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## Formation of amorphous LiCl aggregate regions within Li<sup>+</sup>-ion conducting glasses of (LiCl)<sub>x</sub>(LiPO<sub>3</sub>)<sub>1-x</sub> evidenced by <sup>7</sup>Li MAS NMR

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### Abstract

Li<sup>+</sup>-ion conducting glasses of (LiCl)<sub>x</sub>(LiPO<sub>3</sub>)<sub>1-x</sub> with high LiCl compositions up to  $x = 0.45$  were prepared successfully by using a twin-roller quenching method. <sup>7</sup>Li magic angle spinning (MAS) NMR spectra of the glasses showed a broad signal, and a linear dependence of the chemical shift on LiCl composition,  $x$ , was observed. The chemical shift estimated by extrapolating the linear relation to the LiCl composition limit of  $x = 1$  was very different from that of crystalline LiCl, and was concluded to correspond to that of amorphous LiCl. A linear relation to the LiCl composition was also observed for the linewidth of the signal, and quite a sharp signal was expected for amorphous LiCl from the relation. The glasses with relatively high LiCl compositions of  $x \geq 0.40$  exhibited a sharp signal besides the broad one in the spectra, and the chemical shift of the sharp signal corresponded well with that estimated for amorphous LiCl. This result clearly shows the formation of 'amorphous LiCl aggregate regions' in the (LiCl)<sub>x</sub>(LiPO<sub>3</sub>)<sub>1-x</sub> glasses with increase of the LiCl composition, and the sharp signal was reasonably attributed to the Li<sup>+</sup> ions included in the amorphous LiCl aggregate regions.

Fast ion conducting (FIC) glasses are materials of an interesting class because of their potential applications as electrolytes for constructing solid-state batteries and also solid-state electrical devices. Much effort has been made, especially for metal halide-based FIC glasses, to get information on the structure of the glasses and to understand the mechanism of the ion conduction for producing higher ionic conductivity in the glasses [1–5]. However, the microscopic structure of the glasses, particularly in the high metal halide composition range, has not been clarified yet and is still under debate. Among the glasses, AgI-based AgI–AgPO<sub>3</sub> glasses have been most widely investigated as model materials, and a homogeneous structure,

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where most  $\text{Ag}^+$  ions are coordinated to both I and O anions without the existence of AgI clusters, has been concluded from the study developed by the combination of neutron diffraction, x-ray diffraction and EXAFS data with reverse Monte Carlo modelling [6]. In contrast, the results of precise calorimetry and conductometry for the  $\text{AgI-Ag}_2\text{O-P}_2\text{O}_5$ , including  $\text{AgI-AgPO}_3$ , and  $\text{AgBr-AgPO}_3$  glasses have strongly suggested the formation of an amorphous silver halide aggregate region in high silver halide composition range [7–11].

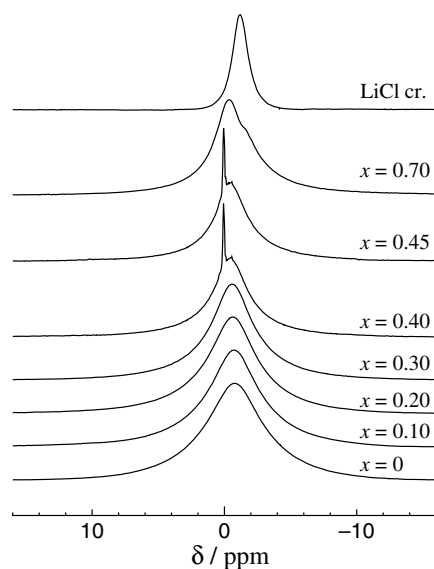
High resolution solid-state NMR potentially serves as a valuable technique for obtaining information about the above issue, and  $^7\text{Li}$  NMR for Li analogues of silver halide-based glasses are expected to be more effective due to the high NMR sensitivity and receptivity of  $^7\text{Li}$  nuclei. Actually,  $\text{LiX-LiPO}_3$  ( $X = \text{Cl, Br, I}$ ) glasses are typical  $\text{Li}^+$ -ion conducting glasses and are known to get higher ionic conductivity with increase of the LiX composition [12]. Therefore, we tried to prepare  $(\text{LiCl})_x(\text{LiPO}_3)_{1-x}$  glasses with extended glass forming LiCl composition regions by applying a twin-roller quenching method, and examined the  $^7\text{Li}$  magic angle spinning (MAS) NMR of the glasses.

