Synthesis of $Li_{3+x}In_{1-x}M_xBr_6$(M=Zn, Co, Fe) by Nano-grinding and their Ionic Conductivity

Yasumasa Tomita, Hideyoshi Matsushita, Yasuhisa Maeda,
Kenkichiro Kobayashi, and Koji Yamada*
Department of Materials Science and Chemical Engineering, Shizuoka University,
3-5-1 Johoku, Hamamatsu, Shizuoka, 432-8561, Japan, ,
Affiliations and address (9 point)
Fax: 81-53-478-1149, e-mail: tytomit@ipc.shizuoka.ac.jp
* Applied Molecular Chemistry, College of Industrial Technology, Nihon University,
1-2-1 Izumicho, Narashino, Chiba, Japan
e-mail: k5yama@cit.nihon-u.ac.jp

$Li_{3+x}In_{1-x}M_xBr_6$ (M=Zn, Co, Fe) was synthesized by nano-grinding. No peak of source materials was observed for all the compounds in XRD measurements. With an increase of x for M=Fe compounds, the lattice constants decreased, because the ionic radius of Fe^{2+} ion are much smaller than that of In^{3+} ion. In the high temperature phase for $Li_{3+x}In_{1-x}M_xBr_6$ (M=Zn, Co), the conductivity decreased with x. In Zn compound, a new phase transition was observed at about 345 K and the conductivity became higher than that of the medium temperature phase. In $Li_{3+x}In_{1-x}Fe_xBr_6$, the conductivity of high temperature phase was almost equal to that for Li_3InBr_6. In ^7Li NMR measurement, the spectra in high temperature phase for $Li_{3+x}In_{1-x}Fe_xBr_6$ was narrowed to be less than 1 kHz. It is indicated that Li^+ ion diffuse fast in the crystal and these compounds are good Li ion conductors.
Key words: Li ion conductor, phase transition, NMR, substitution effect

1. INTRODUCTION

The lithium ion secondary battery has been widely prevalent as a power source of small-sized electronic devices because of the high-energy density characteristics. More improvement of safety, reliability, and capacity are desired to use for a large current power source such as electric vehicles. Instead of organic liquid electrolytes and gel polymer electrolytes used for current lithium ion secondary batteries, a conversion of all solid state batteries by us of lithium ion conductive inorganic solid electrolyte is one of effective methods to improve these performances and many of lithium ion conductors such as Li ion conductive glass [1,2], thio-LISICON[3], and (La, Li)TiO3[4,5], has been studied and attempted to apply to the solid electrolyte in the lithium ion secondary battery[6].

In recent years, we have investigated the structures and dynamics for a series of compounds MBr-M'Br3 (M = Li, Cu, Ag; M' = Al, Ga, In) and found a lithium ion conductor Li_3InBr_6 with $\sigma \sim 10^{-3}$ Scm^{-1} at 330 K [7-9]. This high conductivity appears in the high temperature phase of Li_3InBr_6, its value being much higher than that reported for Li_3MX_6 (M= lanthanoids; X= Cl, Br) and comparable to that of Li_3N (1.2×10^{-3} Scm^{-1} at 298 K) [10]. The diffusional correlation time, estimated from the ^7Li NMR T_1 on the high temperature phase supported the high conductivity due to the Li^+ cation. On the other hand, in the low temperature phase three ^{81}Br NQR lines between 59 and 70 MHz[8] suggested an isolated $InBr_6^{3-}$ anion with an inversion point symmetry. At the phase transition temperature, T_{tr}, toward the high temperature phase the three NQR lines disappeared,

accompanied by a strong endothermic peak on the DTA curve without an appreciate change of the XRD powder pattern. These findings suggest an order-disorder phase transition at T_{tr}. $Li_3InBr_{6-x}Cl_x$ was the compounds partially substituted of Li_3InBr_6 by Cl ion and the volume of crystal lattice was decreased with Cl content. In these compounds, the phase transition temperature lowered to be 285 K and the ionic conductivity was at the maximum around x = 3. The modification of anion improved the ionic conductivity and thermal stability of high conductive phase.

