Medium- and long-range order in binary sodium-silicate glasses simulated by molecular dynamics

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Abstract

Molecular dynamics simulations of $x\mathrm{Na_2O}\cdot(1\text{-}x)\mathrm{SiO_2}$ glasses, for $x = 0, ..., 0.66$, were performed. The obtained structure at the normal temperature was described in frame of Q-species, bridging and non-bridging oxygen distributions, bonding defects, and connectivity. Distributions of Q-species are compared with the "structurally ideal" model glass. In addition, simulated results are compared with the available experimental data.

Introduction

The silicate glass, as a prototype of the covalently bonded glass can be efficiently described by the Continuous Random Network (CRN) Model [1]. The model is based on the assumption of the well ordered short-range arrangement around silicon atoms resulting in SiO_4 tetrahedra, so called Q-units. The Q-units are interconnected via the bonding oxygen (BO), which in ideal case join two SiO_4 tetrahedra. If the alkali species enter the covalently bonded glass, the silicate network includes non-bridging oxygen as a result of the ion bonding between oxygen and alkali species. It was suggested, and now generally accepted, that the network incorporating the alkali species can be described by Modified Random Network (MRN) Model [2]. The model predicts a non-homogeneous alkali distribution inside the silicate network. However, the substance of such non-ideal distribution is not fully understood. Many other questions arise about the shape of the alkali distribution in space, e.g. if alkali species tend to form 3-D clusters, or

clusters of a lower dimensionality; if the clusters tend to percolate the silicate network or prefer to be separated from each other.

One of the possible quantitative glass structure descriptions resides in quantifying the distribution of the so called Q^n-units. Here, Q stands for quaternary, i.e. SiO_4 tetrahedron in case of silicate glasses, and n denotes the number of bridging oxygens (BO). Q-units are well defined, not significantly deviating from their crystalline counterparts. It is a result of strong covalent bonds between Si and O and hence a strong short-range ordering. On the other hand, the alkali species are distributed much randomly in space, even at short ranges. As a result, Partial Pair Radial Distribution Function (PP RDF) of O-Na disables to well define the Na coordination [3]. On the other hand, as each NBO is associated with an alkali species, Q-units be can advantageously used for the description not only of the NBO distribution but also for the distribution of alkali species.

Today, glass characterization in frame of Q-units is well accessible by means of spectroscopic methods, e.g. Raman [4] and ^{29}Si MAS NMR [5] spectroscopy. In addition, theoretical approaches, like molecular dynamics (MD) method or thermodynamic modelling [6] offer alternative approaches giving glass structure expressed in terms of Q-units. Application of these methods to simple (e.g. two- and three component) glass forming systems has provided a substantial part of the current understanding of the relationships between the glass composition, structure and properties.

The present work focuses to the structure of the binary glasses $x Na_2O \cdot (1-x) SiO_2$, 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, described in frame of Q-units. The changes of structural characteristics of the medium- and long-range order with alkali concentration are followed.

Computational details

The MD simulations of the $x Na_2O \cdot (1-x) SiO_2$ 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, were performed by DL_POLY software [7]. Interatomic interactions were described by Buckingham short-range potential and Coulomb long-range potential. BKS parameterization [8] was used; the potential parameters for Si-O, O-O can be found in [8], and for Na-Na, Na-O in [9]. 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

boundaries was used. Newton equations of motion were numerically integrated by the leap-frog algorithm with time step of 2 fs. MD simulations were performed with a constant pressure. The cooling regime comprised a step-by-step temperature decrease (temperature step set to 100 K). The simulation started at 5000 K. Each temperature step consisted of the numeric control of the reached temperature and pressure (NPT, 2500 time steps) followed by equilibration (NVE, 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 from the snapshots by the following way. All oxygen atoms coordinated by one silicon atom within radius 2.46 Å were considered as NBO. Oxygen atoms with more then one silicon within this radius were identified as BO. The value 2.46 Å corresponds to the centre of the zero area after the first peak of PP RDF(Si-O).

