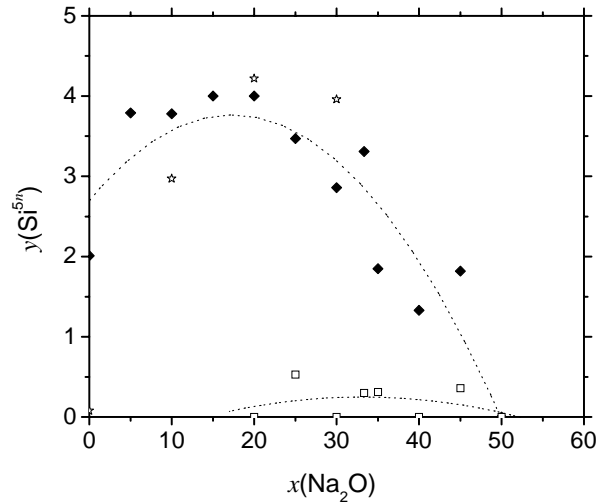
**Fig. 2:** Q-units distribution in sodium silicate glasses: solid line - RBM model; dash-and-dot line - binary model; filled symbols ( $\blacklozenge$   $Q^4$ ,  $\blacksquare$   $Q^3$ ,  $\blacktriangle$   $Q^2$ ,  $\bullet$   $Q^1$ ,  $\times$   $Q^0$ ) - MD simulation; open symbols -  $^{29}\text{Si}$  MAS-NMR data for  $Q^3$  [4]. The dotted lines are only guides for the eye.

## 3 RESULTS AND DISCUSSION

The dependence of relative amount of  $Q^n$ ,  $y(Q^n)$ , in  $\text{Na}_2\text{O}\text{-SiO}_2$  system is shown in Fig. 2. It is evident that the experimental data points ( $Q^3$  units) are much closer to the simple stoichiometric binary model than to the results of MD simulation. The MD simulated glasses reveal higher speciation of  $Q^3$  than the experimental ones. On the other hand, the MD simulation excellently matches the random bonding model

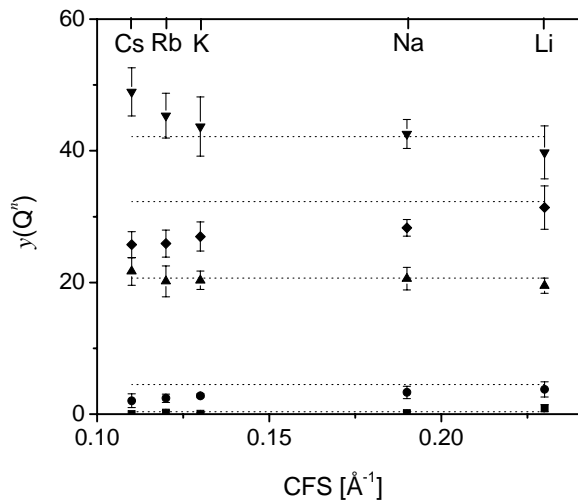
(RBM) [2] up to 45 % Na<sub>2</sub>O. The model considers BO to be randomly placed into silicon atom coordination spheres. Discrepancy between experimental data and MD simulation is usually explained by rapid cooling rate of MD simulated glass (typically 10<sup>12</sup> K/s) fixating a high temperature structure with enormous configurational entropy. Therefore, MD simulation is not suitable for quantitative predictions, but rather for qualitative comparisons.

The MD simulated glass contains a bit higher amount of defects {Si}<sup>5</sup> than experimental rapidly quenched glasses (Fig. 3). Surprisingly,  $\gamma(\text{Si}^5)$  shows the maximum at 20 % of Na<sub>2</sub>O, which is in excellent agreement with earlier experimental findings of <sup>29</sup>Si MAS-NMR. When more alkali oxide added to the system the fraction of {Si}<sup>5</sup> steeply vanishes. This supports the hypothesis about the role of {Si}<sup>5</sup> as an intermediate product of oxygen migration in silicate melts.



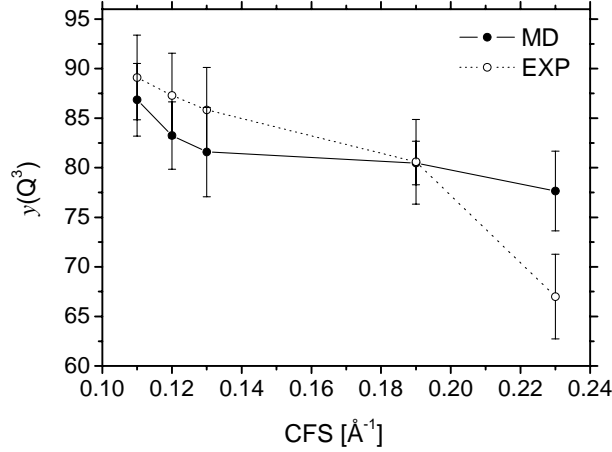
**Fig. 3:** Dependence of {Si}<sup>5n</sup> defects fraction on % of sodium oxide in MD simulated Na<sub>2</sub>O-SiO<sub>2</sub> glassy system. Filled diamonds are {Si}<sup>55</sup> units; open squares are {Si}<sup>54</sup> units and open stars are {Si}<sup>55</sup> taken from [5]. The dotted curves are only guides for the eye.