In the present paper, we synthesized $Li_{3+x}In_{1-x}M_xBr_6$ (M=Zn, Co, Fe) substituted of In^{3+} and the effect of the modification of anion on the ionic conductivity was investigated by means of X-ray diffraction, AC conductivity, and solid state NMR measurements.

2. EXPERIMENTAL

$Li_{3+x}In_{1-x}M_xBr_6$ (M=Zn, Co, Fe) was synthesized by a solid state reaction method. Stoichiometric mixtures of $LiBr$, MBr_2 and $InBr_3$ were ground by planetary ball mill up to about 20 nm and annealed in a quartz tube at 493K. Source materials were purified by sublimation in a vacuum or recrystallization, and all compounds handled in a glove box filled with dry Ar gas. Powder X-ray diffraction patterns were recorded by a Rigaku Rad-B system using a Cu-Kα radiation. The handmade cell was used to protect the samples from the moisture. ^7Li and ^{115}In NMR spectra were observed with a Matec pulsed spectrometer at 6.3 T with corresponding Larmor frequencies of 105.4 and 59.45 MHz, respectively. 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 argon atmosphere.

3. RESULTS AND DISCUSSION
3.1 X-ray diffraction

Figure 1 shows the crystal structure of Li$_3$InBr$_6$ and XRD patterns of Li$_{3.15}$In$_{0.85}$M$_{0.15}$Br$_6$ (M=Zn, Co, Fe; x = 0.15) and Li$_3$InBr$_6$ at 297 K. Li$_3$InBr$_6$ belongs to a monoclinic system with a = 0.6756 nm, b = 1.170 nm, c = 0.6758 nm and β = 110.1° at 297 K. The structure in figure 1 displays a part of the unit lattice and In atoms occupy their sites partially. In Li$_{3+x}$In$_{1-x}$M$_x$Br$_6$, their peak intensity was weakened with an increase of x and no apparent impurity peak could be detected. It was indicated that the crystallinity of the sample becomes poorer slightly with x and each of them was single phase. In Li$_{3+x}$In$_{1-x}$Zn$_x$Br$_6$ and Li$_{3+x}$In$_{1-x}$Co$_x$Br$_6$, no shift could be observed for 2θ value of the peaks. In Li$_{3+x}$In$_{1-x}$Co$_x$Br$_6$, some of weak peaks appeared by substitution, indicating that the crystal structure might be changed. In Fe compounds, 2θ value of the peaks shifted slightly toward the higher angle. The volume of the crystal lattice was reduced due to the substitution with Fe and the lattice constants were changed uniformly. Since ionic radius of Fe, Co and Zn is smaller than that of Indium ion, it was predicted that the substitution of In with Fe, Co, or Zn made the crystal lattice smaller and increase of the amount of Li ion expand the lattice in these substitution. It was considered that the reason why the contraction of the crystal lattice was observed only in Fe substitution is that ionic radius of Fe^{2+} ion is much smaller than that of In^{3+} in comparison to Co^{2+} and Zn^{2+}.
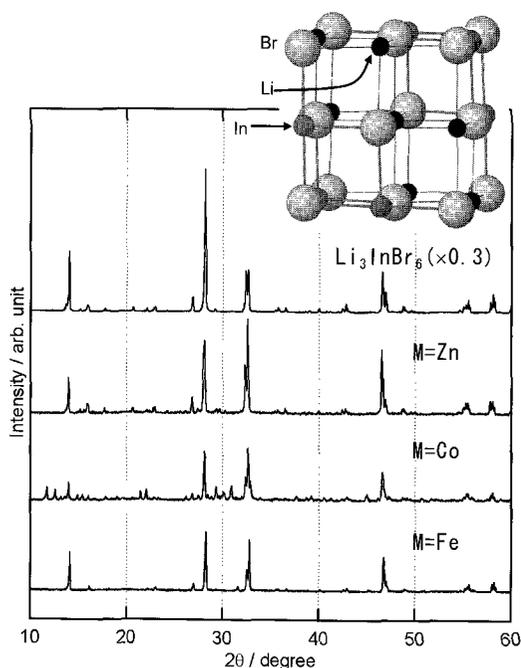

