Li ion conductivity of solid electrolyte, $\text{Li}_{3-2x}\text{M}_x\text{InBr}_6$ (M = Ca, Sr and Ba)

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$\text{Li}_{3-2x}\text{M}_x\text{InBr}_6$ (M = Ca, Sr, Ba; $x = 0-1.0$) was synthesized and the cation substitution effect was investigated by means of X-ray diffraction and AC conductivity measurements. In $\text{Li}_{3-2x}\text{Sr}_x\text{InBr}_6$ ($x \leq 0.7$), the conductivity of high temperature phase decreased with an increase of x and LiSrInBr_6 show almost the same conductivity to Li_3InBr_6 . Intensity of XRD peaks of LiSrInBr_6 was different from those of Li_3InBr_6 and the substitution of Sr was expected to affect the structure and ionic conductivity. In $\text{Li}_{3-2x}\text{Ca}_x\text{InBr}_6$, the conductivity decreased monotonously with an increase of x .

Key Words : Solid Electrolyte, Li Ion Conductor, Ionic Conductivity

1 Introduction

Ionic conductors for lithium ion have stirred up particular interest for possible applications as solid electrolyte lithium ion secondary batteries and many studies have been carried out.¹⁻⁴⁾ In recent years, we have investigated the crystal structures and dynamics for a series of compounds $\text{MBr} \cdot \text{M}'\text{Br}_3$ (M = Li, Cu, Ag; M' = Al, Ga, In) and found a good lithium ion conductor Li_3InBr_6 with $\sigma \sim 10^{-3} \text{ Scm}^{-1}$ at 330 K.⁵⁻⁷⁾ This high conductivity appears in the high temperature phase of Li_3InBr_6 (abbreviated as HT phase), its value being much higher than that reported for Li_3MX_6 (M = lanthanoids; X = Cl, Br) and comparable to that of Li_3N ($1.2 \times 10^{-3} \text{ Scm}^{-1}$ at 298 K).⁸⁻¹⁰⁾ 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. At the phase transition to the superionic HT phase ($T_{\text{tr}} = 314 \text{ K}$) a strong endothermic peak was observed on the DTA curve without an appreciate change of the XRD powder pattern. These findings suggest an order-disorder phase transition at T_{tr} . We also reported that the partial substitution of Li^+ for Mg^{2+} for Li_3InBr_6 made the ionic conductivity a little higher in the LT phase.⁶⁾ In the present paper, the effect of the partial substitution of Li^+ for Ca^{2+} , Sr^{2+} and Ba^{2+} on the ionic conductivity was investigated by means of X-ray diffraction and AC conductivity measurements.

2 Experimental

$\text{Li}_{3-2x}\text{M}_x\text{InBr}_6$ (M = Ca, Sr, Ba; $x = 0-1.0$) was synthesized by a solid-state reaction at 473 K using a quartz tube containing a stoichiometric mixture of LiBr , MBr_2

and InBr_3 . All materials were dried in a vacuum and handled in a glove box filled with dry nitrogen gas. Powder X-ray diffraction patterns were recorded by a Rigaku Rad-B system using a $\text{Cu-K}\alpha$ radiation. The handmade cell was used to protect the samples from the moisture. The conductivity was determined by a complex impedance method measured at 35 frequencies between 42 Hz and 5 MHz (HIOKI 3532-50 LCR high tester) in a dry nitrogen atmosphere.

3 Results and Discussion

3.1 X-ray Diffraction

Figure 1 shows X-ray diffraction patterns of $\text{Li}_2\text{M}_{0.5}\text{InBr}_6$ (M = Ca, Sr, Ba), $\text{Li}_{1.4}\text{Sr}_{0.7}\text{InBr}_6$ and Li_3InBr_6 at 297 K. Original compound, Li_3InBr_6 , belongs to a monoclinic system with $a = 0.6756 \text{ nm}$, $b = 1.170 \text{ nm}$, $c = 0.6758 \text{ nm}$ and $\beta = 110.1^\circ$ at 297 K. In $\text{Li}_{3-2x}\text{Ca}_x\text{InBr}_6$, no apparent impurity peak could be detected. In

Fig. 1 Powder X-ray diffraction patterns of $\text{Li}_2\text{M}_{0.5}\text{InBr}_6$ (M = Ca, Sr, Ba) and Li_3InBr_6 at 297 K.

