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Ionic Conductivity and Structure of New Double Chloride Li_6FeCl_8 in the LiCl-$FeCl_2$ System

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The phase diagram of the LiCl-$FeCl_2$ system was determined. The system contained two intermediate compounds, one the new phase Li_6FeCl_8 with the Mg_6MnO_8-type structure and the other Li_2FeCl_4 with the spinel structure. Electrical conductivity measurements on Li_6FeCl_8 showed a high ionic conductivity of 2.0×10^{-3} S cm^{-1} at 200 °C.

The double chlorides containing lithium have attracted considerable interest because of the high lithium ion conduction at moderate temperature. The spinel, Li_2MCl_4 (M=Mg, V, Mn, Fe, Cd), showed a high lithium ion conductivity, the value of which is comparable to or greater than those for the high lithium ion conductors reported previously.$^{1-5)}$ The Mg_6MnO_8-type compound, Li_6MCl_8 (M=V, Co), also showed a high ionic conduction.$^{6-8)}$

In the previous work on double chlorides containing lithium, we reported that the cubic spinel $Li_{2-2x}Fe_{1+x}Cl_4$ had a high ionic conductivity of 0.1 S cm^{-1} at 400 °C and that the vacancy played an important role for the conduction.$^{4)}$ Recently, we found that the cubic spinel transformed at 126 °C to the low-temperature orthorhombic modification with the ordered cationic arrangement over the octahedral sites.$^{9)}$

The purpose of this study is to search new phases which might have a high lithium ion conductivity and to clarify the phase relationship in the LiCl-$FeCl_2$ system. We found a new intermediate compound Li_6FeCl_8 in the course of the phase diagram study by preparing more than 30 different samples of the LiCl-$FeCl_2$ system. We examined the crystal structure and the electrical conductivity of Li_6FeCl_8.

Samples were prepared in the same manner as described previously.$^{3)}$ X-ray diffraction (XRD) patterns of the powdered samples were obtained using monochromated CuKα radiation. A 7 μm thick aluminum window covered the sample holder to prevent moisture attack during measurement.

We constructed the phase diagram, shown in Fig. 1, using high temperature XRD and DTA measurements. The system contained two intermediate compounds, Li_2FeCl_4 and Li_6FeCl_8. Li_2FeCl_4 had the orthorhombic spinel lattice at room temperature and decomposed to Li_6FeCl_8 and the non-stoichiometric cubic spinel $Li_{2-2x}Fe_{1+x}Cl_4$ at 126 °C.$^{9)}$ The range of solid solution for the orthorhombic spinel was found to be $0<x<\simeq 0.05$ in $Li_{2-2x}Fe_{1+x}Cl_4$ around 70 °C. The non-stoichiometric $Li_{2-2x}Fe_{1+x}Cl_4$ with x=0.05 transformed from the orthorhombic to the cubic structure around 80 °C.

