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Ionic Conductivity and Structure of Double Chloride Li_2ZnCl_4 in the $LiCl-ZnCl_2$ System

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The phase diagram of the $LiCl-ZnCl_2$ system was determined. The system contained one intermediate compound, Li_2ZnCl_4; it transformed from the normal spinel to the olivine structure at 215 °C. Electrical conductivity measurements showed a high ionic conductivity of 2.0×10^{-4} S cm^{-1} at 280 °C.

The double chlorides containing lithium have attracted considerable interest because of high lithium ion conductivity at moderate temperature.[1] The family of the spinels, Li_2MCl_4 (M=Mg, Mn, Fe, Co), for example, showed a high ionic conductivity of 0.1 S cm^{-1} around 400 °C and further showed a phase transition from a low- to a high-ionic conduction state.[2] We recently found new distorted spinels, Li_2MCl_4(M= Cr, Fe, Co), which had higher activation energies for ionic conduction than those of the cubic spinels. This suggests that the lattice distortion is one of the factors influencing the ionic conduction.[3]

In the $LiCl-ZnCl_2$ system, the intermediate compound, Li_2ZnCl_4, was reported to have the olivine structure, characterized by octahedrally surrounded Li^+ ions in hexagonal close-packed chloride ions.[4] The cationic distribution of the olivine structure might lead to a conduction mechanism different from that of the cubic inverse spinel structure. The purpose of this study is to clarify the ionic conductivity of Li_2ZnCl_4 and to discuss its ionic conduction in comparison with other chloride spinels. In the course of the phase diagram study of the $LiCl-ZnCl_2$ system, we confirmed a new low-temperature modification with the normal spinel structure, reported more recently by Lutz et al.[5] No detailed structural data is however reported in the literature. We thus determined its structure by X-Ray Rietveld analysis and the ionic conductivity by ac impedance technique.

Anhydrous lithium chloride and zinc dichloride were used. The appropriate quantities of reactants, which were dried under vacuum at 130 °C, were ground together, pressed into a pellet at 60 MPa in a nitrogen-filled glove box, and heated in an evacuated Pyrex tube at 300 °C for 1 week. X-Ray diffraction (XRD) patterns of the powdered samples were obtained using CuKα radiation. A 7μm-thick Al window covered the sample holder to prevent moisture attack during the measurement.

We constructed the phase diagram, shown in Fig. 1, using DTA and high temperature XRD measurements. The system contained one intermediate compound, Li_2ZnCl_4. No other phase such as the Suzuki-type phase, found in the $LiCl-MCl_2$(M=V, Fe, Co, Ni) system,[6] was observed. The DTA curves of the samples prepared at 300 °C

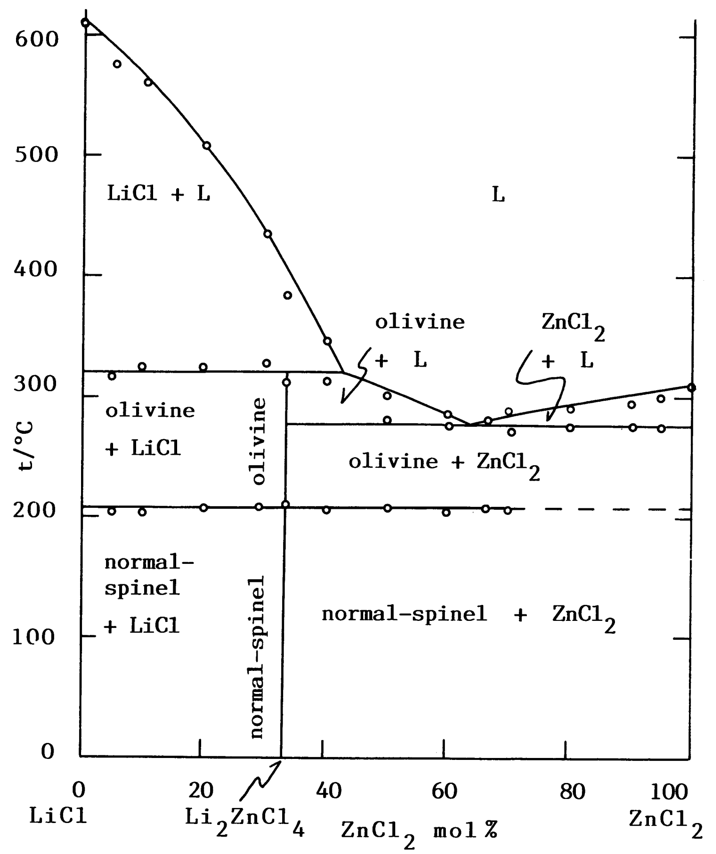

Fig. 1. Phase diagram of the $LiCl-ZnCl_2$ system.