$\text{Li}_{3-2x}\text{M}_x\text{InBr}_6$ ($\text{M} = \text{Sr}, \text{Ba}$), the weak peaks of impurity were observed and they were not single phase. In Ca compound, most Bragg peaks became broader with x and their intensity was weakened. It was indicated that the crystallinity of the sample becomes poorer with an increase of x . 2θ value of the peaks shifted slightly toward the lower angle and so, the crystal lattice was expanded due to the substitution with Ca. The lattice constant was changed uniformly with x though the remarkable variation of the lattice constants of $\text{Li}_{3-2x}\text{Mg}_x\text{InBr}_6$ was observed with an increase of Mg content in the case of substitution with Mg.⁶⁾ In Sr compound, the peaks were shifted toward the lower angle in the same way as Ca compound and the peak intensity was varied drastically in $x \geq 0.7$. Since ionic radius of Ca and Sr is larger than that of lithium ion, the lattice constant of them increased simply with the substitution. In $\text{Li}_{3-2x}\text{Sr}_x\text{InBr}_6$ ($x \geq 0.7$), the change of the crystal structure was expected to be induced by the substitution and produce the increase of the ionic conductivity as follows. In Ba compound, the shift of the peaks was not observed and the intensity for the impurity increased with x . It was considered that Ba could not be substitute for Li due to the large difference between each ionic radius.

3. 2 AC Conductivity

The temperature dependence of the AC conductivity for $\text{Li}_2\text{M}_{0.5}\text{InBr}_6$ and LiMInBr_6 ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) is shown in Fig. 2. The phase transitions are clearly seen around 310–330 K, where the conductivity changes steeply in Sr and Ba compounds. In Ba compounds, the conductivity was increased monotonously with an increase of temperature in the same manner as original compound and the temperature of the steep raise due to the phase transition was not changed as expected from the result of XRD measurement. The phase transition was, however, disappeared in cooling process at $x = 0.5$ and the high conductive phase was stable below 250 K. The sample

Fig. 2 Temperature dependence of AC conductivity for $\text{Li}_2\text{M}_{0.5}\text{InBr}_6$ ($\text{M} = \text{Ca}(\bigcirc), \text{Sr}(\square), \text{Ba}(\triangle)$), LiMInBr_6 ($\text{M} = \text{Ca}(\bullet), \text{Sr}(\blacksquare), \text{Ba}(\blacktriangle)$) and Li_3InBr_6 .

remained in high conductive phase on and after the secondary measurement. This sample, however, returned to the LT phase by grinding in a mortar or maintenance in low temperature for several days. This phenomenon was not observed in other samples of Ba compound, and the origin is not yet elucidated. In Sr compound, the conductivity was increased monotonously with temperature and the temperature of phase transition increased slightly. The slope of the conductivity in HT phase of $x \leq 0.5$ was not changed so much regardless of Sr content. In $x \geq 0.7$, the slope and the value of the conductivity was increased with x as described below. The intensity of XRD peak was different from original compound and the substitution with Sr expected to give effects on the crystal structure and the ionic conductivity. In Ca compound, temperature of phase transition became much higher due to the substitution unfortunately though the reduction of transition temperature was desirable in their practical application. The conductivity of HT phase also became lower and the slope of the conductivity was increased with an increase of x .

The activation energy, E_a , for the conduction was evaluated using the equation,

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

where A and σ is the pre-exponential parameter and the conductivity, respectively.¹¹⁾ The activation energy in Sr compound was not change so much between 25 kJmol^{-1} and 30 kJmol^{-1} , and showed the tendency to increase together with x .

Figure 3 shows the conductivity of the HT phase (400 K) in $\text{Li}_{3-2x}\text{M}_x\text{InBr}_6$ and E_a of the conduction in $\text{Li}_{3-2x}\text{Ca}_x\text{InBr}_6$ against x . In the HT phase of Ca compound, the conductivity decreased and E_a increased monotonously with an increase of x . In Sr compound ($x \leq 0.7$), the conductivity decreased with x as in Ca compound. The substitution of the Li^+ with Ca^{2+} and Sr^{2+} expected to introduce extrinsic vacancies into the crystal lattice and increase the conductivity. These results, however, indicates that the superionic property of the HT phase originates from the intrinsic nature of Li_3InBr_6 due to its structure and no extrinsic vacancy produced by

Fig. 3 Plots of AC conductivity for $\text{Li}_{3-2x}\text{M}_x\text{InBr}_6$ ($\text{M} = \text{Ca}(\bigcirc), \text{Sr}(\square), \text{Ba}(\triangle)$) at 400 K and $E_a(\blacktriangle)$ of the conduction in $\text{Li}_{3-2x}\text{Ca}_x\text{InBr}_6$ against x .

those substitution contributes to the Li^+ conduction in HT phase. Furthermore, the substitution of Ca was considered to disturb the Li^+ diffusion in the HT phase in view of the increase of E_a . The conductivity in Sr compound ($x \leq 0.7$) increased with x and the value of the conductivity in LiSrInBr_6 is almost equal to that in the original compound. From XRD measurements of Sr compound ($x \geq 0.7$), it was considered that the substitution of Sr stimulated the disorder of Li^+ ion and affected the diffusion path of Li^+ ion. Therefore, the Li^+ ion in the crystal could diffuse easily and the conductivity increased due to the change of the crystal structure produced by the substitution.

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