Journal of Non-Crystalline Solids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Bulk, surface structures and properties of sodium borosilicate and boroaluminosilicate nuclear waste glasses from molecular dynamics simulations

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ARTICLE INFO

Keywords:
Molecular dynamics simulations
Borosilicate glass
Boroaluminosilicate glass
Nuclear waste glass
Glass structure
Surface structure
Properties

ABSTRACT

The bulk and surface structures, as well as physical properties such as ionic diffusion and mechanical moduli, of sodium borosilicate and boroaluminosilicate model nuclear waste glasses with composition similar to the international simplified glass (ISG) have been studied using molecular dynamics simulations with the recently developed partial charge composition dependent potentials. Short and medium range structures of these glasses were analyzed and it was found that, for glass former cations, silicon ion is all four-fold coordinated by oxygen, aluminum is also mainly four-fold coordinated, while boron exists in a mixture of 3- and 4-fold coordination, with the fraction of 4-fold coordinated B (N_4 value) close to but slightly higher than the experimental and theoretical values. The medium range structure features such as network former cation oxygen polyhedral connectivity, sodium distribution around the network formers, and network ring size distribution were characterized. The surface structure was generated from the simulated bulk glass structures and showed sodium enrichment on the glass surface. Addition of alumina to borosilicate glasses increased B N_4 value and overall glass network connectivity that led to improved mechanical properties. Ion diffusion properties, mechanical properties as well as surface characteristics for the simplified ISG have also been investigated with simulations and compared with available experimental data. This detailed atomic structure information provides insight of the physical properties of these glasses and a step further in understanding the chemical durability and dissolution behaviors.

1. Introduction

Borosilicate glasses find wide industrial and technological applications with examples ranging from Pyrex® glass for cooking wares and chemistry lab utilities to borosilicate multicomponent glasses for nuclear waste immobilization. Borosilicate glasses have been the preferred composition for immobilization of high level nuclear wastes generated from either the nuclear fuel cycles or defense related nuclear processes in several countries such as U.S., France, UK, Germany, etc. [1]. In order to establish these glasses as reliable nuclear waste hosts, their chemical and physical properties, especially the dissolution behavior and long-term chemical durability must be thoroughly investigated. A lot of research has been done on the dissolution and corrosion behaviors of borosilicate glass over the past few decades [2–4]. To make results from different research groups more comparable, the international community decided to formulate a common glass composition called International Simple Glass (ISG) that will be studied by researchers around the world [1]. ISG is a six oxide borosilicate glass (Table 1) which has the same cation ratios as those for the major components in the SON68 glass (a 30 components model nuclear waste glass composition). SON68 glass is the inactive reference of the actual used French R7T7-type nuclear waste glass, which is likely the most widely studied nuclear waste material in history. Long-term (more than 25 years) alternation experiment data for SON68 glass are already available as references [5–7]. Gin et al. [8] showed that ISG and SON68 glass have similar initial and residual alternation rates. Despite the wide range of experimental studies of these borosilicate glasses as nuclear waste forms, we know essentially very little on the details of the short and medium range structures of these glasses. The purpose of this work is to use molecular dynamics simulations to model simplified ISG glasses in order to understand the structure features of these glasses and their structure-property relations with the recently developed partial charge composition dependent potentials. The success of molecular dynamics (MD) simulations of boron containing aluminosilicate glasses provides trust for future simulations of more complex multicomponent nuclear waste and industrial glass compositions.

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http://dx.doi.org/10.1016/j.jnoncrysol.2017.09.030
Received 19 May 2017; Received in revised form 13 September 2017; Accepted 14 September 2017

Molecular dynamics simulation provided an effective way to understand the structure and properties of glass materials. Lots of simulations have been performed for silicate glasses that have significantly contributed to the understanding of the structure features and behaviors of these glasses. Borate and borosilicate glasses, on the other hand, have been much less studied using MD simulations. This is mainly due to the lack of reliable potentials that can capture the complex composition dependence of boron coordination change, which forms = the basis of many property changes with composition such as well-known boron anomaly. *ab initio* molecular dynamics (AIMD) simulations [9,10], where interatomic interactions are calculated from first principles methods, would be ideal for simulation of boron containing glasses but AIMD is computationally very expensive, which limits the accessible simulation time and system sizes that can be critical for these glasses. Compared with AIMD [9,10], classical MD has the advantage of computational efficiency and accessible to longer time scale and larger length scales, thus is ideal for the simulation of multicomponent borosilicate nuclear waste glasses. Despite the challenges of empirical potentials, several MD simulations have been reported to study the structures of borosilicate glasses [11–15]. Born-Mayer-Hyggins (BMH) potentials together with three-body terms for Si—O—Si, O—Si—O, and O—B—O triplets were commonly employed to simulate these glasses. Connelly et al. [15] investigated the composition-structure relationships in simplified nuclear waste glass with combination of BHW potential and Stillinger-Weber type three-body potential [16]. Compared with earlier potentials used by Delaye and Ghaleb [12], no restriction on the O—B—O bond angle was applied thus making boron coordination change with composition possible. Kieu et al. [17] developed a set of composition dependent partial charge empirical potential for the SiO_2—B_2O_3—Na_2O glass systems by introducing B—O interactions into the Guillot-Sator (GS) potential of oxide minerals [18]. Deng and Du [19] extended this set of potential to include Al_2O_3 to enable the simulations of a wide range of compositions in boroaluminosilicate glass. The main feature of this set of potential is its composition-dependent atomic charges and parameters for B—O pair interactions that enable them to reproduce the boron coordination change with composition, i.e. the K ($[Na_2O]/[SiO_2]$) and R ($[B_2O_3]/[SiO_2]$) values, in agreement with the Dell and Bray model based on NMR studies [19–21]. The developed potential has been tested in wide range of sodium borosilicate glasses and several series of sodium boroaluminosilicate glasses that showed not only the structure features such as B, Al and Si coordination can be captured by the potential but also mechanical properties such as Young's, Bulk and Shear moduli and vibration density of states could be described well [19]. Very few potentials in the literature are capable to simulate boroaluminosilicate glass systems. Ha and Garofalini recently reported a set of potential for boroaluminosilicate glasses that combines BMH two-body and three-body interactions with long range Coulombic interactions with full atomic charges [22]. Some of the structure features were reproduced by the potential, but it predicted over 20% five coordinated Al in per alkali glass compositions while experiments predicted mostly 4-fold coordination [23]. In addition, there was no quantitative comparison of boron coordination with NMR results thus it is difficult to judge the accuracy of the potential. The purpose of this paper is to apply the composition dependent partial charge potential developed by Du and Deng to study borosilicate and boroaluminosilicate glasses with compositions that are close to the ISG model nuclear waste glass system.