Despite the fact that the speciation of Q<sup>3</sup> is very high in MD simulated glasses (Fig. 4), it was found that the trend of speciation over disilicate glasses with varying alkali cations (Fig. 5) is the same as for experiments. The reason for the lower speciation in Li glass and the higher in Cs glass resides in the tendency of small cations to surround themselves with rather flexible NBO atoms located on Q<sup>2</sup> units (generated by Q<sup>3</sup>). Then, formation of Q<sup>4</sup> units guarantees electroneutrality of glassy system. Highly localized charge on small cations is discharged by highly localized charge on a flexible NBO.

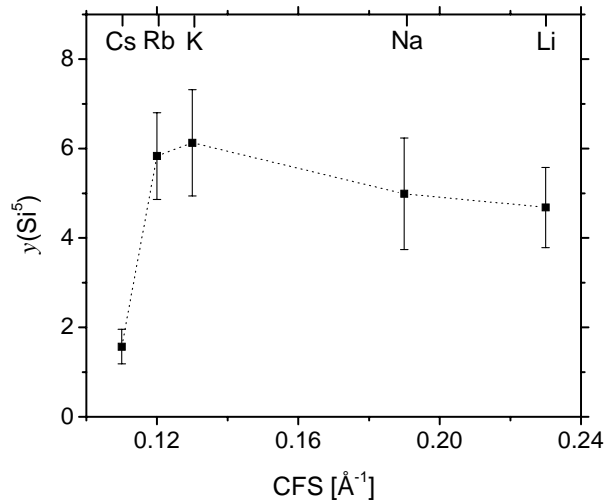


**Fig. 4:** Dependence of Q<sup>n</sup> distribution on cationic field strength in MD simulated M<sub>2</sub>O·2SiO<sub>2</sub> glass (M stands for alkali cation). Q<sup>n</sup> units are distinguished as follows: ◆ Q<sup>4</sup>, ▼ Q<sup>3</sup>, ▲ Q<sup>2</sup>, ● Q<sup>1</sup>, × Q<sup>0</sup>; RBM model - dotted line.  $\gamma(Q^n)$  was obtained by averaging of 4 independent configurations (1494 atoms per each).

In agreement with experimental findings [7], the maximum of  $\{\text{Si}\}^5$  was found in K glass (Fig. 6). It seems that a potassium cation does not match the space generated by the silicate framework and acts as a generator of structural defects. The potassium cation can be considered as a transient element between small cations Li and Na and large cations Cs and Rb.



**Fig. 5:** Comparison of  $Q^3$  fraction in MD simulated and experimental  $M_2O \cdot 2SiO_2$  glass (M stands for alkali cation).  $y(Q^3)_{MD}$  was obtained by averaging of 4 independent MD configurations and  $y(Q^3)_{EXP}$  by averaging of published data (NMR and Raman).  $y(Q^3)_{MD}$  values were raised by 34 %. The solid and dotted lines are only guides for the eye.



**Fig. 6:** Dependence of  $\{\text{Si}\}^5$  defects fraction on cationic field strength in MD simulated  $M_2O \cdot SiO_2$  glass.  $y(\text{Si}^5)$  was obtained by averaging of 4 independent MD configurations. The error bars denote standard deviations. The dashed lines are only guides for the eye.

#### 4 CONCLUSION

MD simulations of binary sodium silicate glasses within a wide composition range were performed. The obtained structures were described in frame of Q-species. Speciation of  $Q^3$  units well agrees with the random bonding model. Structural defects  $\{\text{Si}\}^5$  observed in MD glass modeled with a pair-wise interatomic potential show their maximum at 20 % of  $\text{Na}_2\text{O}$ , which is in excellent agreement with earlier experimental findings of  $^{29}\text{Si}$  MAS-NMR. It confirms a role of  $\{\text{Si}\}^5$  as an intermediate product of oxygen migration in silicate melts. Despite the speciation of  $Q^3$  is much higher in MD simulated

M<sub>2</sub>O·2SiO<sub>2</sub> glasses than in the experimental ones, the similar dependence on alkali cation field strength was found. The reason for the lower speciation in Li glass and higher in Cs glass resides in tendency of small cations to surround themselves with NBO located on Q<sup>2</sup> units. In agreement with experimental findings, the maximum of {Si}<sup>5</sup> was found in K glass.

## 5 ACKNOWLEDGEMENTS

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