# Substitution Effect in the Ion Conductor $Li_3InBr_6$, Studied by Nuclear Magnetic Resonance

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$Li_{3-2x}Mg_xInBr_6$ ($x$ = 0.02 - 0.4) was synthesized, and the cation substitution effect on the conductivity was investigated by means of $^7Li$ and $^{115}In$ NMR, and X-ray diffraction. With increasing $x$ the lattice constants $a$ and $c$ increased, but $b$ and $\beta$ did not show significant changes. The conductivity of the low temperature phase increased with $x$, associated with a narrowing of the $^7Li$ NMR spectra. In the high temperature superionic phase, on the other hand, the conductivity decreased with $x$ accompanied by a broadening of the $^{115}In$ NMR spectra.

*Key words:* NMR; Ionic Conductivity; Lithium Ion Conductor; Quadrupole Effect.

## Introduction

We have investigated the structures and dynamics for a series of compounds MBr-M'$Br_3$ (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 [1 - 6]. 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 $Li_3N$ ($1.2\times10^{-3}$ $Scm^{-1}$ at 298 K) [7 - 9]. The diffusional correlation time, estimated from the $^7Li$ NMR $T_1$ on the HT phase supported the high conductivity due to the $Li^+$ cation. On the other hand, in the low temperature phase (LT phase) three $^{81}Br$ NQR lines between 59 and 70 MHz suggested an isolated $InBr_6^{3-}$ anion with an inversion point symmetry [3]. At the phase transition to the superionic HT phase ($T_{tr}$ = 314 K) 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 $T_{tr}$. On the other hand, in the LT phase $^{115}In$ NMR at showed only an echo signal obove 1 MHz at 77 K due to the higher order quadrupole effect. Above $T_{tr}$ the FWHM line width decreased drastically, and a conventional FT-NMR technique was available to detect $^{115}In$ NMR. The sharp $^{115}In$ NMR signals of about 7 kHz at 400 K suggested a high symmetry of the anionic sublattice, probably due to the fast translational diffusion of the $Li^+$ cation. In the present paper, the effect of the partial substitution of $Li^+$ on the ionic conductivity was investigated by means of X-ray diffraction and $^7Li$, $^{115}In$ NMR measurements.

## Experimental

$Li_{3-2x}Mg_xInBr_6$ was synthesized by a solid state reaction at 493 K using a quartz tube containing a stoichiometric mixture of LiBr, $MgBr_2$ and $InBr_3$. All materials were 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 Cu-$K_\alpha$ radiation. $^7Li$ 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. The conductivity was deter-

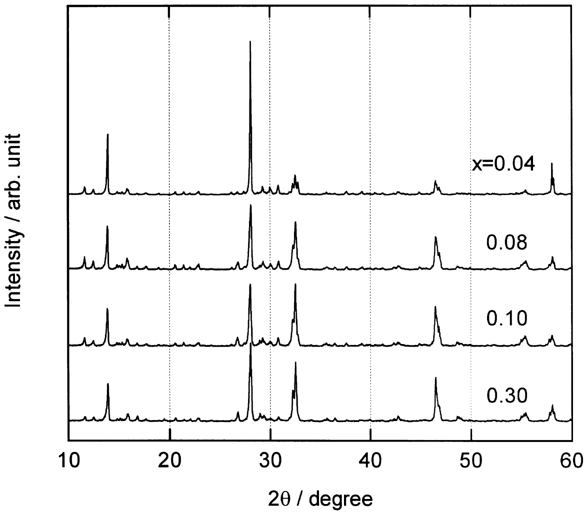

Fig. 1. Powder X-ray diffraction patterns of $Li_{3-2x}Mg_x$-$InBr_6$ at 297 K.

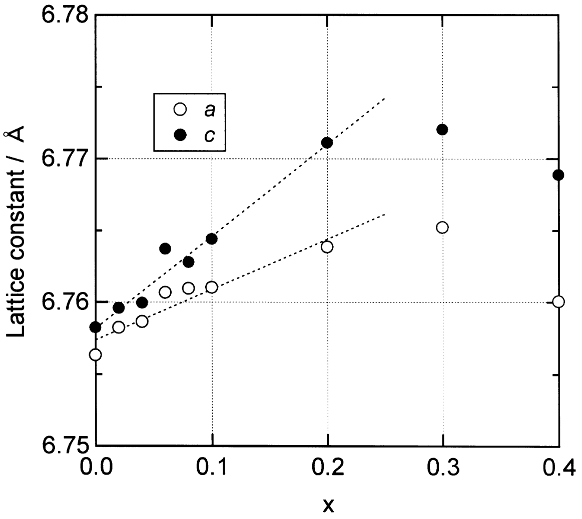

Fig. 2. Plots of lattice constants of $Li_{2-x}Mg_xInBr_6$ against Mg content, obtained form XRD patterns.

mined by a complex impedance method measured at 11 frequencies between 100 Hz and 100 kHz (YHP 4274A) in a dry nitrogen atmosphere.