In this paper, we utilized the recently developed composition dependent partial charge potential [19] to perform molecular dynamics simulations to model sodium borosilicate and sodium boroaluminosilicate glasses with composition similar to the ISG. The purpose of this paper is to generate structure models of these model systems and to understand the short and medium range bulk structure features of the simplified ISG glasses, their surface structures and physical properties by using molecular dynamics simulations.

2. Methodology and simulation details

One of the most important input for MD simulations is the empirical potentials. A set of partial charge pair wise potential was used for the simulations of the borosilicate and boroaluminosilicate glasses [19]. The potential has a short range interaction in the Buckingham form and long range Coulombic interaction with partial atomic charges. Importantly, the atomic charges depend on composition in terms of the R ($[Na_2O]/[B_2O_3]$) and K ($[SiO_2]/[B_2O_3]$) ratios. Additionally, the Buckingham A parameter for the B—O interaction is also dependent on the composition. The potential [19] set has been shown to be able to simulate borosilicate and boroaluminosilicate glasses in wide composition ranges. Detailed description of the potential and parameters can be found in ref. [19].

The composition of the original six component ISG is shown in Table 1. We performed two simplified versions of the ISG compositions named SISG and SBN respectively with composition and density shown in Table 1. The glass density was calculated from the method by A. Fluegel that showed good agreement with a wide range of glass compositions including those for nuclear waste glasses [24]. It can be seen that the SISG composition was derived from the original ISG by converting CaO to Na_2O and ZrO_2 to SiO_2 under the same mole percentage. The SBN glass composition was further derived by converting Al_2O_3 in SISG to B_2O_3 and maintaining other oxide components. Introduction of this reference SBN glass is intended to figure out the role that Al plays in the SISG structure.

Simulation boxes consisting of around 6000 atoms were used for all the simulations. Each initial structure was randomly generated with the corresponding density listed in Table 1. Then it was heated to the melting temperature of 6000 K for 100,000 steps (100 ps) to obtain homogeneous melts. For glass generation, the melt was gradually cooled down to 300 K using NVT ensemble with a cooling speed of 5 K/ps. At 300 K, the glass went through relaxation under constant ambient pressure (NPT ensemble) for 100 ps and then was further relaxed under microcanonical (NVE) ensemble for another 100 ps. Configurations in the last 20,000 steps under NVE were recorded every 50 steps (total 400 configurations) for final structural analysis.

Mean Square Displacements (MSDs) have been calculated at different temperatures to obtain the diffusion and dynamic properties of the ions in glass, which is defined as the distance ion travels over a time interval t averaged overall ions of the same type, that is:

$$\langle r^2(t)\rangle = \frac{1}{n}\left\langle \sum_{i=1}^{n} |r_i(t) - r_i(t_0)|^2 \right\rangle \quad (1)$$

The NVE trajectories after NPT runs at each temperature were recorded for MSD calculations. Specifically, after the initial 20,000 steps equilibration with the NVE ensemble, the following 200,000 steps (a time range of 200 ps) performed with configurations recorded every 10 steps. At long enough times, MSD exhibits a linear relationship versus time and ionic diffusion coefficients (D) were quantitatively extracted from the linear regime of the MSD curve via the Einstein equation:

$$D = \frac{1}{6}\lim_{t\to\infty}\frac{\langle r^2\rangle}{t} \quad (2)$$

Table 1
Glass compositions and density.

Glass	Na_2O	B_2O_3	Al_2O_3	SiO_2	CaO	ZrO_2	ρ
	(mol%)						(g/cm^3)
ISG[a]	12.7	16.0	3.8	60.1	5.7	1.7	2.493
SISG[b]	18.4	16.0	3.8	61.8	–	–	2.426
SBN[b]	18.4	19.8	–	61.8	–	–	2.314

[a] Gin et al. [1].
[b] Density calculated using the method from A. Fluegel [24].