

Loosening of the structure in a mixed alkali glass

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It is known that both loosening of glass structure and reduction of ionic diffusion coefficient occur in the mixed alkali system. We have performed molecular dynamics simulations of the mixed alkali system and have observed both characteristics in different time regions. A large decrease in the ionic diffusion coefficient is due to the interception of the jump where the jump path keeps its characteristics. The contribution of accelerated dynamics due to cooperative jumps decreases in such paths. On the other hand, in longer time regions, the motion of the framework has been found to accompany the small number of jump events of alkali metal ions to unlike ion sites. [S1063-651X(98)03210-3]

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I. INTRODUCTION

In many glasses, such as silicates, transport coefficients fall markedly when an alkali metal ion is mixed with other alkali metal ions; this phenomenon is known as the “mixed alkali effect” [1]. The effect is a key phenomenon in understanding the mechanism of ion conduction in glasses. Ingram [2] has reviewed the recent development of studies related to the mixed alkali effect. He pointed out that the mixing of cations leads both to a loosening of the structure and, at the same time, to immobilization of the cations. The mixed alkali metasilicate glass (LiKSIO_3), which is made up of cations and a framework structure consisting of chains made of SiO_4 units, was examined in our previous work [3]. A distinct part of the Van Hove functions revealed that the Li ion cannot enter a site previously occupied by K and vice versa for at least 192 ps at 700 K in the glass. On the other hand, both cations can enter the sites previously occupied by like ions. These results mean that the lifetime of the former pathway in our simulation is fairly long compared to the jump process of like ions. A similar tendency was observed by Balasubramanian and Rao [4] in related systems. In the present work, the molecular dynamic (MD) simulation has been extended up to 1 ns in order to examine the relationships between the motion of alkali metal ions and that of the framework structure.

II. MD SIMULATION

MD simulations were performed in the same way as in previous studies [3,5–9]: The numbers of the particles in the basic cube was 144 M (72 for Li and 72 for K in the mixed alkali system), 72 Si, and 216 O in M_2SiO_3 . The volume was fixed as that derived by the *NPT* (constant pressure and temperature) ensemble simulation. The glass transition temperatures were approximately 830 and 850 K for the Li and the mixed systems, respectively. Gilbert-Ida-type of pair potential functions [10] plus an r^{-6} term were used. The parameters of the potential used have been derived previously on the basis of *ab initio* molecular orbital calculation [9] and

their validity has been checked in the liquid, glassy, and crystal states under constant pressure conditions. The runs up to 1 ns (250 000 steps) for the Li_2SiO_3 , and K_2SiO_3 systems and for the mixed alkali system at 700 K were analyzed.

III. RESULT AND DISCUSSION

In our previous work [3,5,8], the mechanism of the mixed alkali effect was explained as follows. In LiKSIO_3 glass, each cation has individual jump path. The paths are intercepted by each other. The interceptions of the paths result in a decreased number of cooperative jumps, which was found to be the main mechanism of ion conduction in the pure systems [6]. A log-log plot of the mean square displacement (MSD) of atoms at 700 K up to 1 ns region is shown in Fig. 1(a) for Li_2SiO_3 and in Fig. 1(b) for LiKSIO_3 . The slope of Li in Fig. 1(a) changes at about 300 ps. The inflection is caused by the overlap of the localized motion and the diffusive motion due to cooperative jumps [6]. The accelerated motion due to cooperative jumps is characterized as Lévy flight dynamics [6,11]. The motion of Si and O changes at about 100–200 ps. The slopes in longer time regions are negligibly small, as expected for the glassy state. The larger slopes for Si and O at short times are due to localized motion of the chains. The changes of the slopes for Si and O are not smooth, due to restricted spring motion arising from the chain structure.

On the other hand, the motion of alkali metal ions in the mixed alkali system is one order less than in the pure systems. Simultaneous (or nearly simultaneous) changes of slopes of all species are found at about 600 ps even after an averaging procedure using a large time window (80 ps) and point to the existence of a cooperative motion of all species, although the number of events is small. The cooperative motion of cations with the chain structure is one of the characteristics of loosening of the framework structure.