## Results and Discussion

### *X-ray Diffraction*

Figure 1 shows X-ray diffraction patterns of $Li_{3-2x}Mg_xInBr_6$ ($x$ = 0.04 - 0.3) at 297 K. Several peaks shift toward lower $2\theta$ values suggesting an increase of the lattice with $x$. Most Bragg peaks became broader with $x$, indicating poorer crystallinity of the sample with increasing $x$. Since no apparent impurity peak appears below $x$ = 0.3, the solubility limit of $Mg^{2+}$ is around $x$ = 0.3. Figure 2 plots the lattice constants against x together with those of $Li_3InBr_6$, which belongs to a monoclinic system with $a$ = 6.756 Å, $b$ = 11.70 Å, $c$ = 6.758 Å, and $\beta$ = 110.1° at 297 K. Although lattice constants $b$ and $\beta$ showed no appreciable change, $a$ and $c$ increased with $x$ up to $x$ = 0.3, as is shown in Figure 2.

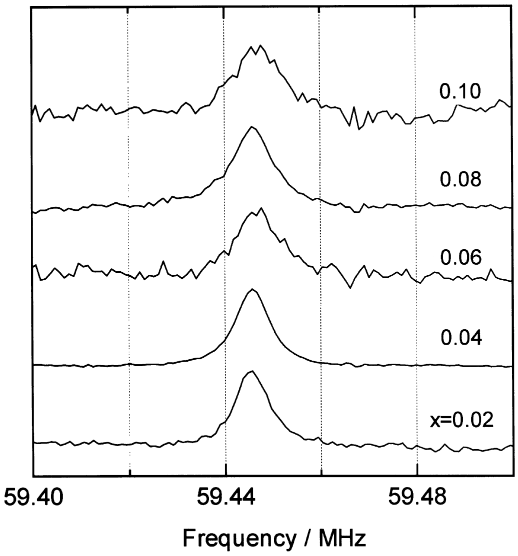

Fig. 3. $^{115}$In NMR spectra of the high temperature phase of $Li_{3-2x}Mg_xInBr_6$ at 350 K.

### *$^{115}$In NMR Spectra*

In the LT phase of $Li_3InBr_6$ only one spin echo $^{115}$In NMR signal was observed above 1 MHz due to the higher order quadrupole effect. On the other hand, in the HT phase, the line width decreased to less than 10 kHz above 350 K. Figure 3 shows the $^{115}$In NMR central transitions ($\Delta m$ = –1/2 ↔ 1/2) for a series of $Li_{3-2x}$ $Mg_xInBr_6$ observed at 350 K. The FWHM line width increases with $x$ associated with a slight shift toward higher frequencies below $x < 0.1$. At $x > 0.1$ no satisfactory spectrum could be observed, probably due to the distribution of the $e^2Qq/h$ at the In site. This finding suggests that the distortion of the anionic sublattice is enhanced by the replacement of $Li^+$ by $Mg^{2+}$.

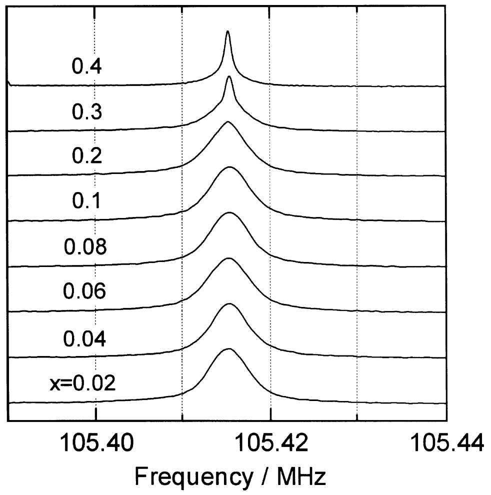

Fig. 4. $^7$Li NMR spectra of the low temperature phase of $Li_{3-2x}$ $Mg_xInBr_6$ at 300 K.