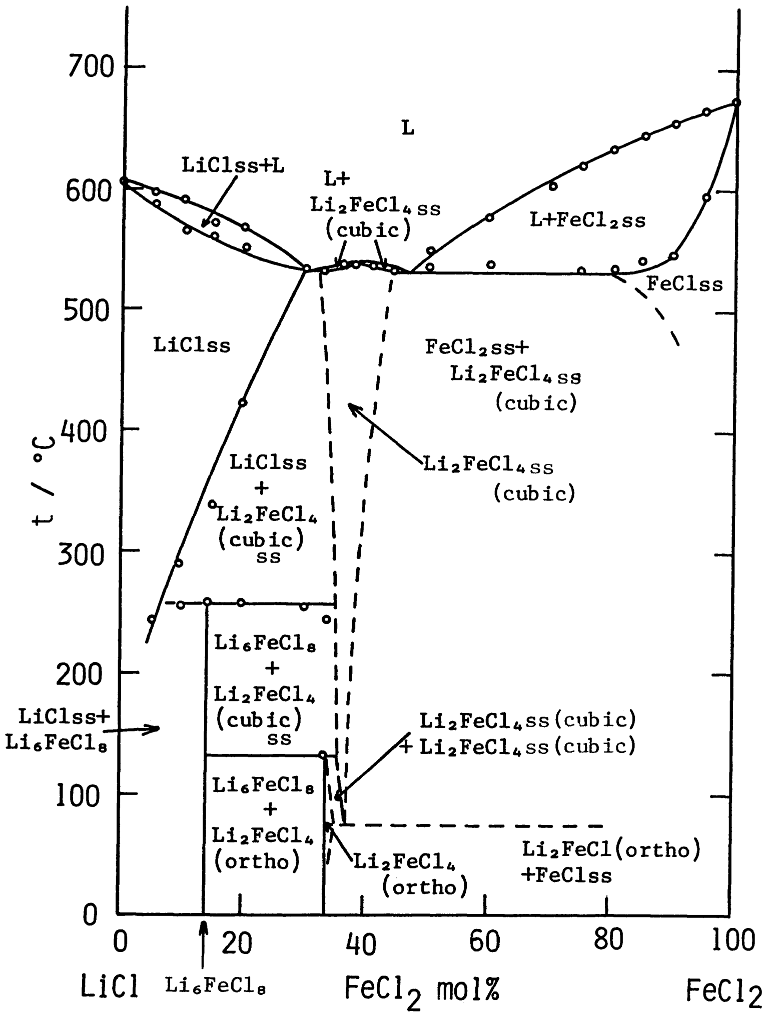

Fig. 1. Phase diagram of the $LiCl-FeCl_2$ system.

Table 1. X-Ray diffraction data for Li_6FeCl_8

h k l	d_{calcd}	d_{obsd}	I_{calcd}	I_{obsd}
1 1 1	5.95	5.96	54	19
2 0 0	5.15	5.15	11	11
2 2 0	3.64	3.65	11	4
3 1 1	3.107	3.108	4	9
2 2 2	2.975	2.975	53	42
4 0 0	2.576	2.577	100	100
3 3 1	2.364	2.365	4	2
4 2 0	2.304	2.305	4	2
4 2 2	2.103	2.104	3	2
5 1 1 3 3 3)	1.983	1.984	13	5
4 4 0	1.8216	1.8217	59	26
5 3 1	1.7418	1.7422	8	3

The range of solid solution for the cubic spinel was $0.05<x<0.2$ around 400 °C.

The XRD pattern of the sample containing 14.3 mol% $FeCl_2$ (Li_6FeCl_8) showed a striking resemblance to that of lithium chloride. However, some additional reflections which could not be indexed by the LiCl structure were observed. The intensities of the additional lines increased with $FeCl_2$ content from 0 to 14.3 mol%. The samples containing more than 14.3 mol% $FeCl_2$ showed additional reflections due to the spinel. These results indicate the existence of the intermediate compound with a formula of Li_6FeCl_8.

The XRD pattern of Li_6FeCl_8 were indexed by a cubic unit cell with a=10.305(5) Å, which is a factor of two larger than the unit cell of LiCl, a=5.1396 Å. The pattern was similar to that of Li_6MCl_8(M=V, Co) with the Mg_6MnO_8-type structure.[6-8)] The structure corresponds to a super-structure of the LiCl-type with an ordered arrangement of cations and vacancies over the octahedral sites. The XRD intensities were calculated under the conditions: space group Fm3m; Fe: 4a (0, 0, 0); Li: 24d (0, 1/4, 1/4); Cl(1): 8e (1/4, 1/4, 1/4); Cl(2): 24e (u, 0, 0). The positional parameter u was fixed at 1/4. Table 1 shows the calculated intensities which are in good agreement with the observed values. This indicates that Li_6FeCl_8 has the Mg_6MnO_8-type structure with the ordered cation arrangement.

Figure 2 shows the XRD patterns of the sample containing 14.3 mol% $FeCl_2$ observed at high temperatures. The XRD pattern at 248 °C is characteristic of the Mg_6MnO_8-type structure, while that at 397 °C is the monophasic LiCl-type structure(LiClss). The pattern at 297 °C, on the other hand, indicates co-existence of two structure types, one the cubic spinel and the other the LiCl-type structure. High temperature XRD results suggest that LiClss with a nominal formula of Li_6FeCl_8 has a random cationic distribution on the octahedral sites.

