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# ELECTRICAL CONDUCTIVITY OF LITHIUM BORATE GLASSES

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The electrical conductivity of the lithium borate glass systems, $LiCl-Li_2O-Al_2O_3-B_2O_3$, has been measured as a function of composition and temperature. The lithium ion conductivity increases with increasing $Li_2O$ and LiCl contents. The highest conductivity of $7 \times 10^{-3} (\Omega \cdot cm)^{-1}$ was obtained at 300°C.

Solid lithium ion conductors are of high interest as the electrolyte for high energy density battery. The conductors reported previously are in the form of poly- or single-crystal and no glassy solid with high lithium ion conductivity has been reported. In this communication, the electrical conductivity of lithium borate glass with and without lithium chloride is described.

Reagent grade boric acid, lithium carbonate, γ-alumina and lithium chloride were used as starting materials. About ten grams of the raw materials were weighed, mixed throughly, and melted in a platinum crucible at the temperatures near 910°C for the batches with lithium chloride and near 1000°C for the batches without lithium chloride for one hour. Then, the melts were quenched to room temperature in a steel mould. The obtained glass was formed in the shape of a tablet of about 10 mm in diameter and about 5 mm in thickness for the conductivity measurement, and gold was evaporated onto the surfaces so as to use as the electrodes. The ac conductivity was measured with conductance bridge mainly at 20 KHz. When the resistance of sample is larger than 100 KΩ, the dc conductivity was measured also. The NMR spectra of $^7Li$ were measured with a JEOL broad-line spectrometer at 16 MHz.

The glass formation in the $Li_2O-B_2O_3$ system was reported by Sastry and Hummel,[1] who showed that a melt could be quenched to glass in the range from 0 to 20 m/o $Li_2O$. In the $LiCl-Li_2O-B_2O_3$ system, however, a melt could be obtained as glass in the range from 0 to 49 m/o $LiCl+Li_2O$ with the maximum LiCl content of 22 m/o as shown in Fig. 1.

Further, the glass with higher lithium content was obtained by adding $Al_2O_3$ to the system. The glass formation in the system $LiCl-Li_2O_3-(3.5 \pm 0.5$ m/o) $Al_2O_3 - B_2O_3$ is shown in Fig. 1, where mol % of the constituents is represented in the ternary system $LiCl-Li_2O-B_2O_3$. At the highest $LiCl + Li_2O$ content of 53 m/o, a glass was obtained in which the upper limit of LiCl content was 24 m/o. The typical temperature dependence of the electrical conductivity of the glass of the system $LiCl-Li_2O-Al_2O_3-B_2O_3$ containing various LiCl and $Li_2O$ contents is shown in Fig. 2. The highest conductivity of $7 \times 10^{-3}$ $(\Omega \cdot cm)^{-1}$ at 300°C and the lowest activation

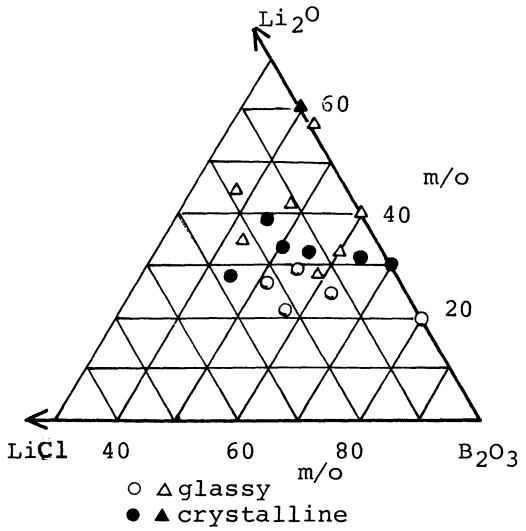


Fig. 1. Glass formation in the LiCl-$Li_2O$-$B_2O_3$ ( ○, ● ) and LiCl-$Li_2O$-$Al_2O_3$-$B_2O_3$ ( △, ▲ ) systems.

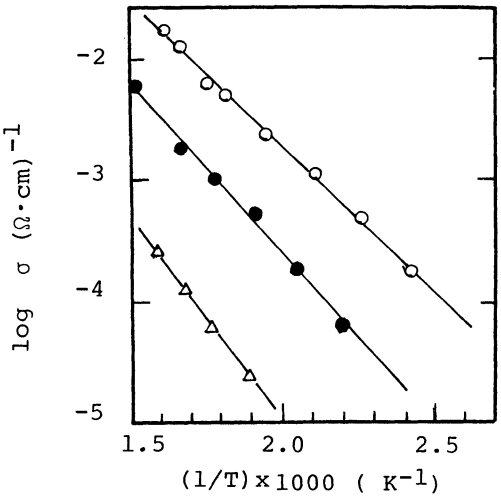


Fig. 2. Temperature dependence of the electrical conductivity ( $\sigma$ ) of 24 LiCl-29 $Li_2O$- 3 $Al_2O_3$- 44 $B_2O_3$ (in m/o) (○), 11 LiCl- 37 $Li_2O$- 4 $Al_2O_3$- 48 $B_2O_3$ (in m/o) (●) and 45 $Li_2O$- 4 $Al_2O_3$- 51 $B_2O_3$ (in m/o) (△).

energy for conduction of 44 K J/mole were obtained by the glass containing 24 LiCl-29 $Li_2O$- 3 $Al_2O_3$- 44 $B_2O_3$ (in m/o). The glass-transition temperature of this glass was 370°C. The conductivity is as high as that of the typical solid lithium ion conductors[2] ever found. It is about one order of magnitude higher than that of the 40 $Li_2O$- 60 $SiO_2$ (in m/o) glass at 300°C[3]. The contribution of electronic conductivity to total conductivity was determined with the help of the emf measurement of the cell, Li/glass/CuCl, Cu. The observed emf of 0.275 V at 20°C is in good agreement with the emf calculated from the free enthalpy change of the reaction Li(s) + CuCl(s) = LiCl(s) + Cu(s), that is 0.273 V, showing that this glass is an essentially ionic conductor. The $^7Li$ NMR spectra were measured between -120°C and 200°C. In the glasses having high conductivities, the narrowing of linewidth at room temperature was 0.5 gauss. As the linewidth decreases as the lithium motion increases[4] these results suggest that the lithium ion moves easily in the glass.

This glass electrolyte with high lithium ion conductivity will be used as the electrolyte for lithium battery because of its easy manufacturing process.

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