Potassium mobility in K2O-SiO2 glasses – energy landscape and migration under the electron beam

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The structure of 15 $K_2O.85\ SiO_2$ glass was obtained with help of molecular dynamics method. The standard MD procedure was adopted so that an electric field and/or momentum transfer, coming from the elastic scattering of primary electrons, can be applied to the particular set of ions. The sections of energy hypersurface constructed for static and dynamic displacement of individual potassium ions from their equilibrium position enables semi-quantitative evaluation of migration characteristics. The method of analysis of the full set of static energy maps enabling the calculation of migration activation energy distribution was developed.

Introduction

Migration of potassium ions was extensively studied for the electron-irradiated glasses, where two regimes with different migration mechanisms were observed[1]. The migration strongly depends on the local structure of potassium ion site as well as on the overall glass structure [2].

Due to the ability of following individual particle trajectories, the method of molecular dynamics (MD) [3] is extraordinary suitable for the theoretical study of the above phenomenon. However, different modes of MD application have to be considered to obtain a sufficient degree of understanding of potassium migration mechanism.

The most straightforward results are obtained when only the equilibrium glass structure is calculated. After that, the shape and the amount of the free volume around the individual potassium cation are investigated from the snapshot of the equilibrium structure [4]. The higher free volume, in comparison with the cation size, the greater mobility of the ion is expected. Moreover, the anisotropy of the free volume determines the preferable migration direction. Some quantitative criteria, like inter-atomic distances, coordination numbers, network connectivity and Voronoi polyhedra (VP) tessellation [5], can be used to determine the free volume and its anisotropy [4].

The more realistic possibility is to simulate, using the method of molecular dynamics (MD), the influence of the electric field and/or the momentum transfer on releasing of individual alkali ions from their original sites [6]. This way the field strength needed to release individual potassium ion can be determined as a function of momentum transferred (i.e. obtained from the collision with external particle and/or the thermal collision) accompanied the release. Moreover, the individual site energy is obtained. Another mode of MD application is represented by the study of potential energy hypersurface [7], which is defined as the dependence of potential energy on the coordinates of all particles. In a static version [8], only the sections of the energy hypersurface corresponding to the movement of individual cations are studied, i.e. all particles except for the studied potassium cation are left in their original positions. The static mapping does not reflect time with respect to movement of potassium ions and corresponds therefore to the limiting case of infinite electric field. Combining the last two approaches the dynamic mapping is obtained. In this approach, the ion is driven by external constant field (electric) and energy maps are constructed similarly as in a static case but the relaxation of surrounding structure is enabled. Of course, the extent of relaxation depends on the field strength. The higher field strength, the lower relaxation extent.

The present work studies the migration of potassium cations in binary potassium silicate glasses. The aim of the work is to give brief, mostly graphic overview of the results obtained by various above-mentioned MD approaches.

Method

The ensembles comprising 900 ions were simulated for the composition 15% K2O + 85% SiO2 (255 Si4+, 555 O2-, 90 K+), referred as K15 glass. The effective pairwise interatomic potential of Born-Mayer type [9] was used to describe the interaction among the ions. Parameters of the potentials taken from Garofalini [10]. Ewald summation [11] of the Coulomb force was used in a cube with periodic boundaries, and leap-frog algorithm with time step of 10-15 s was used for numerical integration of Newton's equations of motion. MD simulation started from a random configuration at 6000 K and the system was equilibrated 10 000 time steps (i.e. 10-11 s). The cooling procedure comprised a sudden decrease of the kinetic energy of all atoms followed by the numeric control of the reached temperature (2500 time steps), and equilibration (7500 time steps). Using this procedure, the system was initially cooled from 6000 K to 4000 K, 3000 K, 2500 K, 2000 K, 1750 K, 1500 K, 1250 K, 1000 K, 750 K, 500 K, and finally 300 K. At each temperature, the density of the system (box size) was adjusted to reach zero pressure (<5 kbar [12])

