New approach to modeling of a local structure of silicate glasses and melts

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Abstract. Structural model of silicate melts and glasses obtained by rapid cooling of the melt is far from complete at present. Modern models suggest the existence of the five different types of silicon-oxygen tetrahedra which are distinguish by the ratio of bridging and terminal oxygen atoms per silicon atom (the so-called basic structural blocks or units) in the structure of silicate glasses and melts and also assume that the several types of such units can exist in the glass and melt structures simultaneously. The knowledge of the concentrations of these units depending on the composition and temperature (the so-called $Q^n$ distribution) is a necessary element for the development of an adequate model of silicate systems and to explaining their physical and chemical properties. Three-parameter statistical method to modeling of $Q^n$ distribution in silicate melts and glasses is present in this paper. This method allows calculating the concentration of structural units in a wide composition range at different temperatures. The method is based on a destruction of a preassigned network as a model of depolymerization of the silicon-oxygen framework in the process its interaction with the modifier oxides. $Q^n$ distribution, distribution of silicon-oxygen tetrahedra according to their next-nearest neighbours, and distribution of bridging bonds in alkali-silicate glasses and melts were obtained in frame of the developed approach.

1. Introduction

The silicate glasses are the typical representative of the covalently bonded glasses and their structure is well described by the continuous random network model (CRN) [1]. According to this model, the structure of vitreous $\text{SiO}_2$ is a continuous network of $\text{SiO}_4$ tetrahedra randomly interconnected via the oxygen apexes. In other words, each silicon atom is surrounded by four oxygen atoms and each oxygen atom is shared between two silicon atoms, forming so-called bridging oxygen (BO) bond in structure of glassy $\text{SiO}_2$. Addition of alkali or alkaline-earth oxides to silica leads to break-up of the bridging bonds and formation of the terminal oxygen atoms each of which is connected only to one silicon atom. In case of alkali silicate glasses, such structural reorganization can be schematically described by $\text{Si-}O-\text{Si} + R_2\text{O} \Rightarrow 2[\text{Si-O}^\text{R}^\text{+}]$ reaction, where $R^+$ is the alkali ion and $O^-$ is the terminal or non-bridging oxygen atom (NBO). At such interaction, four oxygen atoms remain in nearest surrounding of silicon atom but new silicon-oxygen tetrahedra with differ BO/NBO ratio are formed in glass structure. Five types of silicon-oxygen tetrahedra are accepted to distinguish according to BO number per silicon-oxygen tetrahedron (so-called $Q^n$ units, where $n = 0...4$ is the number of BO). The
existence of $Q^n$ units in silicate glasses and melts is universally recognized and no any significant deviations from their crystalline counterparts were found.

At present, $Q^n$ species are widely used in interpretation of experimental data such as Raman and $^{29}$Si MAS NMR spectroscopy [2-6], and can be obtained by method of thermodynamic simulation [7, 8] and molecular dynamic (MD) method [9]. Experimental determination of dependence $Q^n$ concentrations ($Q^i$ distribution) on composition and temperature are is laborious and the high-temperatures experiments require the special equipment to detect the weak signal against the background of the strong thermal radiation from sample. Thermodynamic modeling allows performing calculation in a wide range of compositions and temperatures but knowledge of all crystalline phases and standard Gibbs free energies of their formation are required as input data [10]. The whole set of such data is not always available for researchers and it limits the possibility of using of this method. In addition, more and more attention is paid to not only $Q^n$ distribution but also connectivity of $Q^n$ species, i.e., so-called $Q^{n,a_1,\ldots,a_n}$ distribution ($a_1,\ldots,a_n$ indices denote the type of the structural units which are connected to the given $Q^n$ unit) , lately [11,12]. Such problem does not considered in thermodynamic simulation. The MD allows us to study both $Q^n$ and $Q^{n,a_1,\ldots,a_n}$ distributions. To date, such investigations, however, were performed only in a limited compositional range and do not show the complete picture of distribution of large $Q^{n,a_1,\ldots,a_n}$ groups as a function of glass composition and temperature. From this point of view, the elaboration of other methods in order to study the above mentioned problems is certain interest. An alternative method of study of the local structure of alkali silicate glasses and melts is reported in this paper. It was tested on Li$_2$O-SiO$_2$, Na$_2$O-SiO$_2$ and K$_2$O-SiO$_2$ glass forming systems.