Results and discussion

Analysis of the Si-O coordination numbers reveals a small amount (less than 5%) of the over-coordinated silicon. These structural defects are mostly attributed to the extremely high cooling rate implied by MD method. Over-coordinated silicon atoms were, however, also detected in real alkali-silicate glasses investigated by ^{29}Si MAS NMR [10]. Other type of structural defects, so called lacking NBO's, were identified on base of the comparison between the theoretical number of NBO's (equal to the number of sodium cations) and the actual NBO number obtained from MD snapshot by NBO counting, which is based on the above described distance cut-off algorithm. It was found that the decreasing number of the over-coordinated silicon atoms is strongly correlated with the number of lacking NBO's. Hence, the over-coordination can be attributed to the competition between the alkali cation and silicon for bonding to NBO [10]. The competition is stronger in low-alkali region, as the alkali ion has less opportunity for the creation of the optimised surrounding due to the rigid silicate network. As the silicate network is less and less interconnected, the alkali ion can find a more proper site, optimise it for itself, and simultaneously fulfil the requirements of the silicate network.

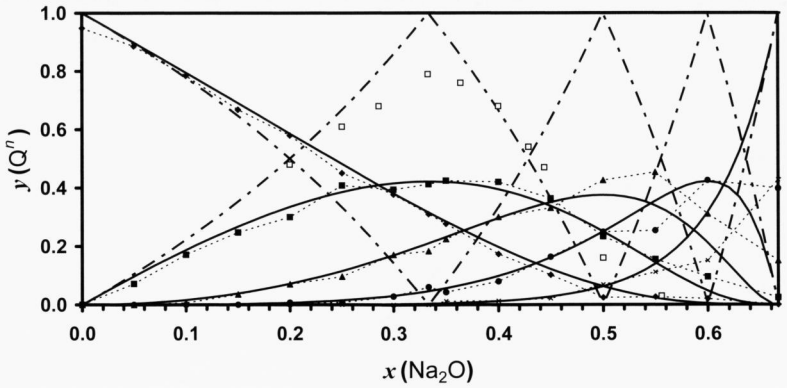

Figure 1. Q-units distribution in sodium silicate glasses: black solid line = random bond model; dashed-dot line = binary model; black filled symbols (◆ Q^4, ■ Q^3, ▲ Q^2, ● Q^1, × Q^0) = MD simulation; open symbols = MAS NMR data for Q^3 [5]. The dashed lines are only guides for the eye.

Most of energy of the silicate glass is deposited in the SiO_4 tetrahedra. Hence, the distributions of Q-units mirror the essential part of thermodynamics in glass. *Binary model* assumes presence of only two different Q^n-units with the highest possible n's according to the stoichiometry. The model stands as a limiting case and provides a basic estimation of Q-units distribution in silicate glass. It breaks down most pronouncedly at glass compositions, where a crystalline counterpart exists. However, the speciation according to the equation $2Q^i \rightleftharpoons Q^{i-1} + Q^{i+1}$, $i = 3, 2, 1$ places an important role there and requires a modification of the above simple model. A *Random model* [11], based on the random distribution of NBO's and half-BO's, admits existence of more than two Q^n units. The distribution of Q-units is obtained fully by random; silicon atom forms four BO or NBO bonds on base of their populations in the sample. Distributions of Q-units obtained by MD are presented in Fig. 1 together with distributions predicted by above mentioned models. In addition, experimental results are included for the comparison. The Figure clearly shows that the MD yields Q-units speciation well corresponding to the Random model. It can be explained by the freezing of the structure at a relatively high temperature. At these

temperatures, the silicon tetrahedra are well formed but the temperature is still high enough to prevent the formation of the structure unit exceeding silicon tetrahedra.