The twin-roller quenching method realizes a high cooling rate of  $\sim 10^5 \text{ K s}^{-1}$  [13, 14], and glassy samples of  $(\text{LiCl})_x(\text{LiPO}_3)_{1-x}$  were successfully prepared up to the LiCl composition  $x = 0.45$ .  $^7\text{Li}$  MAS NMR measurements for the glasses revealed that the glasses with relatively high LiCl compositions of  $x \geq 0.40$  include at least two different kinds of  $\text{Li}^+$  ions; one shows a broad signal in the NMR spectrum, which exists also in the glasses with  $x \leq 0.30$ , and the other exhibits a sharp signal in the spectrum. The latter  $\text{Li}^+$  ion was obviously different in chemical shift from that in crystalline LiCl, and was reasonably concluded to be that included in amorphous LiCl formed within the  $(\text{LiCl})_x(\text{LiPO}_3)_{1-x}$  glasses from the chemical shift and the linewidth of the signal. This is the first and direct experimental evidence for the formation of ‘amorphous metal halide aggregate regions’ in the metal halide-based FIC glasses with increase of the metal halide composition.

$\text{LiPO}_3$  glass was synthesized from  $\text{LiH}_2\text{PO}_4$  of reagent grade by melting  $\text{LiH}_2\text{PO}_4$  in a Pt crucible at 1073 K and quenching the melt to room temperature.  $(\text{LiCl})_x(\text{LiPO}_3)_{1-x}$  glasses were prepared as follows: reagent grade LiCl and the  $\text{LiPO}_3$  glass were weighed to obtain the desired composition and mixed in a Pt crucible, and the mixture was heated to 1073 K; then the melt was quenched to room temperature. In this work, the twin-roller quenching method was applied to quench the melted samples at a high cooling rate; in it, the melted samples were poured between the twin rollers rotating at 4500 rpm at room temperature resulting in thin flakes of the samples with thickness of about 10  $\mu\text{m}$ . Powder x-ray diffractometry was carried out to confirm the successful preparation of glassy samples containing no crystallite. The glass forming LiCl composition region for  $(\text{LiCl})_x(\text{LiPO}_3)_{1-x}$  obtained by the twin-roller quenching method was determined to be  $0 \leq x \leq 0.45$ .

The  $^7\text{Li}$  MAS NMR spectra were acquired at the room temperature of 293 K on a Bruker DMX-300 wide-bore spectrometer operating at 116.6 MHz. A 4 mm broadband MAS probe allowed a spinning speed of 10 kHz to be used for all samples. Spectra were acquired using a 2  $\mu\text{s}$  rf pulse where the  $\pi/2$  pulse length was determined to be 3  $\mu\text{s}$ . Spectra were obtained using 16 signal averages with recycle delays from 15 to 60 s. External 1 M aqueous LiCl was used as a chemical shift reference ( $\delta = 0.00$  ppm). The accuracies of the reported chemical shifts were  $\pm 0.1$  ppm, as determined by repeated experiments and calibrations.

The prepared samples were moderately hygroscopic, and were put in a desiccator immediately after quenched to protect them from moisture. The sample for NMR measurements was packed in a 4 mm MAS rotor and sealed up within a minute after quenching. No change was observed in the NMR spectra between the sample and that exposed to the air for 10 min, showing that possible moistening of the sample during the procedure of packing into the MAS rotor did not affect the NMR property.