Results

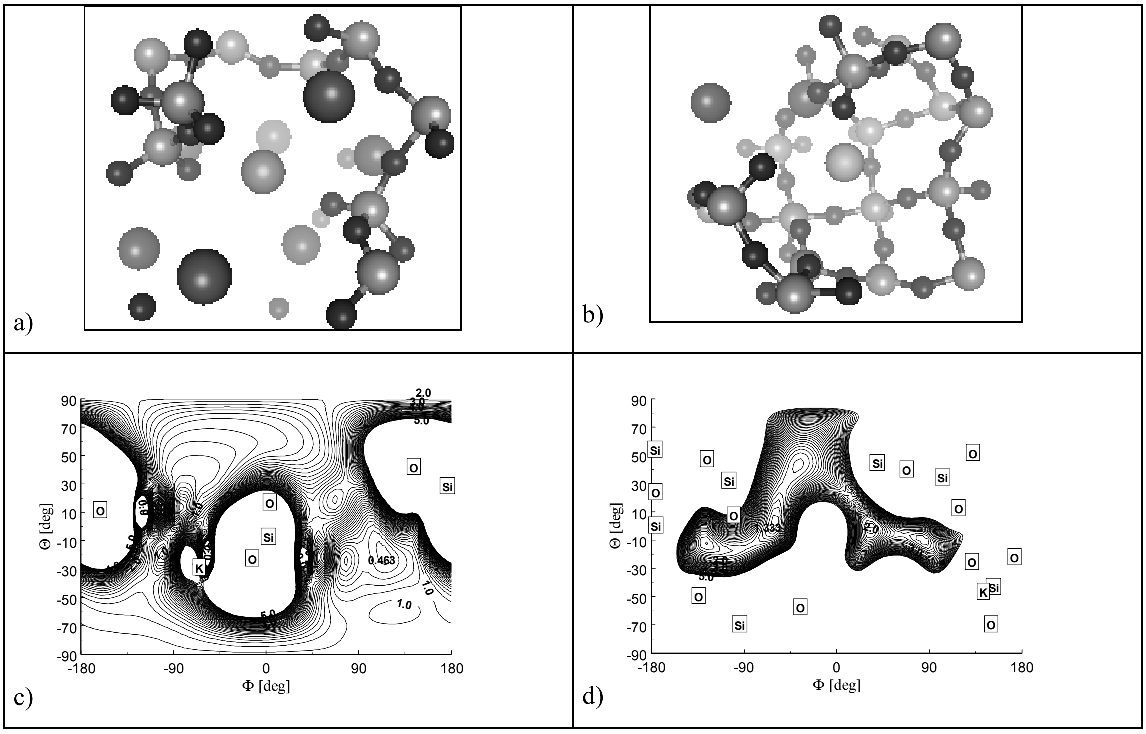

Fig. 1. Stick-and-ball plot around the K^+ ion a) # 1, b) #13 demonstrate a rather open/closed local structure. Corresponding potential energy map at r=2.0 Å for the K^+ ion c) # 1 and d) #13. Energy contour lines plotted from zero to 5 eV with step of 0.1 eV.

The approach reflecting only the snapshot structure around individual K^+ ions illustrates Fig. 1a-b), where the typical examples of closed and open sites were chosen. The strength of the electric field needed to remove the ion away from its original site without the help of momentum transfer is estimated in Fig. 2. Similarly, Fig. 3 demonstrates the release of the ion purely due to the momentum transfer. Migration of three representants among K^+ ions under the combined influence of electric field and momentum transfer is visualised in Fig. 4. The "half-width", z_C, and the depth of the site hole, E_C, (Fig. 5) can be then estimated. In addition, the critical force, F^{crit}, able to release the cation from its site, can be also evaluated. The critical force for the K^+ ion was set to be between 6.10^9 eV/m and 7.10^9 eV/m and the critical half width of the well z_C (corresponding to the critical force) was estimated to be approximately 0.8 Å. It is worth noting that the electric field of the intensity of 6.10^9 V/m pulling the ion 0.8 Å increases its energy about 0.48 eV, while the same displacement caused by the field of intensity 7.10^9 V/m increases the energy of ion about 0.56 eV, so that the energy E_C must be between these two values.

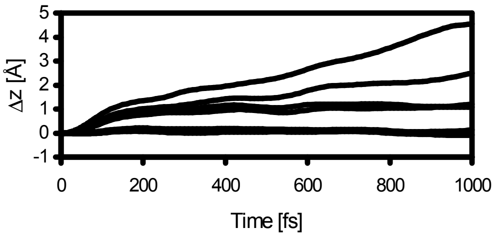

Fig. 2. Averaged displacement from the initial position in the direction of the applied electric field. The curves (from bottom) correspond to the field of intensity 0 V/m, 10^8 V/m, 10^9 V/m, 6.10^9 V/m, 7.10^9 V/m, and 10^{10} V/m. Averaging was performed over 10 potassium ions.

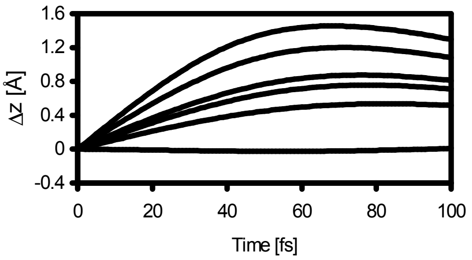

Fig. 3. Averaged displacement from the initial position in the direction of the momentum transfer. The curves (from bottom) correspond to the momentum transfer from elastic scattering of electron with energy of 0 keV, 5 keV, 10 keV, 15 keV, 30 keV, and 50 keV. Averaging was performed over 10 potassium ions.

