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Molecular dynamics simulation of thermodynamic and structural properties of silicate glass: Effect of the alkali oxide modifiers

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ABSTRACT

Molecular dynamics simulation was applied to elucidate the effect of adding alkali oxides $(M_2O)_X(SiO_2)_{(1-X)}$ with M = (Na, Li or K) into silicate glass matrix. We are interested in the study of this effect particularly on structural and thermodynamic properties of the material. Some interesting results were obtained given a new insight on the bridging process and its reliability to the observed depolymerization phenomena affecting the existing Si—O network and depending on both the kind of the alkali modifier and its molar fraction. We observed that the thermodynamic properties are influenced by these structural modifications. Indeed, the glass transition temperature T_g has been found to decrease as the molar fraction of modifier increases depending strongly on the alkali modifier kind. On the other hand, we extracted the fictive temperature from the calculated total energy of the system and determined the glass transition by studying the variation of the fictive temperature as a function of the conventional one using different cooling and heating rates.

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1. Introduction

Silicate glasses and their properties (structural and thermodynamic) are usual topics of condensed matter physics, glass science and materials chemistry. These materials were studied by many physicists and chemists by means of both theoretical and experimental methods as a fundamental and complex problem. Time domain of many experiments through the glass transformation region routinely comes across with non-equilibrium state of the material. The fictive temperature is a common tool to characterize the non-equilibrium state (glassy state) and it is defined as the temperature at which the non-equilibrium values of a macroscopic property (e.g. enthalpy) would equal the equilibrium ones [1]. Alkali elements (e.g. K^+, Na^+, L^+, …) are becoming increasingly essential for improving glasses materials with a greater focus on end-user application requirements, reduction of development costs, and a decrease in the time to market [2,3]. Therefore, alkali silicate glasses are the prototype of multi-component silicate glasses that find wide applications in the glass industry, photonic devices, biomaterials and microelectronics [4]. Recently, the binary alkali silicate glasses have taken much attention not only like an archetype of glassy materials, but also because of its anomalous structural, mechanical, thermal properties [3] and glass transition temperature [5,6]. For example, describing

properties of the glassy state and predicting the glass transition temperature T_g of binary and multicomponent mixtures of molecular and ionic compounds is still poorly understood [7,8]. The present paper represents a modest attempt to provide representative information on this problem.

For silica glass, the number density of Si—O—Si bonds is related to the degree of network polymerization; higher polymerization usually offers the specific properties that are changed by the effect of alkali modifiers. These elements act as bond breakers in the silica network, showing a decrease of the polymerization degree by transforming part of bridging oxygen atoms (*BOs*) into non-bridging oxygen atoms (*NBOs*) [9]. Glass transition temperature, being itself a useful parameter in glass technology, is sensitive to the modification in structure, which can happen due to compositional changes [10]. The aim of this present work, is the understanding of the processes involved in the alkali silicate glassy state and the study of its physical and chemical properties. In many cases these properties are not always easily accessible from experiments, so we need to develop theoretical models and/or simulations in order to investigate the phenomena related to the alkali effects. Classical Molecular Dynamics (CMD) simulation is one of the methods that is generally applied successfully in silicate glass study to shed light on the microscopic processes involved in the transition. However, the quality of a simulation strongly depends on the atom–atom interaction potential [11]. Indeed the choice of the interatomic potential type, describing the interaction between the different constituents in the simulation, is determinant for obtaining a reliable initial structure in which

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the glassy state will be prepared. Another important feature for the MD simulation of glassy systems is related to the dynamics and the rate of cooling and heating of the system and its effect on the glass transition.

In this work, we emphasis on the use of MD to study alkali addition effect on silicate glass proprieties. Born-Mayer-Huggins with long-range coulombic formula [12] is used to compute pairwise interactions in the material. We use the potential parameters developed by Habasaki et al. for describing the silicate materials [13]. We focused on the effect the cooling rate and alkali oxide content on the glass transition to obtain the silicate glassy states. On the other hand, we are interested in studying the structure results of silica and alkali-silicate glasses and their relationship with the change of glass transition temperature.

This paper is arranged as follows. Firstly it starts with introduction followed by a brief description of the used interatomic potential. In Section 3, we describe the used simulation and the glass making method. In the results section, we are interested in characterizing the non-equilibrium (glassy state) by fictive temperature notion in order to show the cooling rate effect on the glass transition temperature T_g. We then present the alkali oxide (Li_2O, Na_2O and K_2O) addition effects on T_g and on the silica glass structures. The discussion of all results and conclusion of this work are given in Sections 4 and 5, respectively.

