



Composition-structure-properties relationship of lithium-calcium borosilicate glasses studied by molecular dynamics simulation

Yueh-Ting Shih, Jau-Ho Jean*

Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan

ARTICLE INFO

Keywords:

Borosilicate glasses
Molecular dynamics simulation
Composition-structure-properties relationship

ABSTRACT

The composition-structure-properties relationship of the lithium-calcium borosilicate (LCBS) glasses, which have a composition of $0.4[(1-x)\text{Li}_2\text{O}-x\text{CaO}]-0.6[(1-y)\text{B}_2\text{O}_3-y\text{SiO}_2]$ with x in the range of 0–1 and y in the range of 0.33–0.83, is investigated by the molecular dynamics (MD) simulation with the Buckingham potential. The structure of the silicon-oxygen tetrahedron is relatively independent of the glass compositions; however, the structure of the boron-oxygen polyhedron and the local environment around the modifier cations change significantly with increasing $[\text{SiO}_2]/[\text{B}_2\text{O}_3]$ ratio (K) and CaO content. The relationships between glass composition and simulated linear thermal expansion coefficient (α_L), glass transition temperature (T_g), self-diffusivity (D), activation energy of electrical conductivity (E_a°) and fragility (m) are strongly affected by the change of glass network structure, and consistent with those of experimental results.

1. Introduction

To investigate the composition-structure-properties relationship of glasses, the molecular dynamics (MD) simulation has been widely used [1–7]. By a series of programmed quenches from a melt, the MD simulation provides a method to closely imitate the forming process of glasses in the laboratory, which yields not only the structural parameters of glasses but also the dynamic properties such as diffusivity and viscosity [8]. To conduct the MD simulation of borosilicate glasses, the Born-Mayer-Huggins (BMH) potential is used [9–11]. Although the simulated structural parameters are in good agreement with experimental results, significant disagreement in Young's modulus is still observed [12]. To minimize the inconsistency, several modified models had been proposed by varying the potential parameters with the coordination number of atoms [13–16], but they are relatively complex to be used. More recently, a simple two-body Buckingham potential is selected for the MD simulation of sodium borosilicate glasses and agrees well with experimental structure and Young's modulus [17]. Similar results are also obtained in the sodium-calcium-strontium-aluminum borosilicate glasses [18].

In this computational research, the lithium-calcium borosilicate (LCBS) glasses are studied by using the MD simulation with the Buckingham potential, and the results are compared with those obtained experimentally. LCBS glasses are industrially important glasses, which can be used as the solid electrolytes in lithium-ion batteries, or the sintering aids in low-temperature co-fired ceramic (LTCC) systems

[19–22]. The composition-structure-properties relationship of the LCBS glasses, which have a composition of $0.4[(1-x)\text{Li}_2\text{O}-x\text{CaO}]-0.6[(1-y)\text{B}_2\text{O}_3-y\text{SiO}_2]$ with x in the range of 0–1 and y in the range of 0.33–0.83, has been investigated previously by using nuclear magnetic resonance (NMR) and X-ray absorption spectroscopy (XAS) [23]. Experimental results show that the fraction of 4-coordinated boron (N_4) increases with $[\text{SiO}_2]/[\text{B}_2\text{O}_3]$ ratio (K) and CaO content, resulting in a decrease in non-bridging oxygen (NBO) and an increase in strength of glass network. The above changes in the glass structure strongly affect the glass properties, of which the activation energy of electrical conductivity (E_a°), glass transition temperature (T_g), dilatometric softening temperature (T_d), Vickers microhardness (H_v), dielectric constant (ϵ), and dielectric loss ($\tan\delta$) deviate from linearity while the CaO substitution increases. The largest deviation is always observed at $[\text{CaO}]/([\text{CaO}] + [\text{Li}_2\text{O}]) = 0.5$, which is enhanced with increasing K value. This interesting phenomenon is referred as the mixed modifier effect (MME). Two mechanisms to explain the MME in the LCBS glasses are proposed, including the weakening bond and the hindrance of ionic transport in the mixed modifier region. In this study, moreover, the structural parameters including radial distribution function (RDF), bond length, bond angle and coordination number, and the glass properties including linear thermal expansion coefficient (α_L), glass transition temperature (T_g), self-diffusivity (D), activation energy of electrical conductivity (E_a°) and fragility (m) of the LCBS glasses are obtained by the MD simulation, and compared with the experimental results to reveal the composition-structure-properties relationship of the LCBS glasses.

* Corresponding author.

E-mail address: jhjean@mx.nthu.edu.tw (J.-H. Jean).

<https://doi.org/10.1016/j.ceramint.2018.03.216>

Received 16 March 2018; Received in revised form 24 March 2018; Accepted 24 March 2018
0272-8842/ © 2018 Published by Elsevier Ltd.

Table 1

The parameter values of the Buckingham potential [14].

Bond	q_i (e)	A_{ij} (eV)	ρ_{ij} (Å)	C_{ij} (eV Å ⁶)
Li–O	0.4725	7042	0.19	0
Ca–O	0.945	155667.9876	0.178	42.259787
B–O	1.4175	15176.81	0.15	9.0821
Si–O	1.890	50306.24729	0.161	46.2979
O–O	–0.945	9022.821263	0.265	85.0924

2. Simulation method

The molecular dynamics program of LAMMPS [24] was used to simulate the composition, structure and properties of the LCBS glasses. The Buckingham potential (U_{BUK}) was used to describe the interaction between ion pairs [18]:

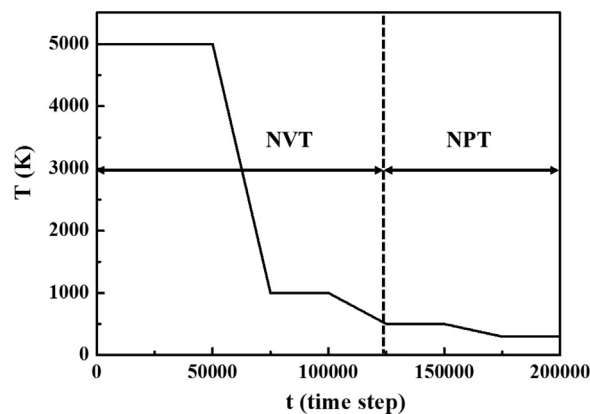
$$U_{\text{BUK}}(r_{ij}) = A_{ij} \exp\left(\frac{-r_{ij}}{\rho_{ij}}\right) + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} - \frac{C_{ij}}{r_{ij}^6} \quad (1)$$

r_{ij} is the distance between two ions of i and j ; q_i and q_j are the effective charges of the ions; A_{ij} , ρ_{ij} , and C_{ij} are the potential parameters describing repulsion and dispersion forces between ions. The potential parameters of Li–O, Ca–O, B–O, Si–O, and O–O are presented in Table 1 [18]. To save the computational resource, the interactions between cations were taken purely Coulombic by setting $C_{ij} = 0$, and $\rho_{ij} = 1$ [17,18]. The parameters for Li–O were fitted to the crystal structure of Li_2O and LiBSiO_4 by using the GULP program [25]. The fitted and experimental lattice parameters are summarized in Table 2. All of the differences between fitted and experimental lattice parameters are less than 5% [26,27]. A short-range cut-off distance of 12 Å was used for all non-Coulombic parts of the Buckingham potential. The Coulombic potential was calculated by using the Ewald sum method with a precision of 10^{-5} [28].

To simulate the forming process of the LCBS glasses, randomly distributed ions (6000–8000 ions) were placed in a simulation box with periodic boundary conditions. The edge length of the box and number of ions were determined by the glass compositions. The simulation was conducted according to the diagram presented in Fig. 1, and the Nosé-Hoover thermostat was used to control the temperature. At the first stage, randomly placed atoms were equilibrated for 50,000 time steps at 5,000 K (1 step = 2 fs) in the constant number of particles (N), volume (V) and temperature (T), i.e., NVT, ensemble. Next, the atoms were gradually quenched to 1000 K for the next 25,000 time steps with a cooling rate of 0.08 K/fs. Throughout the next 25,000 time steps, the system was equilibrated at 1000 K and again quenched to 500 K for the next 25,000 time steps with a cooling rate of 0.1 K/fs. Next 75,000 time steps were conducted in the constant number of particles (N), pressure (P) and temperature (T), i.e., NPT, ensemble to allow the system to fully relax and change the density. In these stages, the glass was relaxed at 500 K, then gradually quenched to 300 K with a cooling rate of 0.004 K/fs and finally relaxed at 300 K. The glass density difference between simulated and experimental results should be controlled less than 10%; otherwise, the edge length of the simulation box and number of ions

Table 2The fitted and the experimental lattice parameters of Li_2O and LiBSiO_4 crystals [18,19].

Lattice parameter	Li_2O			LiBSiO_4		
	Experimental	Fitted	Difference	Experimental	Fitted	Difference
a (Å)	4.61	4.613	0.09%	4.379	4.219	–3.65%
b (Å)	4.61	4.621	0.24%	4.379	4.312	–1.53%
c (Å)	4.61	4.619	0.19%	6.778	6.967	2.79%
α (°)	90	90.02	0.02%	90	88.42	–1.76%
β (°)	90	89.72	–0.31%	90	91.51	1.68%
γ (°)	90	90.47	0.52%	90	91.13	1.45%

**Fig. 1.** The simulated thermal history of glass forming process of the LCBS glasses.

chosen have to be corrected.

The resulting glasses were used to calculate the radial distribution function (RDF), bond length, bond angle and coordination number (CN). The bond length of ion pair was determined at its first peak position in the RDF. The coordination number to oxygen of the specific cation was calculated by integration of corresponding RDF to a certain radius. The radius was determined as a minimum between the first and second peaks of cation-oxygen in the RDF.

The volume expansion curve was calculated by heating the simulation box in the NPT ensemble at a heating rate of 1 K/ps. The volume thermal expansion coefficient (α_v) was determined from the slope of the curve at 298–573 K, and the linear thermal expansion coefficient (α_l) was obtained by $\alpha_v/3$ due to the isotropic nature of glass. The glass transition temperature (T_g) was determined as the intercept temperature of the slope from the curve in solid and supercooling region [29,30].

To calculate the self-diffusivity (D) of glass modifiers, the mean square displacement was calculated in the NVE ensemble and substituted into Eq. (2) [31]:

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \frac{1}{N} \sum_{i=1}^N \langle |r_i(t) - r_i(0)|^2 \rangle \quad (2)$$

where t is time, N is the number of atoms, and r_i is the instantaneous position of an atom. The simulated viscosity was obtained by applying a shearing force onto the simulation box with an engineering shear strain rate of 10^{-3} fs^{-1} in the NVT ensemble. The SLOD algorithm was used to calculate the effect of external force to the equilibrium state [32], and the viscosity was calculated from the ratio of the flux of momentum and its corresponding gradient of velocity [30].

3. Results and discussion

Fig. 2 shows the radial distribution function (RDF) of the first Si–O peak of the LCBS glasses. The Si–O first peak position and its width remain relatively the same with increasing $[\text{SiO}_2]/[\text{B}_2\text{O}_3]$ ratio (K)

Download English Version:

<https://daneshyari.com/en/article/7887131>

Download Persian Version:

<https://daneshyari.com/article/7887131>

[Daneshyari.com](https://daneshyari.com)