Fig. 1. Powder XRD patterns of Li$_3$InBr$_6$ and Li$_{3.15}$In$_{0.85}$M$_{0.15}$Br$_6$(M= Zn, Co, and Fe) at 297 K, and the crystal structure of Li$_3$InBr$_6$.

3.2 AC conductivity

The temperature dependence of the AC conductivity for Li$_{3+x}$In$_{1-x}$M$_x$Br$_6$ (M=Zn, Co, Fe) and Li$_3$InBr$_6$ is
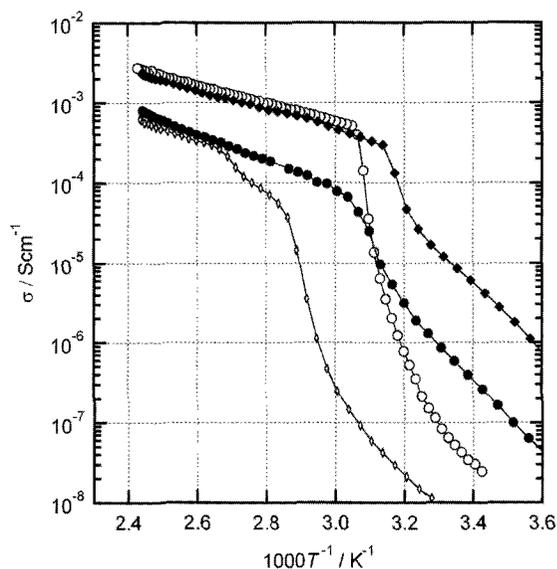
Fig. 2. Temperature dependence of conductivity for Li$_{3.15}$In$_{0.85}$M$_{0.15}$Br$_6$(M= Zn(◊), Co(●), Fe(♦)) and Li$_3$InBr$_6$(○).

shown in Fig. 2. The phase transitions are clearly seen around 310 ~ 330 K, where the conductivity changes in Co and Fe compounds. In Zn compound, phase transition temperature, T$_{tr}$, became much higher due to the substitution unfortunately though the reduction of transition temperature was desirable in their practical application. Furthermore, the conductivity of low temperature phase was also decreased. The low temperature phase must be stabilized by the substitution with Zn. A new phase transition appeared at higher temperature and the conductivity was increased slightly. In Co compounds, the conductivity increased monotonously with an increase of temperature in the same manner as Li$_3$InBr$_6$. The conductivity of high temperature phase became lower and the slope of the conductivity was increased by the substitution. This decrease of the conductivity may be caused by the change of the crystal structure suggested by a little difference in XRD pattern between Co compound and the original one. In Fe compound, the conductivity also increased monotonously with an increase of temperature. The conductivity in high temperature phase was almost equal to that for Li$_3$InBr$_6$ and phase transition temperature where the conductivity raised steeply was lowered. It was found that ionic conductivity was improved and high temperature phase was stabilized by the substitution with Fe.

The conductivity in the low temperature phase was increased in Fe and Co compound. This phenomenon is similar to that of the compounds substituted of Li with Mg. In Mg compounds, the substitution introduced extrinsic vacancies into the crystal lattice and improved the ionic conductivity. In Fe and Co compounds, however, the amount of Li ion was increased and vacancy was not produced by the substitution. The carrier concentration was increased only by a factor of 1.33 but the mechanism of increase of the conductivity is not clear at this moment.