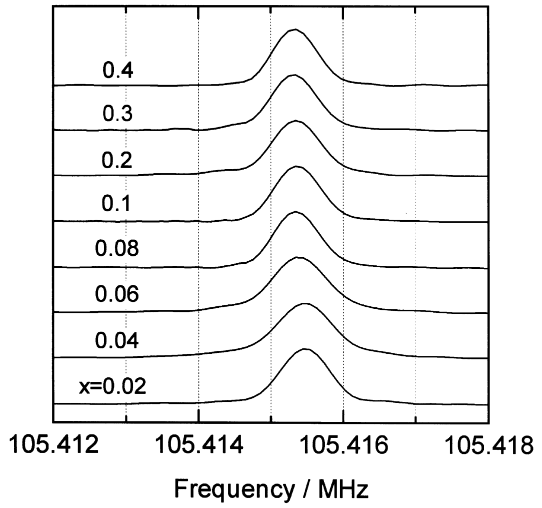

Fig. 5. $^7$Li NMR spectra of the low temperature phase of $Li_{3-2x}$ $Mg_xInBr_6$ at 400 K.

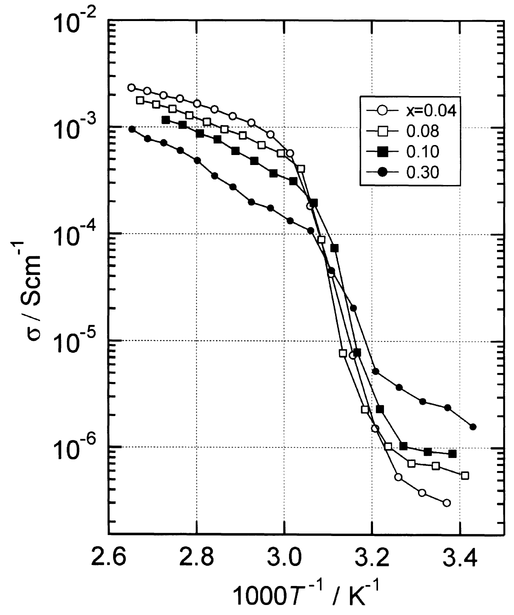

Fig. 6. Temperature dependence of the bulk conductivity of $Li_{3-2x}Mg_xInBr_6$.

### *$^7$Li NMR Spectra*

In the LT phase of $Li_3InBr_6$ the $^7$Li NMR spectrum showed a featureless Gaussian profile with a FWHM line width of about 6 kHz. No apparent quadrupole effect was observed. This line width at $x = 0$ agreed well with the one expected from the van Vleck formula assuming a rigid lattice [10, 11]. On the other hand, the line width in the HT phase reduced to 0.6 kHz. This suggests that the rate of the translational diffusion is much faster than corresponding to the inverse line width parameter of the $^7$Li NMR. Figure 4 shows $^7$Li NMR spectra at 300 K (LT phase) for $Li_{3-2x}Mg_xInBr_6$ ($x$ = 0.02∼0.4). The line width of the LT phase below $x = 0.2$ agrees well with that for $x = 0$ suggesting that the cationic sublattice forms a rigid lattice in the NMR time scale. The spectra observed for $x = 0.3$ and 0.4, however, consist of two components including a sharp one having a FWHM line width less than 1 kHz. This indicates that extrinsic vacancies accelerate the self-diffusion of the $Li^+$ cation. On the other hand, as Fig. 5 shows, all substituted samples show motional narrowing spectra due to the fast translational diffusion of the cation.

### *Conductivity*

The temperature dependence of the conductivity for $Li_{3-2x}Mg_xInBr_6$ is shown in Figure 6. The phase transitions are clearly seen around 310 ∼ 330 K, where the conductivity changes steeply for all samples. In the LT phase, the conductivity increases with increase of the Mg content. This is consistent with the $^7$Li NMR observations at $x = 0.3$ and 0.4, where a narrowing component was observed due to the translational diffusion as described above. Since a substitution of the $Li^+$ by $Mg^{2+}$ is normally used to introduce extrinsic vacancies into the crystal lattice, this tendency agrees well with the expectation. In the HT phase, on the other hand, the substitution does not improve the conductivity but decreases it with $x$. These findings suggest that the superionic property of the HT phase shows the intrinsic structural nature of the $Li_3InBr_6$. The distortion of the crystal lattice with $x$ may prevent the fast diffusion of the cation.

The activation energy, $E_a$, at the HT phase was evaluated using the equation [12],

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

where $\sigma$ is the conductivity. The activation energy increases from 25 $kJ\,mol^{-1}$ ($x$ = 0.1) to 40 $kJ\,mol^{-1}$ ($x$ = 0.4), accompanied by a decrease of the conductivity.

## *Conclusions*

In the LT phase, the ionic conductivity increases with $x$ due to the introduction of the extrinsic vacancies. Although the conductivity of the HT phase is higher than that of the LT phase, the conductivity decreases with the replacement of $Li^+$ by $Mg^{2+}$. The symmetry of the anionic sublattice is closely related to the fast diffusion of the $Li^+$ cation.

## *Acknowledgements*

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