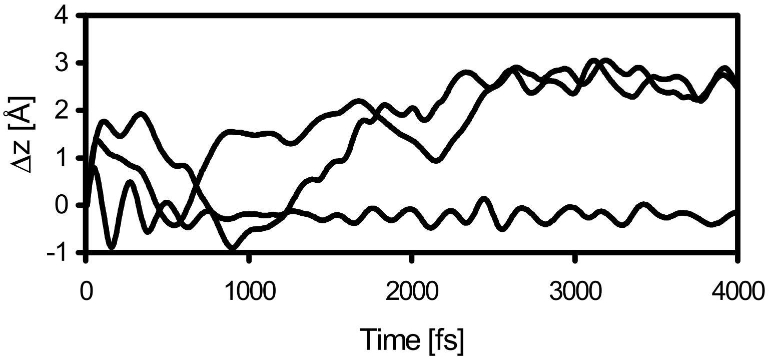

Fig. 4. Trajectories of three different potassium ions with additional momentum transfer corresponding to 50 keV primary electrons and drawn from their initial position by the electric field of intensity 10^8 V/m in the direction of the momentum transfer.

The distribution of activation energies, calculated by static approach from the contour maps, as a minimum energy barrier needed to be overcome by K^+ from its original site to adjacent one, is shown in Fig. 5. The values are influenced by the static approach, which neglects the structure relaxation during potassium transport. This relaxation opens the door for the migrating ion, effectively resulting in a decrease of activation energy. It can be speculated that the overestimation, coming from static approach, is larger for glass with higher content of alkalis (K15 glass) due to less connectivity of network.

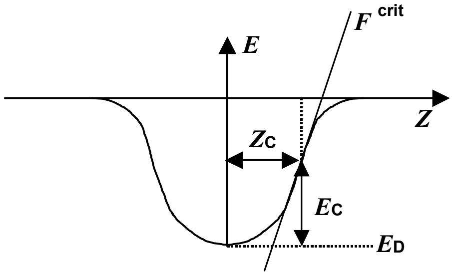

Fig. 5. Potential well characterised by its depth E_D and by a critical force F^{crit}.

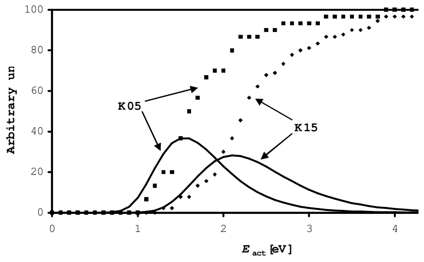

Fig. 6. Distributions of potassium activation energies in K05 and K15 glasses - solid lines, and the corresponding function of the relative number of K^+ ions.

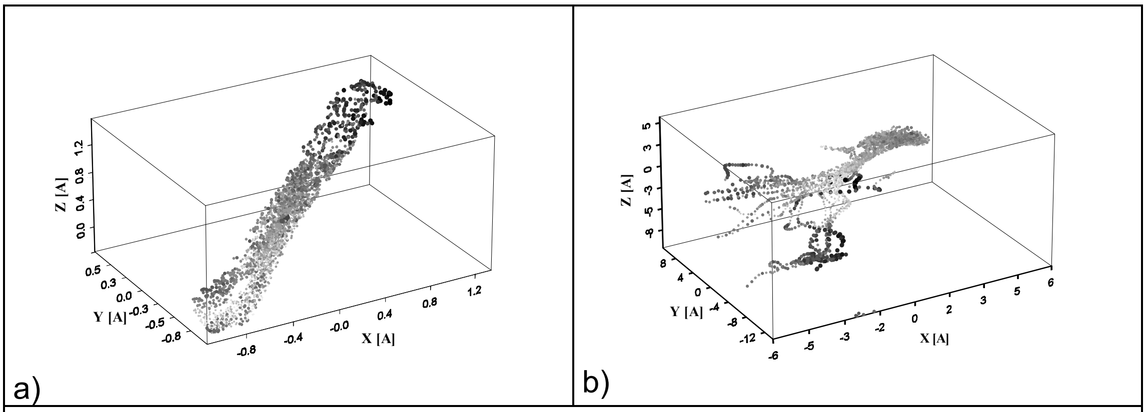

Fig. 7. Accumulated K+ ion #1 position snapshots. The ion is driven by the electrostatic field of the strength a) 10^9 V/m, and b) 10^{10} V/m. The resulted pictures are accumulations over all field directions.

The last figure, Fig. 7, demonstrates the anisotropy of energy landscape around the potassium. The anisotropy is present not only for larger distances where an influence of neighbours is expected, but also for a close surrounding of the equilibrated position of K^+ ion. The energy mapping is in this case performed by the variation of the strength of the electric field, so that the lower strength is chosen, the more sensitive is the K^+ response. Moreover, low strength maps only close surrounding of the ion, while higher strength is able to reflect the surrounding network structure.

Acknowledgment

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