Figure 2 shows the changes with time of the framework structure made up of SiO_4 units for (a) Li_2SiO_3 and (b) LiKSIO_3 , both at 700 K. In spite of the large movement of

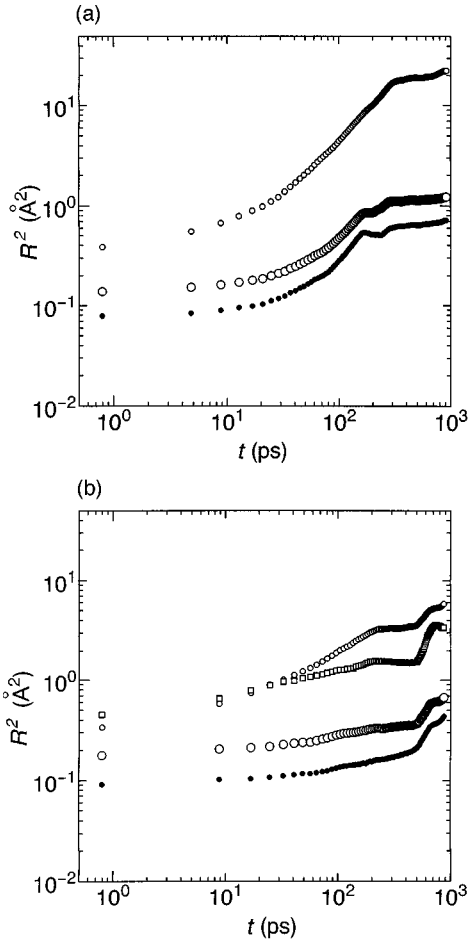


FIG. 1. A log-log plot of the mean square displacements of atoms at 700 K for (a) Li_2SiO_3 and (b) LiKSiO_3 : Li, \circ ; O, \square ; Si, \bullet ; and K, \square .

oxygen atoms, the position of the Si atoms is fairly fixed in Fig. 2(a). On the other hand, the motion of both O and Si is smaller, but the chain structure seems to move collectively for LiKSiO_3 . To learn the details of these motions, Van Hove functions have been examined. In Figs. 3(a), 3(b), and 3(c), the Van Hove function (distinct part) of the Li-Li, Li-K, and K-Li pairs for LiKSiO_3 at 700 K from 0 to 800 ps are shown, respectively. The distinct part of the Van Hove function is defined by

$$G_d^{\alpha'\beta'}(r,t) = (1/N_{\alpha'}) \sum_{i=1}^{N_{\alpha'}} \sum_{j=1}^{N_{\beta'}} \langle \delta(\mathbf{r} - \mathbf{r}_i^{\alpha'}(0) + \mathbf{r}_j^{\beta'}(t)) \rangle. \quad (1)$$

In Fig. 3(a) peaks at $r=0$ appear in the functions, which indicates that ions move into sites previously occupied by the same kind of ions. We observed broadening of the first peak of the Van Hove function at 3.6 Å for Li-Li pairs and new shoulders appeared at 1.5 Å with the lapse of time. New shoulders were also observed for the K-K pair. These results mean that the paths of both cations change gradually over 1 ns. Figures 3(b) and 3(c) show the Li/\bar{K} (\bar{A} means the site previously occupied by A) and $\text{K}/\bar{\text{Li}}$ jumps during a 800 ps run, although we did not observe such events over 192 ps in the previous work [3]. Such jumps are also observed at

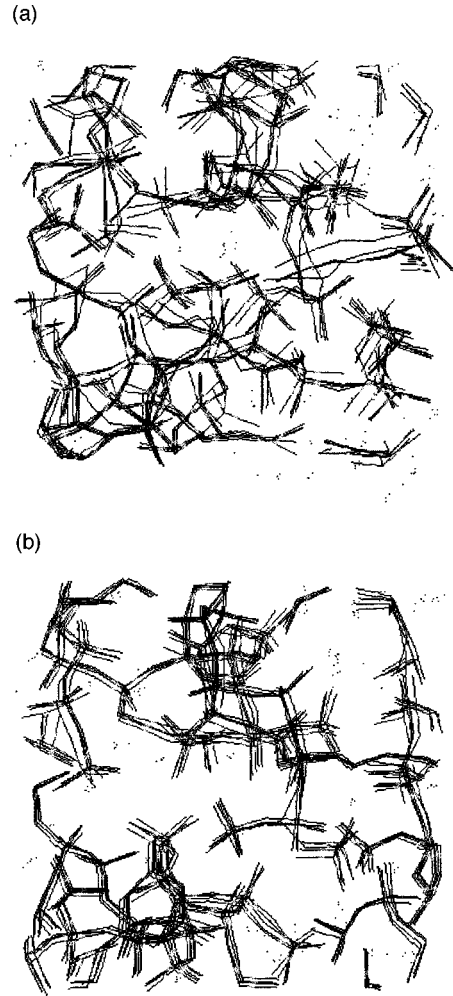


FIG. 2. Framework structures of (a) Li_2SiO_3 and (b) LiKSiO_3 at 700 K. The Si-O within 2 Å are connected at $t=0, 200, 400, 600,$ and 800 ps.