The DTA curves for Li_6FeCl_8 showed two endothermic peaks around 259 and 335 °C, which correspond to the decomposition of Li_6FeCl_8 to the non-stoichiometric spinel $Li_{2-2x}Fe_{1+x}Cl_4$ and LiClss, and to the phase change from two phase region to the monophasic LiClss.

Electrical conductivities of 0.5 g pressed pellets were measured by the ac impedance method over a frequency range of 5 Hz-500 kHz. Figure 3 shows the Arrhenius plots of the conductivity of Li_6FeCl_8. The conductivity of 5.0×10^{-2} S cm^{-1} at 400 °C is almost comparable to that of Li_6CoCl_8, while a value of 2.0×10^{-3} S cm^{-1} at 200 °C is slightly higher than that of 3.8×10^{-4} S cm^{-1} for Li_6CoCl_8.[8)] The change in slope of the conductivity curve around 300 °C corresponds to the phase change from Li_6FeCl_8 to the two-phase region and from the two-phase region to the monophasic LiClss. The activation energies are calculated to be 70.4 kJ mol^{-1} (room temperature - 259 °C) for Li_6FeCl_8 and to be 16.7 kJ mol^{-1} (335 - 450 °C) for LiClss. The lower activation energy observed for the high-temperature disordered phase confirmed that the cation arrangement on the octahedral sites played an important role for lithium ionic motion. The results are consistent with the previous data for Li_6CoCl_8 that the ordered phase had a higher activation energy (E=82 kJ mol^{-1}) than the disordered one (E=36 kJ mol^{-1}).[8)]

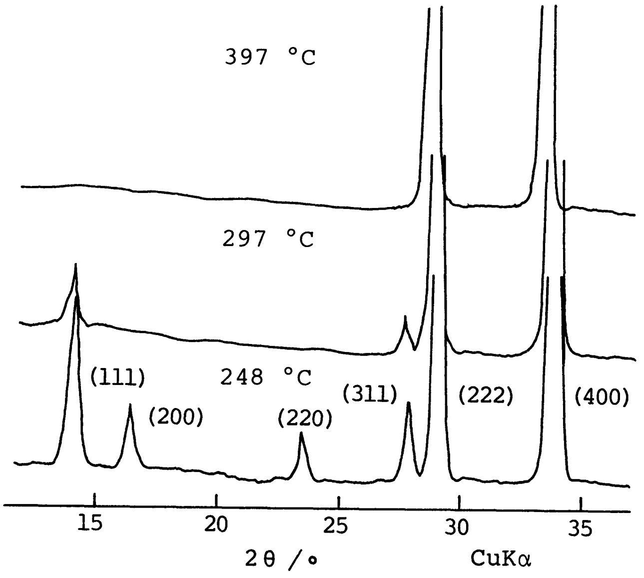

Fig. 2. XRD patterns at high temperatures.

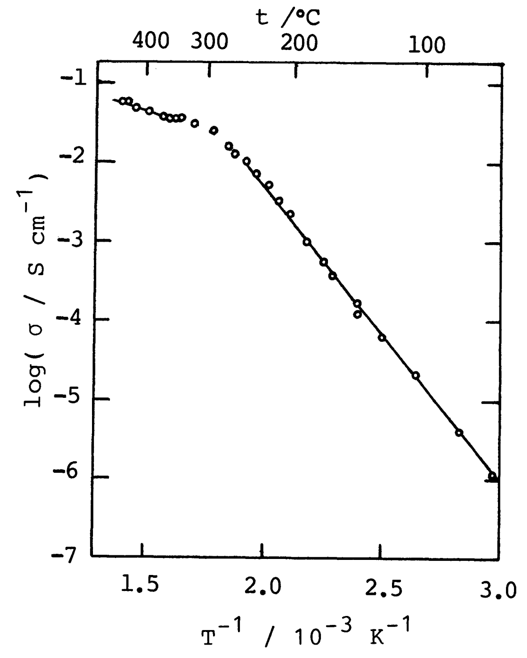

Fig. 3. Thermal evolution of the conductivity for Li_6FeCl_8. The two lines in the Figure correspond respectively to Li_6FeCl_8 and LiClss.

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