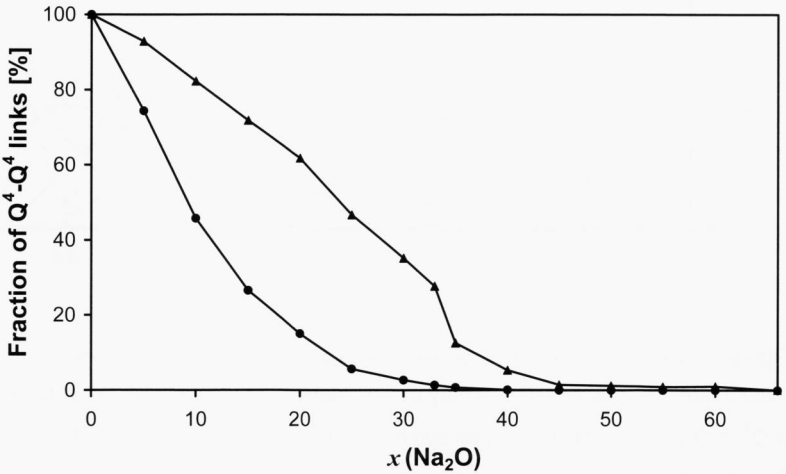

Fig. 2. Population of Q^4-units connected only with Q^4-units (full triangles). Result of a random interconnection (closed circles), based on found Q^n distributions, is presented to demonstrate the preferential Q^4-Q^4 connection.

The Q-unit distributions offer important information about the local clustering of alkali ions, formally described by the speciation equation. The question, if the local clustering creates larger super-structures can be answered only by tracking the grouping of alkali ions in space. Because of not well defined short-range order of alkali ions, it is more advantageous to keep track of connectivity of Q-units associated with alkali ions. In other words, two alkali ions are considered as connected, if their corresponding Q-units, e.g. Q^3-units, are connected by BO. Due to the rather poor statistic of the Q^3 ,Q^2-, Q^1-, Q^0-links, the alkali ion clustering can be most easily tracked via the clustering of Q^4-units, which actually represents the complementary, i.e. alkali free, part of the structure. The Figure 2 reveals preferential Q^4-Q^4 connections in comparison with a random distribution. Hence, Q^4-units create larger structures than expected from their purely random space distribution. The same holds for the inverse (alkali cation associated) Q-units; they have to prefer interconnect each other rather than to connect with Q^{n4} (alkali absent

unit). Hence, the space clustering of alkali ions are demonstrated in binary silicate glass. The question about their shape will be addressed in future as it needs larger size of the simulation box.

Conclusion

Molecular simulations of binary sodium silicate glasses in a wide composition range were performed. The obtained structure was described in frame of Q-species. Speciation of Q-species well agrees with a Random model. The space distribution of alkali ions are found to be non-homogeneous as the alkali associated Q-units prefer to interconnect among themselves rather than to connect with Q^4-units.

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References

[1] Zachariasen, W.J.: J. Am Ceram. Soc. **54** (1932), p. 3841.
[2] Greaves, G.N., Fontain, A., Lagarde, P., Raoux, D., Gurman, S.J., *Nature* **293** (1981) 611.
[3] Machacek, J., Gedeon, O., Phys. Chem. Glasses **44** (2003) 308.
[4] Bykov, V.N., Osipov, A.A., Anfilogov, V.N., *Phys. Chem. Glasses*, **41** (2000) 10.
[5] Maekawa, H.; Maekawa, T.; Kawamura, K.; Yokokawa, T., J. Non-Cryst. Solids **127** (1991) 53.
[6] Shakhmatkin, B. A.; Vedishcheva, N. M.; Shultz, M. M.; Wright, A. C., J. Non-Cryst. Solids **177** (1994) 249.
[7] Smith, W.; Forester, T.R.: http://www.dl.ac.uk/TCSC/Software/DL_POLY, 2000.
[8] van Beest, B., Kramer, G.J., van Santen, R.A., Phys. Rev. Lett. **64** (1990) 1955.
[9] Yuan, X.; Cormack, A. N., J. Non-Cryst. Solids **283** (2001) 69.
[10] Stebbins, J. F.; McMillan, P., J. Non-Cryst. Solids **160** (1993) 116.
[11] Phillip, H.R.: J. Phys. Chem. Solids **32** (1971) 1935.