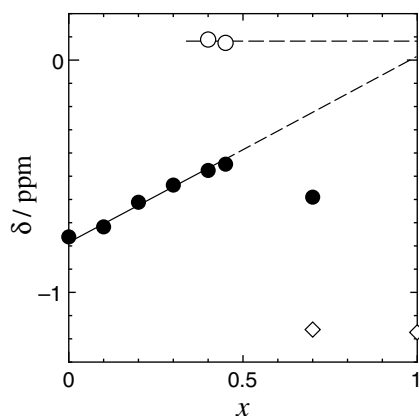


**Figure 1.**  ${}^7\text{Li}$  MAS NMR spectra for  $(\text{LiCl})_x(\text{LiPO}_3)_{1-x}$  glasses ( $0 \leq x \leq 0.45$ ), a  $(\text{LiCl})_{0.70}(\text{LiPO}_3)_{0.30}$  sample containing LiCl crystallites, and crystalline LiCl.

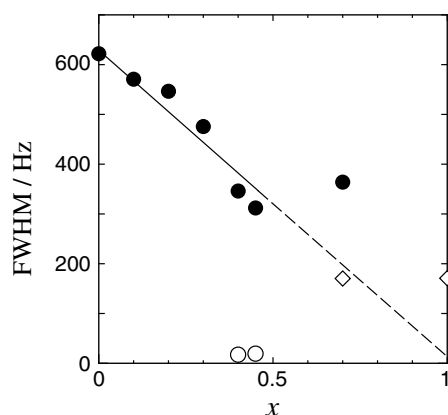
Figure 1 shows the  ${}^7\text{Li}$  ( $I = 3/2$ ) solid-state MAS NMR spectra for  $(\text{LiCl})_x(\text{LiPO}_3)_{1-x}$  glasses from the  $+1/2 \leftrightarrow -1/2$  central transition, along with the spectra for  $(\text{LiCl})_{0.70}(\text{LiPO}_3)_{0.30}$  sample which includes LiCl crystallites and for crystalline LiCl. The glasses with the LiCl composition,  $x$ , lower than 0.40 exhibited only a broad signal in the spectra. However, the glasses with  $x = 0.40$  and  $0.45$  showed a sharp signal beside the broad signal. The sharp signal disappeared with further increase of  $x$ , and the signal due to crystalline LiCl appeared instead.

The broad signal of the glassy samples shows a high frequency shift and linewidth narrowing with increase of the LiCl composition. The chemical shift,  $\delta$ , of the broad signal and the full width at half-maximum (FWHM) of the signal are plotted against the LiCl composition,  $x$ , in figures 2 and 3, respectively. The signal is assignable to the  $\text{Li}^+$  ions interacting with both the glass forming phosphate anion,  $(\text{PO}_3^-)_n$ , and  $\text{Cl}^-$  ions brought in by the addition of LiCl to  $\text{LiPO}_3$ . The interaction of  $\text{Li}^+$  ions with  $\text{Cl}^-$  ions in the glasses is enhanced with increase of the LiCl composition, and this is considered as the origin of the change of  $\delta$ . The enhanced interaction between  $\text{Li}^+$  and  $\text{Cl}^-$  ions produces higher mobility for  $\text{Li}^+$  ions in the glasses, as evidenced by the higher  $\text{Li}^+$ -ion conductivity of  $(\text{LiCl})_x(\text{LiPO}_3)_{1-x}$  glass with higher LiCl composition [12], and thus the change of the linewidth is considered as the result of motional narrowing. The spin-lattice relaxation time  $T_1$ , which was estimated roughly from the preliminary NMR experiments to determine recycle delays for signal acquisition, was observed to be shortened from  $\sim 10$  s to a few seconds with increase of the LiCl composition  $x$  from 0 to 0.45, and the result also supports the assertion that the sharpening of the signal with increase of the  $x$  is due to the motional narrowing.

The change of  $\delta$  is rather linear with  $x$  as shown in figure 2, and a chemical shift of  $\delta = 0.0$  ppm was estimated for the  $\text{Li}^+$  ions interacting only with  $\text{Cl}^-$  ions by extrapolating the linear relation to the LiCl composition limit of  $x = 1$ . This chemical shift is very different from that of  $\text{Li}^+$  ions in LiCl crystal, and is reasonably concluded to correspond to that of  $\text{Li}^+$  ions in LiCl having an amorphous structure, which has never been obtained experimentally.



