CHEMISTRY LETTERS, pp. 367-370, 1991.

Preparation and Ionic Conductivity of the Rapidly-Quenched Glasses in the System $Li_2O-TiO_2-P_2O_5$

Nobuya MACHIDA,* Kazuko FUJII, and Tsutomu MINAMI
Department of Applied Chemistry, University of Osaka Prefecture,
4-804 Mozu-Umemachi, Sakai, Osaka 591

Li^+ ion-conducting glasses were prepared in the system $Li_2O-TiO_2-P_2O_5$ by rapid quenching. These glasses had high ionic conductivities of 10^{-2}-10^{-5} S m^{-1} at 400 K. The conductivities of these glasses increased and the activation energy for conduction decreased with an increase in the Li_2O content of the glasses. At a given Li_2O content, the conductivities at 400 K increased with substituting TiO_2 for P_2O_5.

For several years many investigations have been made in the field of Li^+ ion solid electrolytes for their application to high energy density batteries, electrochromic devices, sensors, and so on. A desirable electrolyte for practical use requires the high ion conductivity over 10^{-1} S m^{-1}, the chemical and electrochemical stability, low cost, and ease of preparation. Some of the solid electrolytes, such as Li_3N[1] and sulfide based glasses,[2-4] have high Li^+ ion conductivities of the order of 10^{-1} S m^{-1} at room temperature, but they are unstable in air. Other solid electrolytes like LISICON[5] and oxide based glasses,[6-7] which are stable in air, have lower conductivities in the range of 10^{-3} to 10^{-5} S m^{-1}.

Recently, Aono and co-workers[8-10] reported that the $LiTi_2(PO_4)_3$ based solid solutions, $Li_{1+x}Ti_{1-x}M_x(PO_4)_3$ (M = Al, Cr, Fe, In, Ga, Sc), showed remarkable high Li^+ ion conductivities in the range of 10^{-2} to 10^{-1} S m^{-1} at room temperature, and that the highest conductivity, 7 x 10^{-2} S m^{-1} at 298 K, was found in $Li_{1.3}Ti_{0.7}Al_{0.3}(PO_4)_3$. However, $LiTi_2(PO_4)_3$ (x=0) sintered pellets were reported to be poor in the Li^+ ion conductivity. In order to obtain the high ion conductivity, the addition of some lithium compounds, such as Li_2O, Li_3PO_4, Li_3BO_3, and Li_2SO_4, was necessary as sintering agents for the $LiTi_2(PO_4)_3$ polycrystalline pellets. These results suggest that the grain boundary of sintered pellets seriously affects to the total conductivity. It is interesting to investigate the Li^+ ion conducting properties of the glasses in the system $Li_2O-TiO_2-P_2O_5$, since glassy or amorphous materials have some advantages compared to crystalline materials; for example, isotropic properties, no grain boundary, a wide range of selection of composition, and thereby a wide range of property control, and so on.

In this paper, we report the preparation and electrical properties of the rapidly quenched glasses in the system $Li_2O-TiO_2-P_2O_5$.

A mixture of reagent-grade Li_2CO_3, TiO_2, $(NH_4)_2HPO_4$ of appropriate compositions was heated in a platinum crucible for 12 h at a temperature in the range of 870 to 1270 K, depending on composition. The product was ground and pressed to form a rod and then sintered at a temperature in the range of 870 to 1270 K. The sintered rod was melted and the melt was quenched by the rapid-quenching apparatus, which was previously reported in detail[11]. The conductivity was measured for the glasses, on which two parallel gold electrodes apart by 0.5 mm were evaporated. The measurements were carried out in a dry nitrogen atmosphere in the frequency range of 110Hz to 1MHz by use of a G-C bridge (Ando Denki, TR-1C). The values of conductivity were determined by employing the complex impedance analysis.

Figure 1 shows the glass-forming region in the system $Li_2O-TiO_2-P_2O_5$ by rapid quenching; the glass-forming region by the usual melt quenching determined by Kishioka et al.[12] is shown by the broken line in the figure for comparison. In the

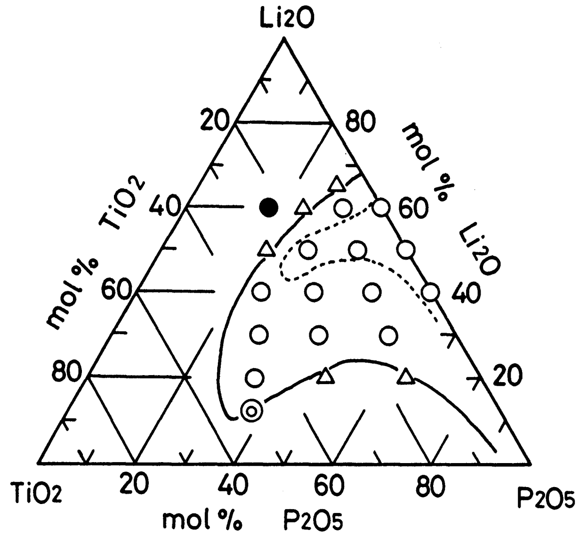

Fig. 1. Glass-forming region in the system $Li_2O-TiO_2-P_2O_5$ by rapid-quenching; (o) glassy, (△) partially crystalline, (●)crystalline. The glass-forming region by usual melt quenching is shown by the broken line.[12]