higher temperature (at 800 K) [5,8]. Since no shoulders in the function of Li-Li and K-K pairs were observed for a 1 ns run with pure salts at 700 K, the change must be related to the jump events among unlike ion sites. In Fig. 4 the Van Hove functions (distinct part) of the Si-Si pair in both Li_2SiO_3 and LiKSiO_3 are shown. In Li_2SiO_3 , the heights of the first peak were nearly constant from 200 to 800 ps. This and the flat part in the corresponding MSD mean that the structural relaxation of the chain is nearly frozen. On the other hand, in the Van Hove functions (distinct part) of the Si-Si pair in the LiKSiO_3 system, the first peak became lower and broader with the lapse of time. A similar tendency was observed for the Li-O, O-O, and Li-Si pairs. These results mean that the structural relaxation of the chains still occurs at longer times in the mixed alkali system, i.e., a loosening of the framework structure occurs. Direct calculations of the viscosity of the moving structures have not been done yet since these require much longer simulations. The structural changes in the chain are accompanied by the jump events among unlike ion sites because the large size difference of Li and K causes strain, as has been discussed by LaCourse [12]. He assumed the formation of mixed alkali defects in mixed alkali glass, which decreased viscosity. The magnitude of the effect will depend on the electrical and

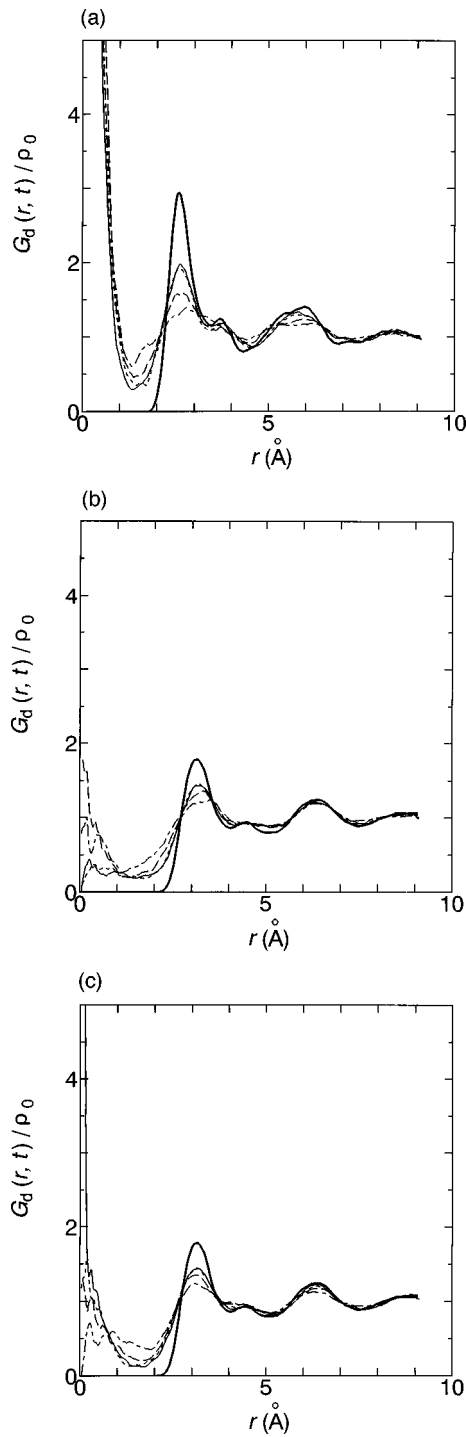


FIG. 3. Van Hove function (distinct part) for (a) Li-Li pairs, (b) Li-K pairs, and (c) K-Li pairs in LiKSiO_3 at 700 K. The curves, from top to bottom at the original first peak, are for $t=0, 200, 400, 600,$ and 800 ps.

mechanical strain caused by defect formation and the rate of stress relaxation in the neighborhood of the defects.

Jumps among unlike ion sites were also suggested in the dynamic structural model by Maass *et al.* [13]. They assume that ions A^+ and B^+ were able to visit each other's sites and thus actively interfere with each other's conducting pathways. They tried to explain the sharp decrease in the host cation mobility in the dilute foreign alkali region by such