showed a small endothermic peak near 200 °C, suggesting a transition from a new low-temperature modification to the olivine type structure. We thus annealed the sample at 150 °C for one week: the annealing just below the transition temperature would facilitate equilibrium and enable the monophasic low-temperature modification to be obtained. The samples after being annealed at 150 °C showed sharp DTA endothermic peaks at 215 °C. The XRD pattern of the low-temperature phase of Li_2ZnCl_4 was indicative of a cubic cell with a cell constant, a = 10.3400(2) Å, with space group Fd3m. Recently, Lutz et al. found a low-temperature modification of Li_2ZnCl_4 below 186 °C,$^{5)}$ the transition temperature of which is slightly lower than that obtained in this study. The discrepancy of the transition temperature is probably due to a different preparation or annealing temperature.

We determined the structure of the low-temperature modification by XR powder Rietveld analysis. XRD data for Rietveld analysis were collected with CuKα radiation using a high-power XR powder diffractometer (Rigaku RAD 12kW) equipped with a graphite monochromater. The structural refinement was performed using the Rietveld analysis computer program RIETAN.$^{7)}$ Refinement proceeded in a straightforward manner with space group Fd3m using the normal spinel, as a model. Initial refinement using the normal spinel as a model did not proceed to low R-value. We repeated the refinement cycles with an extra condition, taking into account a partial disorder of the Li^+ and Zn^{2+} ions. Refinement proceeded to the agreement factors R_{wp}=14.85, R_p=11.36, and R_I=7.41. Table 1 shows the final structural parameters for Li_2ZnCl_4. The interatomic distances and bond angles are listed in Table 2.

Electrical conductivities of pressed pellets were measured by the ac impedance

Table 1. Fractional coordinates for Li_2ZnCl_4 spinel

Atom	Site	Occupancy	x	y	z	B/Å^2
Li(1)	16d	0.95(2)	0.625	0.625	0.625	13(5)
Zn(1)	16d	0.05(2)	0.625	0.625	0.625	13(5)
Zn(2)	8a	0.89(2)	0	0	0	1.1(2)
Li(2)	8a	0.11(2)	0	0	0	1.1(2)
Cl	32e	1	0.3770(6)	0.3770(6)	0.3770(6)	1.9(2)

Table 2. Bond lengths(Å) and angles(°) for Li_2ZnCl_4 spinel

Li(1) - Cl	2.564(6)
Zn(2) - Cl	2.274(6)
Cl - Zn(2) - Cl	109.5(2)
Cl - Li(1) - Cl	89.1(2)

method. Figure 2 shows the temperature dependence of the conductivity for Li_2ZnCl_4. A break in the curve observed around 215 °C corresponds to the phase change from the cubic spinel to the olivine structure. The activation energy was calculated to be 82 kJ mol^{-1} and 72 kJ mol^{-1} below and above the transition temperature, respectively.

The high-temperature modification of Li_2ZnCl_4 has the olivine structure with space group Pnma. Two kinds of octahedral sites, 4a and 4c for Li(1) and Li(2), respectively (Fig. 3), share faces to interstitial tetrahedral sites and connected with each other on the ab-plane. They connected also with each other along c-axis through interstitial octahedral sites by sharing faces. The conduction pathway plausible is, therefore, 1) Li(1) to Li(1) sites and Li(1) to Li(2) sites through tetrahedral voids on the ab-plane, and 2) Li(1) to Li(1) sites and Li(2) to Li(2) sites through octahedral voids along c-axis.

For the normal spinel, the lithium ions on the octahedral 16d sites participate in ionic conduction, because most of the lithium ions are situated on these sites. The conduction pathway is, therefore, through the interstitial tetrahedral 48f sites (Fig. 4). The structural results obtained in this study, however, suggest a partial disorder on the cationic distribution: a part of the lithium ions on the tetrahedral 8a sites, which are found to be suitable for conduction on the inverse spinels,[3)] may participates in the ionic conduction.

The zinc double chloride showed lower conductivity and higher activation energy (σ=2.0x10^{-4} S

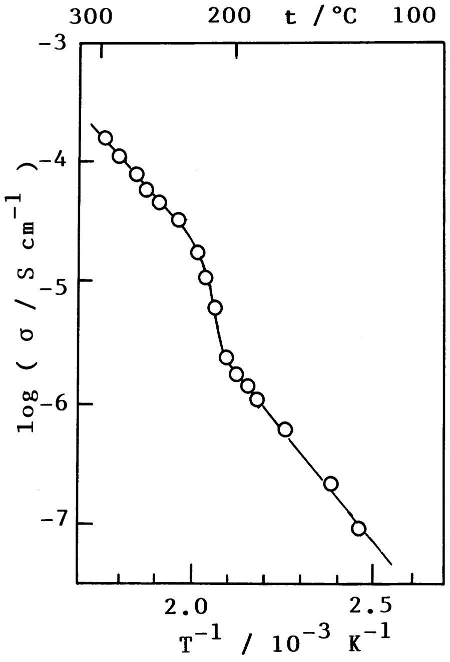

Fig. 2. Temperature dependence of the conductivity for Li_2ZnCl_4.

