New Lithium Ion Conductor Li_3InBr_6 Studied by ^{7}Li NMR

Yasumasa Tomita, Aya Fuji-i, Hiroshi Ohki, Koji Yamada,* and Tsutomu Okuda
Department of Chemistry, Faculty of Science, Hiroshima University, Kagamiyama 1-3-1, Higashi-Hiroshima 739

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Super ionic conductor Li_3InBr_6 ($\sigma=10^{-3}$ Scm^{-1} at 297 K) due to lithium ions was synthesized and characterized by temperature dependence of the ^{7}Li NMR T_1. The substitution effect of the cation and the temperature behavior of T_1 suggested that the high ionic conductivity resulted from the considerably disordered state of the cationic sublattice.

Ionic conductors are widely used in electrochemical devices such as chemical sensors and solid state batteries. Especially Li$^+$ ion conductors have attracted much interest recently because of the development of a solid-state secondary cell. We have studied systematically the ionic conductivity for the double salts between alkali halides and trihalides of 13th group elements (Al, Ga and In).[1,2] In this process, a high conducting phase was found for Li_3InBr_6 associated with the phase transition at 314 K on heating. The high temperature form of Li_3InBr_6 remained unchanged down to 270 K as expected from DTA measurement and showed the conductivity in the order of 10^{-3} Scm^{-1} at 297 K. This value is much higher than those reported for Li_3MX_6 (M= lanthanoids; X= Cl, Br)[3,4] and is comparable to that of Li_3N (1.2×10^{-3} Scm^{-1} at 298 K).[5] This indicates that Li_3InBr_6 is one of the best Li$^+$ ion conductors at room temperature. In this study, we investigated the temperature dependence of the conductivity for Li_3InBr_6 and the substitution effect of a divalent cation. Furthermore, the diffusional motion of the Li$^+$ ion was confirmed by means of ^{7}Li NMR.

Li_3InBr_6 and $Li_{3-2x}Ca_xInBr_6$ (x=0.05, 0.07, 0.10 and 0.15) were prepared by a solid state reaction (473±5 K for 2 weeks) in evacuated silica tubes containing stoichiometric amounts of LiBr, $CaBr_2$ and $InBr_3$. All samples were handled in a glove box under dry nitrogen atmosphere. ^{7}Li NMR was observed using a Matec pulsed spectrometer at 105.41 MHz (6.37 T). The spin-lattice relaxation time T_1 was determined by applying the 90°-τ-90°-pulse sequence. The electric conductivity was determined by means of a complex impedance method using 10 different frequencies (100 Hz~100 kHz, ANDO LCR meter AG-4311B).

Li_3InBr_6 seems to be isomorphous with Li_3ErBr_6 (space group: C2/c).[4] X-ray diffraction pattern of low temperature phase was almost the same with that of high temperature phase.

Figure 1 plots the conductivities of Li_3InBr_6 and $Li_{2.86}Ca_{0.07}InBr_6$ against inverse temperatures. A steep raise of conductivity from 10^{-7} to 10^{-3} Scm^{-1} at ca. 314 K was observed for Li_3InBr_6 on heating. For the doped sample, a similar jump on the conductivity was confirmed at almost the same temperature, and an additional phase transition occurred at 360 K on heating. This is verified to be the first-order transition. The high conductivity of the order of 10^{-3} Scm^{-1} is maintained even at room temperature. On the other hand, the conductivity of the doped sample is lower than that of Li_3InBr_6 just above the phase transition to the conducting phase. These findings suggest that the vacancies produced by doping with the divalent cation do not enhance the diffusion of the Li$^+$ ion above the phase transition point, i.e., the high ionic conductivity results from the intrinsic nature of the cationic sublattice. The activation energy, E_a, for the conduction is determined by the following equation,[6]

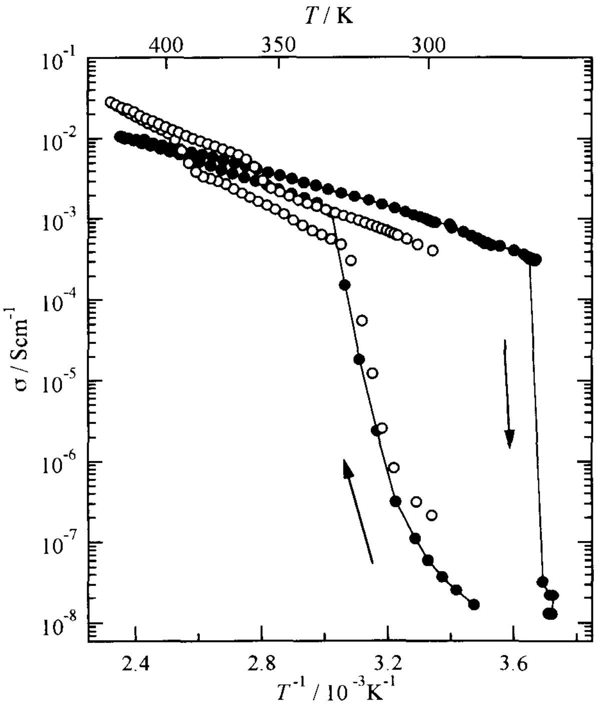

Figure 1. Temperature dependence of electric conductivity for Li_3InBr_6 (solid circle) and $Li_{2.86}Ca_{0.07}InBr_6$ (open circle).

$$\sigma T = A \exp(-E_a/RT), \qquad (1)$$

where A is the pre-exponential parameter. The activation energy evaluated from this equation is 25 kJmol^{-1} for Li_3InBr_6.