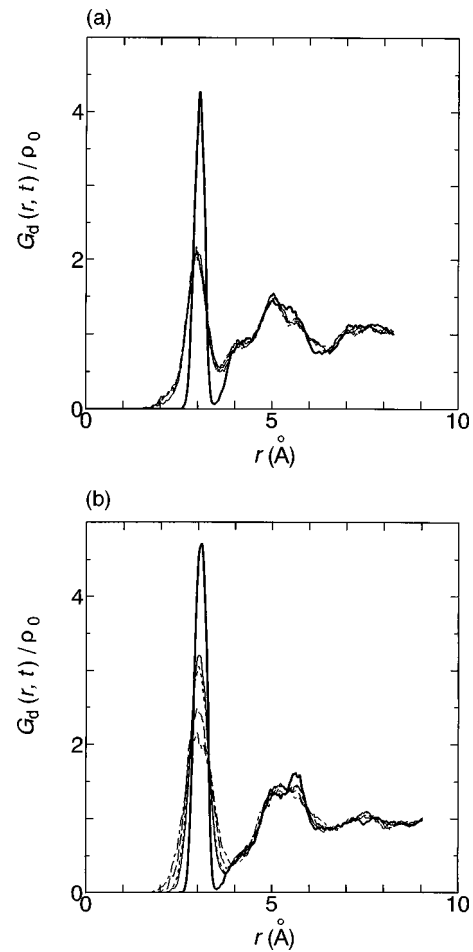


FIG. 4. Van Hove function (distinct part) for Si-Si pairs in (a) Li_2SiO_3 at 700 K and (b) LiKSiO_3 at 700 K. The curves, from top to bottom at the original first peak, are for $t=0, 200, 400, 600,$ and 800 ps.

motion. However, at least in a system having a network former and modifier, the jumps among unlike ion sites contribute to the loosening of the structure rather than decreasing the mobility. The situation is quite similar to that observed in the molten state, where a fixed pathway is not observed [5]. Another possible explanation of the sharp decrease in the host cation mobility is the fact that cooperative jumps are highly sensitive to blockage of the path. Evidence of this effect will be shown in a separate paper, where Monte Carlo simulations considering cooperative jumps were performed. Cooperative jumps of the same kind of cations were confirmed to be the main mechanism of ionic diffusion in a pure system [6] and interception of the jump paths resulted in a decrease of the cooperative jump motion.

Therefore, we must consider the role of cooperative jumps in the mixed alkali effect. In the dynamic structure model, an A ion has a large probability to enter the site previously occupied by the same kind of ion. Such motion will be made more difficult by the existence of other ions. Thus the tendency observed by them is similar to some extent to that expected for the existence of the cooperative motion of ions.

We can explain the difference of dynamics for pure and mixed alkali glasses as follows.

(i) In the pure alkali metal glass, the conduction relaxation time ($\tau_c = \tau_{LiLi}$) is much shorter than that of the framework (τ_f), namely, $\tau_c \ll \tau_f$. The motion of alkali ions is accompanied by the motion of oxygen, but is not coupled with the motion of the whole chain structure (the positions of Si atoms are almost fixed).

(ii) In the mixed alkali glass, the relaxation time due to jumps among unlike sites is on the same order as that in the chain structure because these motions are cooperative, i.e., the size difference of unlike cations causes successive and/or simultaneous relaxation of chain structures. Even in the mixed alkali system, the relaxation of Li/\bar{Li} and K/\bar{K} jumps can be faster than that of the framework, but the relaxation times of jumps among like ion sites decreases considerably compared to the pure systems, that is, $\tau_c (= \tau_{LiLi}, \tau_{KK}) \leq \tau_{LiK} \sim \tau_{KLi} \sim \tau_f$. (τ_{LiK} and τ_{KLi} mean the relaxation times by Li/\bar{K} and K/\bar{Li} jumps, respectively.)

The concept of coupling and decoupling has been discussed by Angell [14]. He has pointed out that the ionic transport and dielectric loss processes are decoupled with the viscous flow relaxation in high conduction pure alkali metal glasses. The decoupling index is known to decrease in mixed alkali systems considerably. Our observations are consistent with these findings. Therefore, the mechanism observed in the present work will probably be applicable to many pure and mixed alkali glasses.

IV. CONCLUSION

In the simulation up to times of 1 ns, the structural relaxation of the framework of the mixed alkali glass is confirmed. This relaxation can explain the loosening of the chain structure in the mixed alkali system. The loosening of the structure and decreased mobility of cations in the mixed alkali system can be explained as follows.

In a pure alkali system, cooperative motion of the like ions causes accelerated dynamics and this motion is decoupled with the motion of the glass forming structure. On the other hand, the jump paths of both kinds of alkali ions are independent, at least on a shorter time scale, but are intercepted by each other in the mixed alkali system. This causes more localized motions of the alkali ions and decreases transport. This effect is larger for the cooperative jump motion than for single ion motion. At longer time scales, Li/\bar{K} and K/\bar{Li} jumps occur accompanied by the changes in chain structures. This results in loosening of the frame structure in spite of the slowing down of the ion dynamics.

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