The activation energy, E$_a$, for the conduction was

evaluated using the equation,

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

where A and σ is the pre-exponential parameter and the conductivity, respectively [11]. The activation energy in the high temperature phase was obtained from the conductivity at cooling process by use of equation (1). E_a in Fe compound was not change so much between 24 kJmol^{-1} and 28 kJmol^{-1}. For Co compounds, E_a was 35 kJmol^{-1} for $Li_{3.15}In_{0.85}Co_{0.15}Br_6$ and showed the tendency to increase together with x, indicating that diffusion of Li ion was disturbed by the substitution.

3.3 ^{7}Li NMR spectra

In Figure 3, spectra (a), (b) and (c) are ^{7}Li NMR spectra at 330 K (high temperature phase) and (d) is at 295 K (low temperature phase). In Co compounds, NMR signal was very weak and any clear spectra could not be obtained. In the low temperature phase of Li_3InBr_6 the ^{7}Li NMR spectrum (d) showed a featureless Gaussian profile with a FWHM linewidth of about 6 kHz. No apparent quadrupole effect was observed. This linewidth in low temperature phase of Li_3InBr_6 agreed well with the one expected from the van Vleck formula assuming a rigid lattice [12,13]. On the other hand, the linewidth of spectra(c) in the high temperature phase reduced to be 0.6 kHz. This suggests that the rate of the translational diffusion is much faster than that corresponding to the inverse linewidth parameter of the ^{7}Li NMR. The linewidth of the spectra in the low temperature phase for Fe and Zn compounds coincides with that for Li_3InBr_6, suggesting that the cationic sublattice forms a rigid lattice in the NMR time scale and Li ion diffusion was very solw. The linewidth of (a) for $Li_{3.15}In_{0.85}Fe_{0.15}Br_6$ and (b) $Li_{3.15}In_{0.85}Zn_{0.15}Br_6$ are narrowed to less than 1 kHz, indicating that the diffusion rate of Li ion became large in both compounds just as Li_3InBr_6. It was found that these compounds are Li ion conductors.
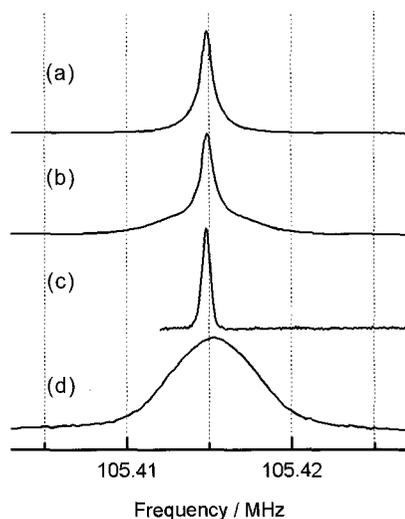

Fig. 3. ^{7}Li NMR spectra of $Li_{3.15}In_{0.85}M_{0.15}Br_6$ (M= Fe (a), Zn (b)) at 330 K and Li_3InBr_6 at 330 K (c) and 297 K(d). (a)-(c) are spectra in high temperature phase and (d) is low.
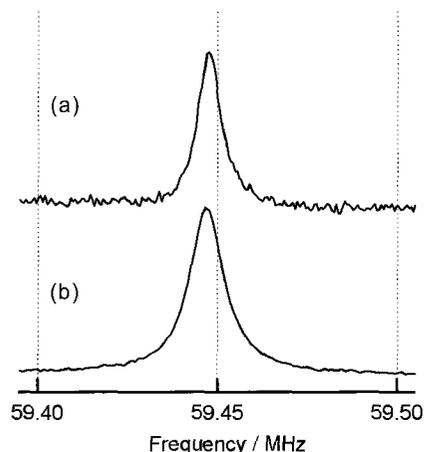

Fig. 4. ^{115}In NMR spectra in high temperature phase of $Li_{3.15}In_{0.85}Fe_{0.15}Br_6$ (a) and Li_3InBr_6 (b) at 330 K.