2. The used interatomic potential

We adopt, in this work, a pair-wise additive effective potentials [14–15] to model the interatomic interactions. The potential is based on the Born–Mayer–Huggins potential [10] which has the general analytical form:

$$U_{ij}(r_{ij}) = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} + f_0(b_i + b_j)\exp\left(\frac{(a_i + a_j) - r_{ij}}{(b_i + b_j)}\right) - \frac{c_i c_j}{r_{ij}^6} + \frac{D_i D_j}{r_{ij}^8} \quad (1)$$

where q_i is the fictive charge number for each atom (Si, O, Na, K and Li) given in Table 1. The charge neutrality of the total system is imposed to the system by the relationship between molar fractions of alkali oxide and oxygen charge in accordance to Eq. (2). r_{ij} is the interatomic distance and f_0 is a normalization constant or standard force equal to $f_0 = 1$ Kcal° [16]. a, b, c and D are parameters characterizing the material. The two terms containing r_{ij}^6 and r_{ij}^8 represent respectively dipole-dipole and dipole-quadrupole dispersion energies. The exponential repulsion term allows us to find a good agreement with experiment [14]. This potential form was used by Bauchy [17] and has shown hopeful results in the study of aluminum and calcium modified silicate properties by means of MD simulations. For our alkali silicate materials we use the parameters developed by Habasaki et al. [11] where the potential of silica glass was proposed by Matsui [18] and was adapted to alkali silicate. All parameters are presented in Table 2. The parameter D is zero for all atoms in the original version of the potential.

To ensure the electro-neutrality of the whole system the different charges are linked to each other by the following relation:

$$q_O = \frac{(1-X)q_{Si} + (2 \times q_M \times X)}{(2-X)} \quad (2)$$

where X is the molar fraction of the alkali oxide in the silicate material.

3. Simulation technique

As mentioned above, our system contains two constituents; alkali oxides which play the role of the modifiers (alkali oxides) and raw

material matrix which consists of silica. The formulation of our chemical compound is written as $(M_2O)_X(SiO_2)_{(1-X)}$; with M: (Na, Li or K) and X represents the molar fraction of the modifier. The X values taken in our simulation vary from 0 to 33%. All the simulations were performed with the LAMMPS package [19], using periodic boundary conditions and an integration time-step of 1 fs. Coulomb interactions were evaluated using a cutoff distance equal to 12 Å. The short-range interaction cutoff was chosen to be 8.0 Å. We know that the choice of these values is very important in molecular dynamics; we note that the values of the used cutoff distances are often omitted in publications for silicate glasses [17]. We started our simulation by placing 2400 atoms as two layers each one contains a given chemical constituent. Then we equilibrated this system for 1 ns by using NVT ensemble at temperature of 300 K. After that, the material is equilibrated at temperature between 3600 K and 5000 K using NPT ensemble for 1 ns. This temperature interval is chosen higher than the melting temperature to insure the fusion of the system. At this temperature range the system reaches a steady state where it loses its memory. Finally we obtain the glassy state by quenching our system from high temperature (liquid) to room temperature 300 K with a cooling rate of 1 K/ps. All atomic visualizations have been done using OVITO [20].

4. Results and analyses

4.1. Fictive temperature determination and glass transition temperature of silica material

As mentioned above, we used 2400 atoms matrix of silicate SiO_2 which is initially generated by placing the atoms in two adjacent surfaces, one contains silicon atoms and the other contains oxygen atoms Fig. 1a. This allowed us to obtain a 3-dimension structure of silicate crystal (Fig. 1b). The system is gradually equilibrated for 1 ns in order to reach liquid equilibrium state. The caloric curves of total energy, as a function of temperature, presents many interesting proprieties directly related to quenching (cooling) process. After this simulation experiment, the obtained liquid is quenched by a cooling rate of 1 K/ps and 0.1 K/ps. The dependence of the fictive temperature T_f (extracted from the caloric curve) as function of conventional temperature is marked by a linear dependence with a slope change at the glass transition temperature. This concept of the fictive temperature T_f can be extracted easily from the caloric curves corresponding to cooling. T_g parameter can be defined, in this case, as the glass transition temperature, which manifests itself by a change of the slope of the total energy as a function of the temperature during the cooling process [21–25]. The fitting correlation coefficient of both total energy curve limits corresponding to low and high temperatures is > 0.99. In this part of the work, we are interested in extracting the fictive temperature through the variation of total energy, in order to define the glass transition.

The system is cooled to temperatures below the transition region and the fictive temperature is determined at low temperatures where the structural relaxation becomes too slow to be detected experimentally as shown in Fig. 2 [26]. During the fictive temperature variation, we can distinguish two limits as was described by Cornelius et al. [26]:

- At high temperatures (liquid state) above the transition region (or transition temperature T_g),

$$\lim_{T \gg T_g} T_f = T$$

- At low temperatures (glassy state) well below the transition region,

$$\lim_{T \ll T_g} T_f = T_f^L$$

Table 1
Effective charges for the different atoms used in this work [16].

	Si	O	Li	Na	K
Effective charge	2.4	X	0.87	0.88	0.85