**Figure 2.** The dependence on the LiCl composition,  $x$ , of the chemical shift of the  $^7\text{Li}$  NMR signal,  $\delta$ , for  $(\text{LiCl})_x(\text{LiPO}_3)_{1-x}$  glasses: ●, broad signal; ○, sharp signal. ◇ represents the result for crystalline LiCl.



**Figure 3.** The dependence on the LiCl composition,  $x$ , of the full width at half-maximum (FWHM) of  $^7\text{Li}$  NMR signal for  $(\text{LiCl})_x(\text{LiPO}_3)_{1-x}$  glasses: ●, broad signal; ○, sharp signal. ◇ represents the result for crystalline LiCl.

The linewidth of the broad signal also depends rather linearly on the LiCl composition  $x$  as exhibited in figure 3, and quite a sharp signal is expected for amorphous LiCl from the extrapolation of the linear dependence to  $x = 1$ .

The chemical shifts of sharp signals observed for  $x = 0.40$  and  $0.45$  glasses were  $0.09$  and  $0.07$  ppm, respectively, and are plotted in figure 2. They are almost identical, and correspond well to that of amorphous LiCl estimated above within the experimental error. In  $(\text{LiCl})_x(\text{LiPO}_3)_{1-x}$  glasses,  $\text{Li}^+$  and  $\text{Cl}^-$  ions introduced by LiCl are dispersed between the glass network former of  $\text{LiPO}_3$  having one-dimensional chain structure. In the low LiCl composition range,  $\text{Li}^+$  ions in the glass are interacting with both  $(\text{PO}_3^-)_n$  and  $\text{Cl}^-$  ions. The interaction between  $\text{Li}^+$  and  $\text{Cl}^-$  ions is enhanced with increase of the LiCl composition, and when the LiCl composition reaches some critical value, for instance  $x \sim 0.4$ , LiCl aggregate regions containing only  $\text{Li}^+$  and  $\text{Cl}^-$  ions are considered to be formed naturally within the interstices between the  $\text{LiPO}_3$  networks. The LiCl aggregate is expected to have an amorphous structure developing in size with increasing LiCl composition, and to crystallize within the

glass matrix when the size exceeds some critical magnitude with further increase of the LiCl composition. Therefore, the sharp signal is assignable to the  $\text{Li}^+$  ions included in the amorphous LiCl aggregate region formed within the glasses. The linewidths (FWHM) of the sharp signals were evaluated to be  $\sim 20$  Hz for both cases of the glasses with  $x = 0.40$  and  $0.45$ , as plotted in figure 3. The magnitude corresponds well to that expected for amorphous LiCl. The  $T_1$  of the sharp signals was roughly estimated to be about 1 s, which is somewhat shorter than those of the broad signals. These results also indicate the validity of the assignment of the sharp signal to the  $\text{Li}^+$  ions included in amorphous LiCl aggregate regions.

The formation of an amorphous silver halide aggregate region has been indicated in the high silver halide composition range for  $\text{AgI-Ag}_2\text{O-P}_2\text{O}_5$  and  $\text{AgBr-AgPO}_3$  glass systems [7–11]. In this work, we observed successfully for  $(\text{LiCl})_x(\text{LiPO}_3)_{1-x}$  glasses the  $^7\text{Li}$  NMR signal which corresponds directly to amorphous LiCl. This result shows more clearly the formation of ‘amorphous LiCl aggregate regions’ within LiCl-based FIC glasses, and strongly suggests that the formation of such an amorphous metal halide aggregate region is a common structural feature of metal halide-based FIC glasses in the high metal halide composition range.

To obtain more precise information about the dynamical properties of  $\text{Li}^+$  ions in  $(\text{LiCl})_x(\text{LiPO}_3)_{1-x}$  glasses and especially of those in the amorphous LiCl aggregate regions in the glasses, studies on the temperature dependence of the NMR spectra and  $T_1$  are in progress in our laboratory.

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