3.4 ^{115}In NMR spectra

Figure 4 shows the ^{115}In NMR central transitions ($\Delta m = -1/2 \leftrightarrow 1/2$) for $Li_{3.15}In_{0.85}Fe_{0.15}Br_6$ and Li_3InBr_6 observed at 330 K. In the low temperature phase of Li_3InBr_6, only a spin echo of ^{115}In NMR signal was observed with more than 1 MHz width due to the higher order quadrupole effect. On the other hand, in the high temperature phase, the linewidth decreased to be 12 kHz at 330 K due to the reorientation of $InBr_6^{3-}$ anion as shown in figure 4(b). In low temperature phase of $Li_{3.15}In_{0.85}M_{0.15}Br_6$, ^{115}In NMR spectra were broad and their line width was more than 1MHz. In Fe compound, the spectra of high temperature phase became sharp as shown in figure 4(a). The linewidth of (a) was narrower than that of (b). This is because phase transition temperature of $Li_{3.15}In_{0.85}Fe_{0.15}Br_6$ was lower than that of Li_3InBr_6 and rate of $InBr_6^{3-}$ reorientation in $Li_{3.15}In_{0.85}Fe_{0.15}Br_6$ was a little faster. At much higher temperature, ^{115}In NMR linewidth were almost same in both Li_3InBr_6 and $Li_{3.15}In_{0.85}Fe_{0.15}Br_6$. In high temperature phase of $Li_{3.15}In_{0.85}M_{0.15}Br_6$(M=Co, Zn), ^{115}In NMR spectra were much broader than that of Li_3InBr_6 and spectrum such as (a) or (b) could not be obtained, indicating that the substitution with Co or Zn distorted $InBr_6^{3-}$ anion and/or made a reorientation of $InBr_6^{3-}$ anion slower. In our previous paper[9], $InBr_6^{3-}$ anion was distorted with x in $Li_{3-2x}Mg_xInBr_6$ and the conductivity was decreased with an increase of x. In Co and Zn compounds, the conductivity was decreased and ^{115}In NMR spectra was broadened in high temperature phase, suggesting that the substitution may cause a distortion of the crystal lattice and disturb the Li ion diffusion.

References
[1] A. Hayashi, S. Hama, F. Mizuno, K. Tadanaga,T. Minami, M. Tatsumisago, *Solid State Ionics*, **175**, 683 (2004)
[2] N. Machida, H. Yamamoto, S. Asano, T. Shigematsu, *Solid State Ionics*, **176**, 473 (2005)
[3] M. Murayama, R. Kanno, M. Irie, S. Ito, T. Hata, N.

Sonoyama, and Y. Kawamoto, *J. Solid State Chem.*, **168**, 140 (2002)

[4] M. Yashima, M. Itoh, Y. Inaguma, and Y. Morii, *J. Am. Chem. Soc.*, **127**, 3491 (2005)

[5] C.H. Chen, K. Amine, *Solid State Ionics*, **144**, 51 (2001)

[6] Seung-Joo Lee a, Hong-Koo Baik a, Sung-Man Lee, *Electrochem. Commun.*, **5**, 32 (2003)

[7] Y. Tomita, K. Yamada, H. Ohki and T. Okuda, *Bull. Chem. Soc. Jpn.*, **70**, 2405 (1997)

[8] Y. Tomita, K. Yamada, H. Ohki and T. Okuda, *Z. Naturforsch.* **53a**, 466 (1998)

[9] Y. Tomita, H. Yonekura, Y. Yamauchi, K. Yamada, and K. Kobayashi, *Z. Naturforsch.* **57a**, (2002) 447.

[10] R.A. Huggins, *Electrochim Acta* 22, 773 (1977)

[11] S. Chandra, Superionic Solid, Principles and Applications, North-Holland Publishing Company, Amsterdam 1981, p.225

[12] J.H. van Vleck, *Phys. Rev.* **74**, (1948) 116

[13] C.P. Slichter, Principles of Magnetic Resonance 3rd ed., Springer-Verlag, (1990) pp. 71