Effect of Cl Substitution on the Lithium Ion Conductivity of Lithium Indium Bromide

Y. Tomita,[a] H. Matsushita,[a] K, Kobayashi,[a] and K. Yamada[b]
[a] Shizuoka University

Department of Materials Science and Chemical Engineering, 3-5-1 Johoku, Hamamatsu, Shizuoka, Japan
[b]Hiroshima University
Graduate School of Science, 1-3-1 Kagamiyama, Higashi-Hiroshima, Hiroshima, Japan

Ionic conductors for lithium ion have attracted the particular interest for possible applications as solid electrolyte of lithium ion secondary batteries and many studies for them have been carried out. In recent years, we have investigated the crystal structures and the dynamics of component ions for a series of compounds $MBr\text{-}M'Br_3$ (M = Li, Cu, Ag; M' = Al, Ga, In) and found a good lithium ion conductor Li_3InBr_6 with □ ~ 10^{-3} Scm^{-1} at 330 K. This high conductivity appears in the high temperature phase of Li_3InBr_6 (abbreviated as HT phase). Its value is much higher than that reported for Li_3MX_6 (M= lanthanoids; X= Cl, Br) and comparable to that of Li_3N (1.2×10^{-3} Scm^{-1} at 298 K). The diffusional correlation time, estimated from the 7Li NMR spectra and spin-lattice relaxation times, T_1, on the HT phase supported the high conductivity due to the Li^+ cation. On the other hand, the low temperature phase (LT phase) showed the much lower conductivity than HT phase. In this study, Br^- ion in Li_3InBr_6 was substituted with Cl^- ion and the substitution effect on the ionic conductivity has been investigated by means of X-ray diffraction, ^{7}Li, ^{115}In NMR spectra and AC conductivity measurements to improve the ionic conductivity for an application to the lithium ion battery.

$Li_3InBr_{6-x}Cl_x$ was synthesized by a solid state reaction method. Stoichiometric mixtures of LiBr, LiCl, $InBr_3$, and $InCl_3$ were milled and annealed in a quartz tube at 473K. Source materials were purified by sublimation in a vacuum or recrystallization, and all compounds handled in a glove box filled with dry nitrogen gas. ^{7}Li and ^{115}In NMR spectra were observed with a Matec pulsed spectrometer at 6.3 T with corresponding Larmor frequencies of 105.4 MHz and 59.4 MHz, respectively.

In XRD measurements, no apparent impurity peak could be detected in $Li_3InBr_{6-x}Cl_x$. Figure 1 shows XRD patterns of $Li_3InBr_{6-x}Cl_x$ and Li_3InBr_6 at 297 K. Original compound, Li_3InBr_6, belongs to a monoclinic system with a = 0.6756 nm, b = 1.170 nm, c = 0.6758 nm and □ = 110.1° at 297 K. With an increase of x, the peak shifted toward higher angle indicating that the lattice constants decreased with x. The remarkable variation of the lattice constants was observed in the substitution. Figure 1 shows the plots of the unit lattice volume of $Li_3InBr_{6-x}Cl_x$ obtained from the analysis of the XRD patterns against x. The volume was naturally decreased with an increase of Cl amount due to the difference of the ionic radius of Cl^- and Br^-. However, the gradient of the volume change of x ≥ 3.0 was steeper from that below x= 3.0. It was indicated from the Rietveld analysis that Cl ion selectively substituted Br ion adjacent to Li ion.

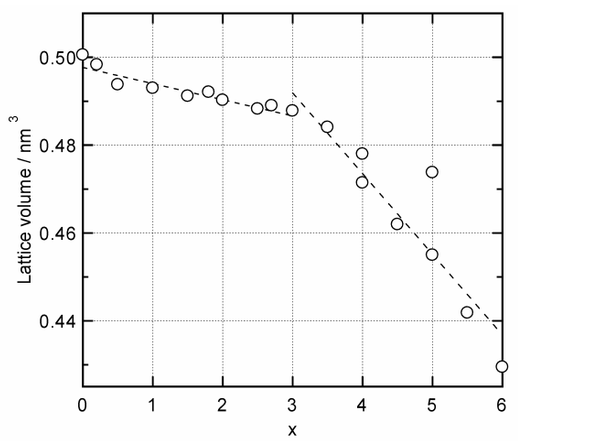

Fig. 1. Plots of the unit lattice volume of $Li_3InBr_{6-x}Cl_x$ against x at 297 K. The lattice volume of x=6 was obtained from single crystal data.

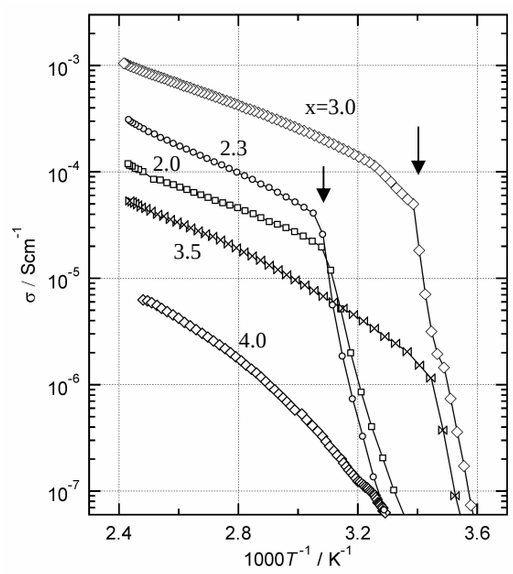

Fig. 2. Temperature dependence of AC conductivity for $Li_3InBr_{6-x}Cl_x$. Arrows indicate the phase transition temperature.

The temperature dependence of the AC conductivity for $Li_3InBr_{6-x}Cl_x$ is shown in Fig. 2. The phase transitions are clearly observed around 320 K in x < 3.0 and became lower temperature in x ~ 3 compounds, where the conductivity changed abruptly. The conductivity in $Li_3InBr_3Cl_3$ was higher than that of Li_3InBr_6 and the transition temperature in $Li_3InBr_{2.5}Cl_{3.5}$ was lowest among the all compounds. In x>3, the conductivity decreased with an increase of x and the phase transition disappeared in x ≥ 4.0. This phenomenon accorded with the tendency observed in the XRD measurement. The conductivity also decreased and phase transition temperature changed above x=3 corresponding to the steep decrease of the lattice volume. When Cl substituted for Br adjacent to Li, the conductivity was highest in $Li_3InBr_{6-x}Cl_x$. In NMR measurement, ^{7}Li spectra was already narrowed at 295 K in x=3. It was confirmed that the phase transition temperature was lowered and the fast diffusion of Li^+ ion arise at room temperature.