Mg^{2+} Ion-exchange with the Li^+ Ion in a Fast Li Ion-conducting Perovskite $La_{0.55}Li_{0.35}TiO_3$

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Mg^{2+} ion-exchange with the Li^+ ion in a fast Li ion-conducting perovskite $La_{0.55}Li_{0.35}TiO_3$ was successful using $MgCl_2$–KCl molten salt. The lattice parameter decreased as a result of the ion-exchange. These results suggest that the driving force of the ion-exchange reaction depends primarily on a decrease in the lattice energy, accompanied by the substitution of the smaller Mg^{2+} for the larger Li^+ ion. A polycrystalline ion-exchanged sample was found to show considerable Mg^{2+}-ion conductivity (4.1×10^{-6} S cm^{-1}) at a lower temperature, 285 °C, than the synthesis temperature, 450 °C.

The field of lithium ion-conducting materials has been widely studied because of their potential applications for solid electrolytes in high-energy batteries and other electrochemical devices. Among these materials, much attention has recently been paid to lithium ion-conducting perovskites (general formula ABO_3) first reported by Latie et al.[1] and Belous et al.,[2] due to their high conductivity, ever since a perovskite lanthanum lithium titanate (La, Li)TiO_3 was found to show lithium-ion conductivity as high as 10^{-3} S cm^{-1} at room temperature.[3] The high conductivity originates from the diffusion of Li ions via vacancies in the A-site-deficient perovskites.

The present study was motivated by the hypothesis that the skeleton of perovskite is also likely to give fast diffusion paths for other kinds of ions with an ionic radius close to that of the Li^+ ion, e.g. Mg^{2+}.[4] However, in a preliminary study, perovskites including Mg^{2+} in the A-site, e.g., (La, Mg)TiO_3, were not successfully synthesized by the conventional solid-state reaction under ambient pressure. Yao and Kummer have reported that the sodium ions in a fast two-dimensional Na^+ ion-conductor Naβ-Al_2O_3 have been exchanged in molten salts with K^+, Ag^+, Rb^+, and Li^+ ions.[5] On the basis of these results, Mg^{2+} ion-exchange with the Li^+ ion in a fast Li ion-conducting perovskite $La_{0.55}Li_{0.35}TiO_3$, among $La_{2/3-x}Li_{3x}TiO_3$ was attempted in the present study using $MgCl_2$-KCl molten salt.

$La_{0.55}Li_{0.35}TiO_3$ (abbreviated as LLT below) was prepared by a conventional solid-state reaction with the starting materials La_2O_3(4N), Li_2CO_3(3N), and TiO_2(3N). The metal content of La_2O_3 was determined by chelatometry with EDTA. Other materials were heated to 130 °C in an oven prior to weighing. A mixture of the raw materials (the molar ratio of metals was La : Li : Ti = 0.55 : 0.35 : 1) was calcined at 600–800 °C for 4 h, and 1100 °C for 12 h in air with intermediate grindings. The calcined powder was pressed into pellets (about 1 mm in thickness, 7 mm in diameter) and sintered at 1150 °C for 6 h in air, and then furnace-cooled. The pellets or ground powder were used for ion-exchange experiments. The ion-exchange reaction was carried out as follows. The reaction mixture, the powder or pellet of LLT and $MgCl_2$ (case 1), or the mixture of 40 wt%$MgCl_2$ and 60 wt%KCl (case 2) was evacuated in a silica glass tube at 200 °C for 1 h and then sealed under vacuum. The sealed tube was heated at 720 °C (case 1) or 450 °C (case 2), higher than the melting or eutectic temperature of chloride.[6] After cooling, the chloride was dissolved with distilled water. The product was filtered and washed with distilled water and dried in an oven at 130 °C. The molar ratio of the metals for the sample was determined by inductive-coupled plasma (ICP) spectroscopy using a SEIKO SPS1500 instrument or a Horiba Ultima2. The sample was then dissolved as follows. A small amount of sample (approximately 10 mg) and 1 ml conc. HCl (35 wt%) were sealed in a Pyrex glass tube and kept at approximately 130 °C for about 10 h in an oven, or 10 ml conc. H_2SO_4 with 10 mg of sample and 1 g of $(NH_4)_2SO_4$ was heated.

The phase identification and determination of lattice parameters were carried out by the powder X-ray diffraction method using a Rigaku RINT2100 diffractometer (graphite-monochromatized Cu Kα). In determining the lattice parameters, Si powder(5N) was used as an internal standard.

The ionic conductivity at 285 °C of the pellet ion-exchanged was measured by a complex impedance method using a HP 4192A impedance analyzer in the frequency range of 5 Hz to 13 MHz and a d.c. method. The electrodes were attached to both surfaces of the pellet with pasted Au or evaporated Mg.

Figure 1 shows the powder X-ray diffraction patterns of (a) pristine LLT, (b) the powder exchanged at 720 °C for 1 h using $MgCl_2$ (case 1, the molar ratio of Mg to Li in LLT, Mg/Li = 1), and (c) the powder exchanged at 450 °C for 1 h using $MgCl_2$-KCl (case 2, molar ratio Mg/Li = 5). LLT shows the tetragonal

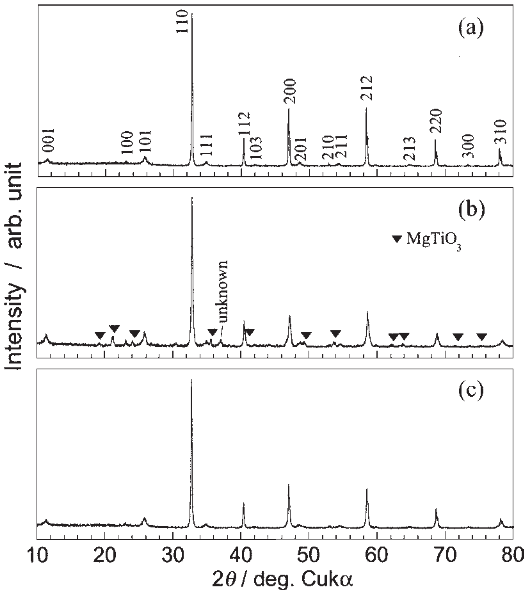

Figure 1. X-ray diffraction patterns of (a) LLT, (b) the powder exchanged at 710 °C for 1 h using $MgCl_2$, and (c) the powder exchanged at 450 °C for 1 h using $MgCl_2$-KCl.