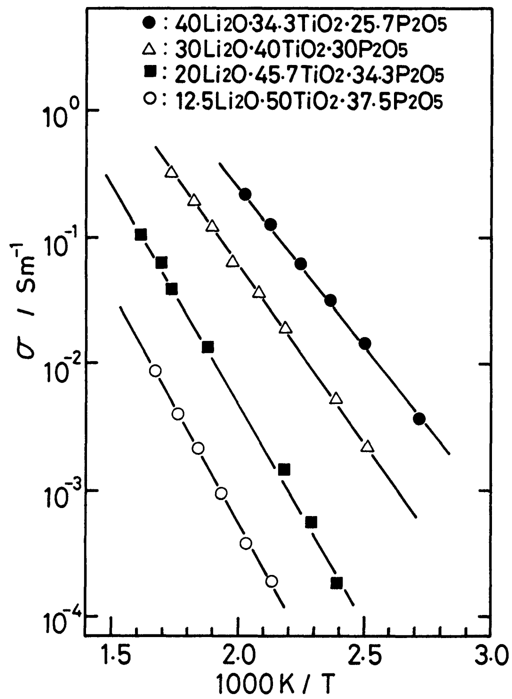

Fig. 2. Temperature dependence of conductivity of glasses in the system $Li_2O-TiO_2-P_2O_5$.

figure open circles, open triangles, and closed circles denote glassy, partially crystalline, and crystalline samples, respectively. The composition of $LiTi_2(PO_4)_3$ is denoted by a double circle, and at this composition we obtained the partially crystalline sample. The glass-forming region by rapid quenching is larger than that by usual melt quenching. The obtained glasses in the system Li_2O-TiO_2-P_2O_5 are stable in air.

Figure 2 shows some examples of the temperature dependence of the conductivities of glasses in the system Li_2O-TiO_2-P_2O_5. The conductivities, σ, are a good fit to the Arrhenius type equation; $\sigma T = A \exp(-Ea/RT)$, where A is the preexponential factor, Ea the activation energy for conduction, and R the gas constant.

Figure 3 shows the composition dependence of the conductivity at 400 K, σ_{400}, of the glasses in the system Li_2O-TiO_2-P_2O_5. In this figure, the composition parameter, x, denotes the ratio of the number of titanium atoms to the total number of titanium and phosphorus atoms included in the glasses; i.e. x = [Ti] / ([Ti] + [P]). The conductivities, σ_{400}, of the glasses logarithmically increase with an increase in the Li_2O content in each x value. The σ_{400} of the sintered $LiTi_2(PO_4)_3$ (x=0) pellet without sintering agents is shown by a closed square for comparison.[9] The σ_{400} of the polycrystalline $LiTi_2(PO_4)_3$

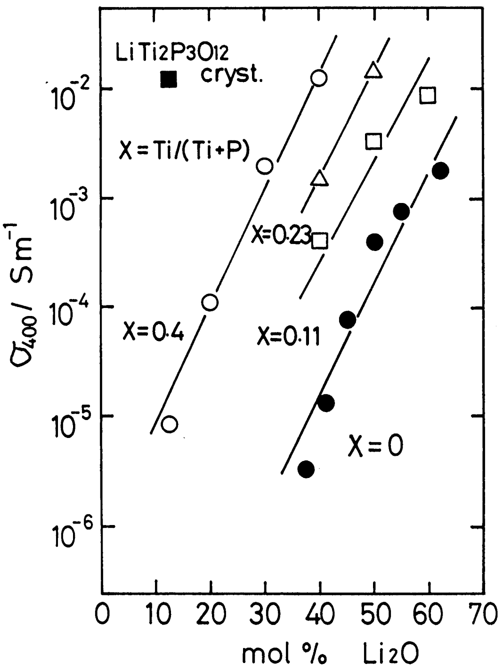

Fig. 3. Conductivity at 400 K, σ_{400}, of the glasses in the system Li_2O-TiO_2-P_2O_5 as a function of composition.

