



Channel diffusion in a lithium–potassium metasilicate glass using the isoconfigurational ensemble: Towards a scenario for the mixed alkali effect



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ARTICLE INFO

Article history:

Received 18 June 2014

Received in revised form 25 August 2014

Accepted 1 September 2014

Available online 19 September 2014

Keywords:

Silicate glasses;
Molecular Dynamics;
Transport channels;
Ionic conductivity;
Mixed alkali effect

ABSTRACT

Performing Molecular Dynamic simulations and using the isoconfigurational ensemble method, we studied the effect of the potassium cation replacing the half part of lithium ions in glassy Li_2SiO_3 . This so-constructed glassy system has the main ingredients present in an immediate forthcoming definition of mixed alkali effect (MAE) in glasses. We show the existence of dynamic correlations among the cations of the same species, i.e. Li–Li and K–K, whereas a very weak correlation was observed between a distinct pair of cations. With this novel approach we can put into evidence that the alkali ion diffusion evolves in specific channels for the ions: a Li ion prefers the lithium ion channel and a K ion prefers the potassium ion channel. This result is coincident with previous simulational studies using the bond–valence technique to reverse Monte Carlo and recent experimental findings using quasielastic neutron scattering.

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1. Introduction

Relaxation processes in glasses and their inherent manifestations as electrical (ionic) conductivity are still far from being understood at the microscopic scale. Their comprehension plays at present an increasingly urgent role in technology, where considerable progress has been made recently on (for instance): solid-oxide fuel cells, thin film solid electrolytes, electrochemical sensors, supercapacitors, electrochromic windows, etc. For a closer understanding of the ion dynamics in glasses, the study of paradigmatic systems appears as pertinent because (beyond its particular importance) it allows us to extract the essential ingredients of the dynamics, and consequently propose a theoretical scenario for this drama. Silicate glasses are in this direction an appropriate candidate for these purposes in the particular chapter of oxide glasses.

One of the usual concepts inherent to the ion dynamics in oxide glasses, is the concept of “channel” for the diffusion of the moving alkali cations. This concept is closely bounded to the Modified Random Network scenario proposed by Greaves [1] and it proves to be useful to rationalize experimental results. Of course, the concept of channel in glasses is quite different from that employed in crystalline solid electrolytes where the periodic structure plays an essential role in its definition.

The existence of the channels in silicate glasses has been put into evidence theoretically by using the Molecular Dynamics formalism [2], [3], [4], [5], [6], [7], [8] and both theoretically and experimentally in silicate melts [9], [10], [11].

The present authors have shown the existence of these channels in lithium metasilicate glasses in a completely alternative manner to the usual approach [12], [13] by using the isoconfigurational ensemble method (ICEM) proposed by Harrowell et al. [14]. In fact, the use of the ICEM allowed us to put into evidence the existence of similar channels (the same portion of the space) which are found using the pioneering way by Jund et al. [15]. Besides, this methodology has revealed how the local structure and dynamics of the mobile particles in the ‘cage regime’ are the precursors of the dynamics in the diffusive regime [16]. Moreover, it allows us to put into evidence the dynamical connectivity among the ions moving inside the channels [17].

Then the purpose of the present work is to extend our procedure as used on single (lithium) metasilicate glasses to metasilicate mixtures (lithium–potassium). This subject appears pertinent because it defines one of the long standing puzzles of the glass science whose origins are poorly understood: the mixed alkali effect. In a few words, when at a given temperature in a single alkali silicate glass (among many other examples) a systematic substitution by a second alkali oxide occurs, it leads to drops in conductivity of many orders of magnitude before increasing again to the ionic conductivity values corresponding to the second alkali silicate [18]. From different experimental studies [19], [20], [21] it is commonly accepted that the origin of MAE has structural

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character. A recent reference to the “state of the art” of the MAE (among other topics of the ion conduction in disordered solids) can be found in the review by Dyre et al. [22].

One attempt to explain this effect is found in the dynamic structure model (DSM) [23], [24] which invokes the mismatch concept: each type of cation generates its own characteristic local environment corresponding to an energy minimum. In this model (and its successive improvements) the relaxation time and the potential energy associated with the ion site depend on the type of ion, each ion creating its own preferred pathway in the network, and participating in the evolution of the energy landscape.

On the other hand, Swenson and Adams, using the Bond Valence analysis of transport pathways to Reverse Monte Carlo method, showed that the two types of alkali ions were randomly mixed and have distinctively different conduction static pathways of low dimensionality [25], [26].

Thus in the present paper we will address the dynamical aspects emerging in a system consisting of a mixture of alkali cations silicate glasses, by comparing them with the two related single alkali glasses. To do that we use the formalism of the Molecular Dynamics (MD) and the ICeM applied to the study of the mixture $(\text{Li}_2\text{O})_{0.5}(\text{K}_2\text{O})_{0.5}(\text{SiO}_2)$.

From the dynamic/structural approach undertaken in this paper, we note that the existence of the dynamic correlation between the mobile ions and the presence of dynamic pathways, allow us to support the scenario proposed in [26] to describe the mixed alkali effect model.