2. Modeling details

As it is known, the Zachariasen’s rules [1] of formation of continuous random glass network are focused only on the local configuration of cation-oxygen polyhedra and their connectivity to each other (via corners, not edges or faces). According to this, it is possible to assume that the most important point in modeling of the above mentioned distributions is a coordination number of glass forming cation rather than the network dimensionality and topology as a whole. Any regular or random network where each knot is linked to four nearest knots and each link is shared only two knots completely reproduces the $Q^n$, $Q^{n,a_1,\ldots,a_n}$ and $Q^i$-$Q^j$ (various types of Si-O-Si bonds, $i,j = 1,\ldots,4$) distributions in glassy SiO$_2$ if the knots and links between them are interpreted as silicon atoms and Si-O-Si bridging bonds, respectively. In this case, a break of the link between two knots simulates the depolymerization process of SiO$_2$ network that can be schematically represented by the follow reaction:

$$Q^i + Q^j + R_2O \rightarrow Q^{i-1} + Q^{j-1}, \quad i,j = 1,\ldots,A$$

Thus, in order to calculate all above distributions it is necessary to break the preassigned number of bonds (determined by the glass composition) and then derived configuration must be analyzed.

It is known, that the $Q^n$ distribution strongly depends on alkali cation type. Therefore, three parameters, $w_1$, $w_2$ and $w_3$, were introduced into the model in order to achieve the best agreement between experimental and calculating data. Figure 1 shows an importance of these parameters in the simulations algorithm. As it is follows from the equation (1), ten different bonds may exist in the system when $R_2O \neq 0$. The choice of the bond that should be broken is absolutely random and does not depend on type of structural units which share this bond when $w_1 = w_2 = w_3 = 1$. The break of the $Q^i$-$Q^j$ bonds with the highest values of $i$ and $j$ will preferentially occur when $w_3 > 1$.

Three different initial networks (2-D regular square network, 3-D quartz-like regular network and network in form of table of the random bonds (TRB)) were used in calculation in order to test the assumption that the $Q^n$, $Q^{n,a_1,\ldots,a_n}$ and $Q^i$-$Q^j$ distributions are independent from the network dimensionality and topology. The TRB was generated in such a manner that each bond belongs to two knots and each knot was joined to four nearest neighbours. Thus, the condition of four-fold coordination of glass forming cation remained but such network has no any real geometry. Results of all experiments were identical when we used the same $w_k$ parameters. It can be explained by the fact...
that both 2-D flat square and 3-D quartz-like regular networks are special cases of the TRB. Therefore, the results only for TRB are reported in this paper.

Figure 1. Block-diagram of simulation algorithm.

3. Results
The $Q_i^{}$-$Q_j^{}$ distributions, several examples of $Q_{n,a_1,...,a_n}^{a_1,...,a_n}$ distributions ($Q_{n,a_1,...,a_n}^{a_1,...,a_n}$ distributions were calculated as ratio of $Q_{n,a_1,...,a_n}^{a_1,...,a_n}$ groups relative the total amount of Q species) and $Q^r$ distributions are shown in figures 2, 3 and 4.

Figure 2. $Q_i^{}$-$Q_j^{}$ distributions in $Li_2O$-SiO$_2$, $Na_2O$-SiO$_2$ and $K_2O$-SiO$_2$ glasses.

Figure 3. Examples of $Q_{n,a_1,...,a_n}^{a_1,...,a_n}$ distributions in $22.5R_2O$-$77.5SiO_2$ and $35R_2O$-$65SiO_2$ glasses ($R = Li, Na$ and $K$).
Figure 4. \(Q^n\) distributions in glasses of \(R_2O-SiO_2\) systems (\(R = \text{Li, Na, K}\)). Solid lines are simulation results, symbols are experimental data [2,4-6,14-19].

4, respectively. It is obvious, that dispersion of all distributions increases with decrease in radius of alkali cation. It is known, that dynamic equilibrium between \(Q^n\) species in alkali silicate melts can be described by

\[
2Q^n \rightleftharpoons Q^{n-1} + Q^{n+1} \quad (n = 1, 2, 3)
\]

equilibrium reaction. The \(Q^n\) distribution is practically independent from the temperature in the \(\text{Li}_2O-SiO_2\) system while it strongly depends on the temperature in the \(\text{Na}_2O-\) and \(\text{K}_2O-SiO_2\) systems (above mentioned equilibrium is shifted to the right with increase in temperature). Thus, it is possible to assume that the \(Q^n\), \(Q^1-Q^4\) and \(Q^{111-1000}\) distributions in the \(\text{Li}_2O-SiO_2\) glasses may be considered as analogous of corresponding distributions in sodium and potassium silicate melts.

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4. References

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