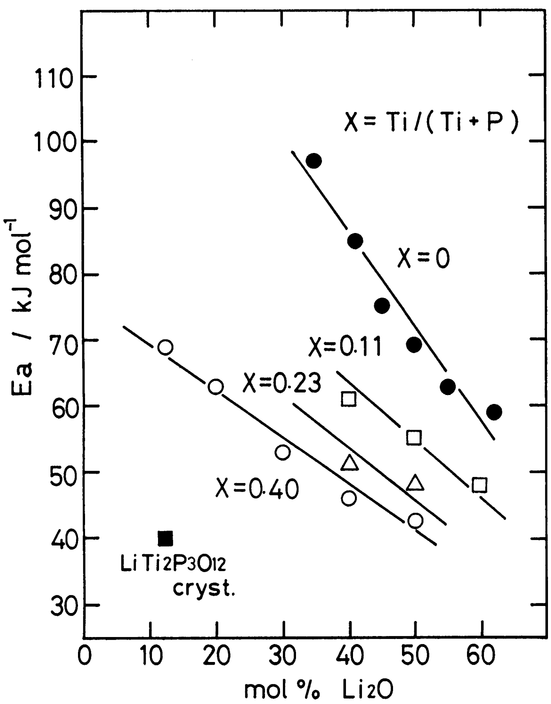

Fig. 4. Activation energy for conduction, Ea, of the glasses in the system Li_2O-TiO_2-P_2O_5 as a function of the composition.

(x=0) is higher by 3 orders of magnitude than that of the partially crystalline glass of the same composition. The highest σ_{400} of glasses in the system Li_2O-TiO_2-P_2O_5 is higher than 10^{-2} S m^{-1}, and this conductivity is as large as that of $LiTi_2(PO_4)_3$ polycrystalline pellet.

At a given Li_2O content, σ_{400} increases with an increase in the x value and also with a substitution of TiO_2 for P_2O_5. This increase in conductivity is probably concerned with the structural change of the glasses. The non-bridging oxygens in the glasses decrease with a substitution of TiO_2 for P_2O_5, because the titanium atoms are probably present as TiO_6 octahedra in the glasses. The structural study of these glasses will be published elsewhere.

Figure 4 shows the composition dependence of the activation energies for conduction, Ea. The Ea decreases with an increase in the Li_2O content of the glasses in each x value. At a constant Li_2O content, Ea decreases with an increase in the composition parameter x. The behavior of Ea with composition is very similar to that of the conductivity at 400 K.

In conclusion, the glasses in the system Li_2O-TiO_2-P_2O_5 were prepared by rapid quenching. These glasses showed high ionic conductivities of 10^{-2} to 10^{-5} S m^{-1} at 400 K. The σ_{400} of the glasses logarithmically increased with an increase in the Li_2O content in each x value. For the glasses with a constant Li_2O content, σ_{400} of the glasses increased and Ea decreased with substitution of TiO_2 for P_2O_5. These behavior of σ_{400} and Ea were probably concerned with the concentration of non-bridging oxygens in the glasses.

This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas, New Functionality Materials —— Design, Preparation and Control, the Ministry of Education, Science and Culture of Japan (No. 02204015).

References

1) U. von Alpen, M. F. Bell, and T. Gladden, Electrochim. Acta, 24, 741 (1979).
2) H. Wada, M. Menetrier, A. Levasseur, and P. Hagenmuller, Mat. Res. Bull., 18 189 (1983).
3) J.H. Kennedy and Y. Yang J. Solid State Chem., 69, 252 (1987).
4) J.H. Kennedy, Mat. Chem. Phys., 23, 29 (1989).
5) U. von Alpen, M.F. Bell, and W. Wichelhaus, Electrochim. Acta, 23, 1395 (1978).
6) D. Ravaine, K. Nassau, and A. M. Glass, Solid State Ionics, 13, 15 (1984).
7) M. Tatsumisago, K. Yoneda, N. Machida, and T. Minami, J. Non-Cryst. Solids, 95/96, 857 (1987).
8) H. Aono, E. Sugimoto, Y. Sadaoka, N. Imanaka, and G. Adachi, J. Electrochem. Soc., 136, 590 (1989).
9) H. Aono, E. Sugimoto, Y. Sadaoka, N. Imanaka, and G. Adachi, Chem. Lett., 1990, 331.
10) H. Aono, E. Sugimoto, Y. Sadaoka, N. Imanaka, and G. Adachi, J. Electrochem. Soc., 137, 1023 (1990).
11) M. Tatsumisago, T. Minami, and M. Tanaka, J. Am. Ceram. Soc., 64, C-97 (1981).
12) A. Kishioka, Bull. Chem. Soc. Jpn., 51, 2259 (1978).

(Received November 19, 1990)