The conductivities of $Li_{3-2x}Ca_xInBr_6$ (x=0.07 and 0.10) were somewhat higher than that of Li_3InBr_6 above the additional phase transition point. Figure 2 plots the conductivities in the high temperature phases of $Li_{3-2x}Ca_xInBr_6$ as a function of composition at two temperatures. The ionic conductivity for x=0 is highest at 300 K. On the other hand, the conductivity at 400 K showed a maximum between x=0.07 and 0.10.

As was expected from the steep rise of the conductivity, the full width at half maximum (FWHM) of the ^{7}Li NMR spectrum changed discontinuously from 6.3 kHz to 0.59 kHz at the transition point. This narrowing phenomenon above the transition point indicates that the fast diffusional motion of the Li$^+$ ion averages out both the magnetic dipole and the quadrupole interaction.

Figure 3 shows the temperature dependence of ^{7}Li NMR

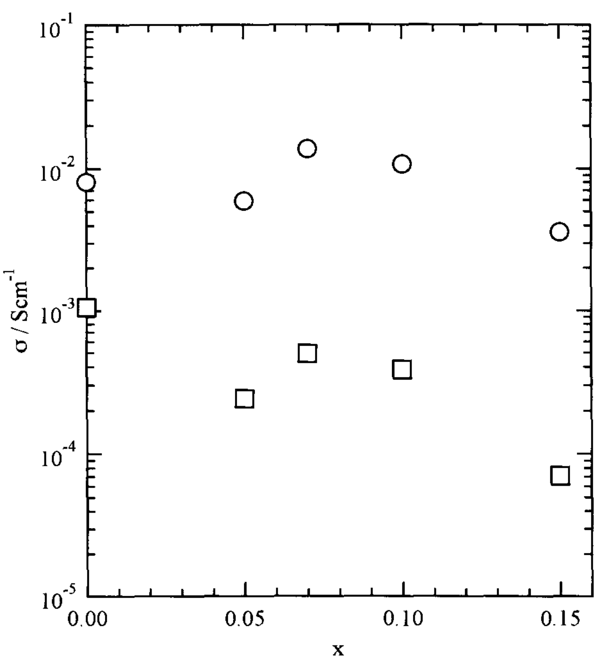

Figure 2. Plots of electric conductivity for high temperature phase of $Li_{3-2x}Ca_xInBr_6$ against x at 300 K (square) and at 400 K (circle).

spin-lattice relaxation times T_1 for Li_3InBr_6. In accordance with linewidth mesurement, the T_1 changed discontinuously at 314K on heating and at 270K on cooling. The slope of the T_1 vs. $1/T$ curves changed its sign at the phase transition point. In general according to the BPP formula, T_1^{-1} is expressed as,[7]

$$T_1^{-1} = C\,(\tau_c\,(1+\omega_0^2\tau_c^2)^{-1}+4\tau_c\,(1+4\omega_0^2\tau_c^2)^{-1}), \qquad (2)$$

$$\tau_c = \tau_0 \exp(E_a/RT), \qquad (3)$$

where C is a constant and ω_0, τ_c and τ_0 are Larmor frequency, correlation time of the motion and pre-exponential parameter, respectively. The T_1 behavior on temperature suggests that a high temperature approximation $\omega_0\tau_c \ll 1$ is satisfied at the high temperature phase of Li_3InBr_6. Then, equations (2) and (3) reduce to a simple relation,

$$T_1^{-1} = C\,\tau_0 \exp(E_a/RT). \qquad (4)$$

The activation energy of the Li^+ ion diffusion was evaluated to be 24 kJmol^{-1} from this equation and its value is in good agreement with that from the conductivity measurement. The narrowing phenomena and the very short correlation time ($\tau_c \ll 1/\omega_0$, $\omega_0 = 10^8$ Hz) at high temperature phase indicate that the Li^+ ion diffusional rate increase several orders at the transition point.

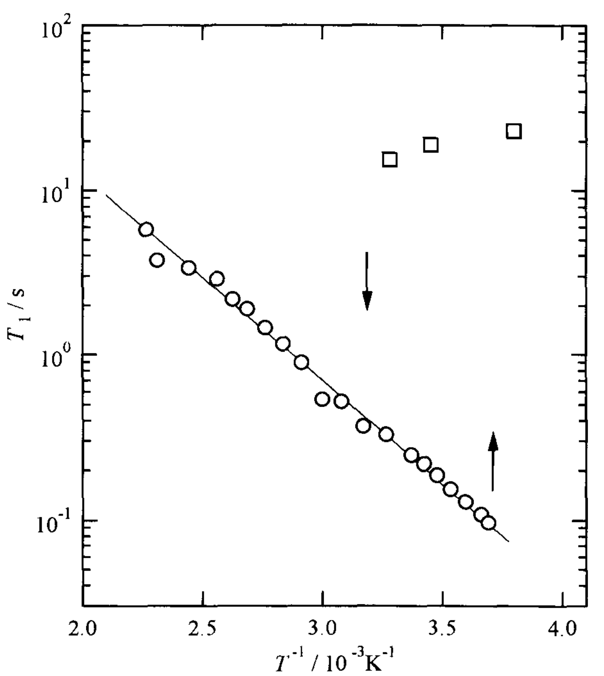

Figure 3. Temperature dependence of ^{7}Li NMR spin-lattice relaxation times for low(square) and high(circle) temperature phases of Li_3InBr_6.

Both conductivity and NMR measurements suggest that the cationic sublattice and vacancies are considerably disordered in the high temperature phase of Li_3InBr_6.

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References and Notes

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