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perovskite structure with the partially ordered distribution of La ions on the perovskite A-sites along the *c* axis, which doubles the cell parameters $c (c = 2a)$.[7] When the reaction temperature was high, the second phases, $MgTiO_3$ and the unknown phase, except for the perovskite phase, were observed as shown in Figure 1(b). On the other hand, a single phase with the same structure as LLT was obtained at 450 °C using $MgCl_2$–KCl molten salt (Figure 1(c)). The composition and lattice parameters before and after the ion exchange using $MgCl_2$–KCl molten salt are listed in Table 1. The result indicates that the ion-exchange reaction is advanced as in equation (1).

$$2Li^+ \text{ in LLT} + MgCl_2 \rightarrow Mg^{2+} \text{ in the perovskite} + 2LiCl \tag{1}$$

The lattice parameters after the ion-exchange decreased, which can be attributed to the smaller ionic radius of the Mg^{2+} ion than that of the Li^+ ion.[4] Furthermore, the potassium with larger ionic radius than Li^+ was not detected within a measurement error. These results imply that the reduction in lattice energy by the lattice contraction promotes the ion-exchange reaction.[8]

Table 1. The composition and lattice parameters, *a*, before and after the ion exchange at 450 °C using $MgCl_2$–KCl molten salt

Sample	Composition	*a*/nm
LLT	$La_{0.56(1)}Li_{0.34(1)}TiO_{3.01(2)}$	0.38701(1)
Exchanged	$La_{0.56(1)}Li_{0.05(1)}Mg_{0.13(1)}TiO_{3.00(2)}$	0.38639(2)

The uncertainties are shown in parentheses, following the last significant figure to which they are attributed.

The pellet for measuring the conductivity was obtained twice by ion-exchange at 450 °C for 12 h using $MgCl_2$–KCl (molar ratio Mg/Li = 2.5). The reaction also yielded a single perovskite phase with the composition $La_{0.56(1)}Li_{0.02(1)}Mg_{0.16(1)}TiO_{3.01(2)}$ and decreased the lattice parameter, *a*, to be 0.38617(3) nm. The conductivity at 285 °C was measured to be 2.0×10^{-6} S cm^{-1} by the d.c. method using Mg electrodes. Figure 2 shows the complex impedance plane plots at 285 °C of the sample with the electrodes of Au and Mg. These results indicate that Au electrodes are blocking, while Mg electrodes are reversible and the sample shows the Mg^{2+}-ion conductivity. Judging from the capacitance, *C*, the small semicircle in the high-frequency region ($C = 14$ pF) and the large semicircle in the low-frequency region ($C = 7$ nF) in the case of the Mg electrodes are thought to correspond to the bulk crystal part and the grain boundary part of the sample, respectively. It was also confirmed that Mg electrodes are blocking for Li^+ ions of LLT by the impedance measurement. Accordingly, the total Mg^{2+}-ion conductivity at 285 °C can be estimated to be 4.1×10^{-6} S cm^{-1} from the impedance plot in the case of the Mg electrodes, which parallels the value measured by the d.c. method using Mg electrodes. This value is comparable to that (2×10^{-5} S cm^{-1} at 500 °C) of the fastest Mg^{2+} ion-conducting inorganic solid, $Mg_{1+x}Zr_4P_6O_{24+x}+xZr_2O(PO_4)_2$ ($x = 0.4$) composite, reported by Imanaka et al.[9] It could not be confirmed whether the bulk crystal conductivity at 285 °C as high as 4.1×10^{-4} S cm^{-1} estimated from the plot in the high-frequency region is due only to Mg^{2+}-ion migration. The diffusion process of the ion-exchange reaction and the Mg^{2+}-ion conductivity will be reported in the future in more detail.

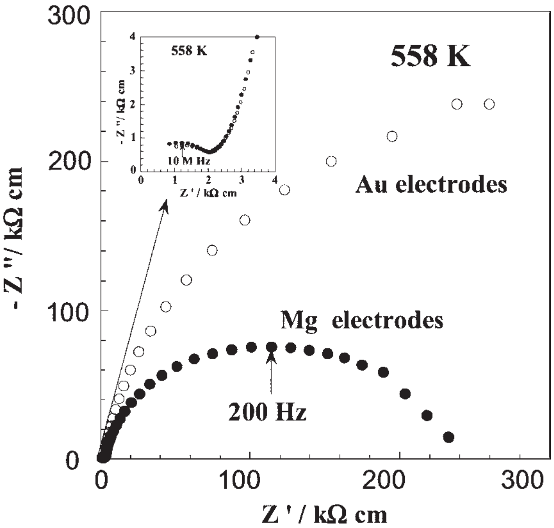

Figure 2. Complex impedance plane plots at 285 °C of a polycrystalline $La_{0.56(1)}Li_{0.02(1)}Mg_{0.16(1)}TiO_{3.01(2)}$ with the electrodes of Au(○) and Mg(●). Inset shows data in the high-frequency region.

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