2. Computer simulations

Classical molecular dynamics calculations were performed on a system of 3456 particles (576 Li, 576 K, 576 Si and 1728 O). The system particles interact by the pair potential of Gilbert-Ida type [27] including the r^{-6} term:

$$U_{ij}(r) = \frac{q_i q_j e^2}{4\pi\epsilon_0 r} - \frac{c_i c_j}{r^6} + f_0 (b_i + b_j) \exp\left(\frac{a_i + a_j - r}{b_i + b_j}\right) \quad (1)$$

The first term in Eq. (1) is the Coulomb interaction with the effective charge numbers q_i , the second term is a dispersive interaction and present for interactions involving only oxygen ions and the last term is a Born–Meyer type potential and takes into account the repulsive short-range interactions.

The parameters of the potentials used were derived on the basis of ab-initio molecular orbital calculations by Habasaki, and the volume of the simulational box ensures that the density corresponds to the experimental density of the glass [28], [29].

The system was prepared by putting the atoms on a cubic box and assigning to each atom velocities drawn from a Maxwell–Boltzmann distribution corresponding to a temperature of 3000 K. The Verlet Algorithm with a time step of 1 fs was used to integrate the equations of motion. Simulations were performed on a cubic box with periodic boundary conditions using the LAMMPS package [30] at two temperatures (700 K and 950 K) well below from the calculated Tg which is equal to 1150 K.

The system was equilibrated at 3000 K in a 2 ns run using the NVE ensemble. Then to reach the working temperature, the system was cooled down from 3000 K to its two final temperatures 950 K or 700 K in 2 cooling steps. Each cooling step (from 3000 K to 2000 K, and from 2000 K to 950 K or 700 K) consists of a 2 ns run using a thermostat to decrease the temperature linearly in the NPT ensemble. Two intermediate periods of equilibration consisting of a 2 ns run in the NPT ensemble were included at 2000 K and at 950 K and 700 K to verify no pressure and temperature drifts. After cooling the system, alternate runs of 100 ps each in the NVE and NVT ensemble were successively repeated to complete 2 ns. Then, the system was equilibrated in a 2 ns run using the NVE ensemble. After this equilibration procedure, trajectories

of 2 ns length were generated in the NVE ensemble for analysis. We calculate the Tg value from the change in the slope in a volume–temperature curve by performing our simulations in the NPT ensemble. The cooling rate was $4.75 \cdot 10^{12}$ K/s.

The usual quantities of interest, such as mean square displacement (MSD): $\langle r^2(t) \rangle$, the non-Gaussian parameter: $\alpha_2(t)$ were calculated. The mean square displacement $\langle r^2(t) \rangle$ is defined as:

$$\langle r^2(t) \rangle = N^{-1} \sum_{j=1}^N \left\langle \left| \vec{r}_j(t) - \vec{r}_j(0) \right|^2 \right\rangle \quad (2)$$

Where $\vec{r}_j(t)$ is the position vector of particle j at instant t and N is the number of the j -particles. The non-Gaussian parameter $\alpha_2(t)$ is defined as:

$$\alpha_2(t) = \frac{3 \langle r^4(t) \rangle}{5 \langle r^2(t) \rangle^2} - 1 \quad (3)$$

The non-Gaussian parameter $\alpha_2(t)$ was introduced by Rahman in his pioneering work, and it is a measure of the deviation from the Gaussian form of the van Hove self-correlation function defined in Eq. (5). Then, the time when $\alpha_2(t)$ reaches its maximum value t^* defines a time interval in which the behaviour of the system is dynamically heterogeneous [31]. This quantity is located roughly at the crossover from the caging to the diffusive regime [12].

As mentioned above, we introduced the isoconfigurational ensemble method (ICeM) proposed by Harrowell et al. [14]. In it, one performs a series of equal length MD runs from the same initial configuration; that is, always the same structure but each one with different initial particle momenta chosen at random from the Maxwell–Boltzmann distribution at the appropriate temperature. Then, having been averaged over the initial influence of the momenta, the observed spatial correlations must be configurational in origin. Accordingly, the propensity of a particle for motion in the initial configuration for a fixed time interval t , has been defined as [14]:

$$\langle \Delta r_j^2 \rangle_{IC} = \left\langle \left| \vec{r}_j(t) - \vec{r}_j(0) \right|^2 \right\rangle \quad (4)$$

Where $|\vec{r}_j(t) - \vec{r}_j(0)|^2$ is the squared displacement of particle j (in such time interval) and $\langle \rangle$ indicates the average over the ensemble (typically 1000 trajectories).

The self space–time correlation function—the van Hove function— $G_s(r, t)$ gives the probability that a particle has moved a distance r in time t . For an isoconfigurational ensemble is written as [32]:

$$G_s(r, t) = N_{type}^{-1} N_{IC}^{-1} \sum_{j=1}^{N_{IC}} \sum_{i=1}^{N_{type}} \left\langle \delta(r - |\vec{r}_{ji}(t) - \vec{r}_{ji}(0)|) \right\rangle \quad (5)$$

Where N_{IC} is the number of trajectories of the ensemble and N_{type} is the total number of i -particles.

3. Results and discussion

3.1. Preliminialia

We have calculated the non-Gaussian parameter $\alpha_2(t)$ for lithium and potassium ions at two temperatures 950 K and 700 K respectively. The non-Gaussian parameter quantifies the deviation of the van Hove function from the Gaussian behaviour. From the results plotted in Fig. 1 we learn that at both temperatures both t^* s for both kinds of cations are coincident. In the same manner, there is a shift of the peaks to lower times when temperature increases. These similarities strongly

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