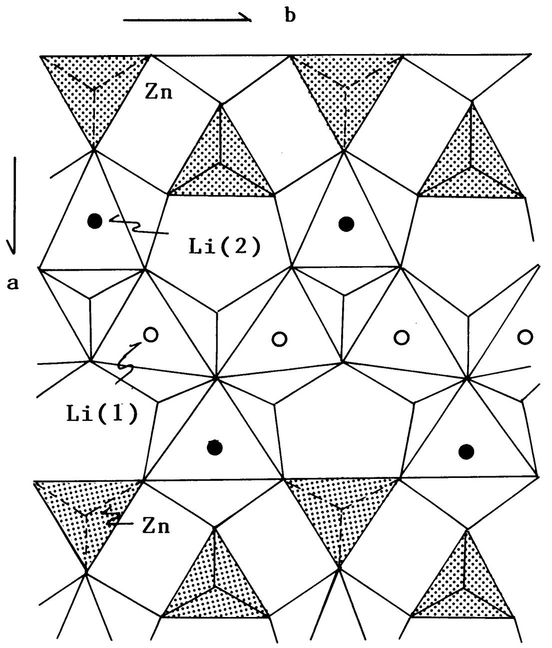

Fig. 3. The olivine structure.

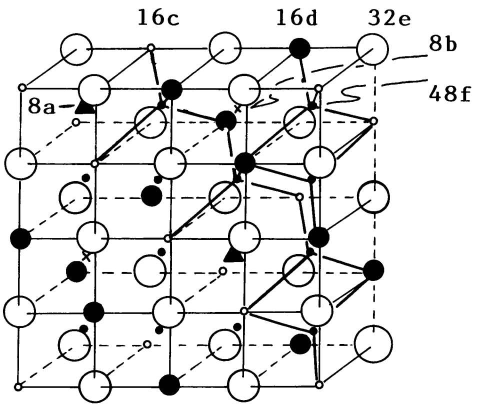

Fig. 4. The spinel structure. The interstitial sites and the ionic conduction pathway are indicated.

cm^{-1} at 280 °C with E=82 kJ mol^{-1} for the olivine and $\sigma=1.0\times10^{-6}$ S cm^{-1} at 200 °C with E= 72 kJ mol^{-1} for the spinel) than that of the cubic inverse spinels, Li_2MCl_4 ($\sigma=5\times10^{-3}$ S cm^{-1} at 200 °C, $\sigma=3\times10^{-2}$ S cm^{-1} at 280 °C, E= 30-40 kJ mol^{-1}). The tetrahedral 8a and the interstitial octahedral 16c sites in the inverse spinel mainly participate in the ionic conduction, while the octahedral 16d sites do not.[2] Since the lithium ions on the 16d sites are responsible for conduction in the normal spinel, it is natural that the normal spinel has lower ionic conduction than the inverse spinels. The conduction pathway through the tetrahedral 48f interstitial sites, which are closely situated to the tetrahedral Zn sites, is less acceptable for conduction of lithium ions.

The olivine structure showed a lower activation energy than the cubic spinels. This is also caused by the fact that the octahedral sites are responsible for ionic conduction. However, the conduction pathway through the octahedral voids leads to a slightly lower activation energy than that of the normal spinel; the interstitial octahedral voids between two lithium sites are favorable for conduction along c-axis. The olivine, furthermore, has lower calculated density(d=1.529) than the spinel(d=1.601), suggesting that the former is more open structure than the latter.

We concluded in the previous studies on the Li_2MCl_4 spinels that the lithium ions on the tetrahedral sites play an important role for ionic conduction on the basis of the following results: 1) vacancy in the tetrahedral sites enhances the conductivity,[1] 2) the tetrahedral 8a and interstitial octahedral 16c sites participate in the conduction,[2] and 3) the distorted spinels, Li_2MCl_4 (M=Cr, Fe, Co), having lithium ions only on the octahedral sites showed lower ionic conduction than the cubic inverse spinels.[3] Both the olivine and the normal spinel showed lower ionic conduction than the inverse spinels; this confirmed the conclusion that the mobile species on the tetrahedral sites are responsible for high ionic conduction in the close packed anionic arrays.

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