Formation and Growth of Spinel-type $LiMn_2O_4$ Single Crystals by LiCl–$MnCl_2$ Flux Evaporation

Weiping Tang,* Xiaojing Yang,† Hirofumi Kanoh,† and Kenta Ooi†
Research Institute for Solvothermal Technology, 2217-43 Hayashi-cho Takamatsu, 761-0301
†Marine Resources and Environment Research Institute, National Institute of Advanced Industrial Science and Technology, 2217-14 Hayashi-cho Takamatsu, 761-0395

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Octahedral and rectangle-like $LiMn_2O_4$ single crystals larger than 0.1 × 0.1 × 0.1 mm^3 in size were synthesized by evaporating a melt of LiCl and $MnCl_2$ at 750 °C. The nucleation and growth of the crystals proceeds on the wall of a pure alumina crucible. Phase analysis showed that purity of phase was affected by $MnCl_2$ partial pressure.

$LiMn_2O_4$ crystals, especially of millimeter size, are attractive as a model compound for the refinement of their crystal structure and for studying the diffusion process of Li^+ in the solid and at the solid–liquid interface. They are also expected to have applications as single crystal cathodes for micro-size rechargeable batteries or as Li^+-sensors. $LiMn_2O_4$ crystals, which generally have been prepared by a solid-state reaction,[1–4] or chemical processes such as hydrothermal reaction or sol–gel process,[5,6] are a polycrystalline material existing as a fine powder. We have prepared octahedral $LiMn_2O_4$ crystals of a size larger than 20 μm by using LiCl as a flux and γ-MnOOH as a Mn source.[7,8] Recently, an octahedral $LiMn_2O_4$ crystal, 30 × 30 × 30 μm in size, prepared by using LiCl as a flux and $LiMn_2O_4$ powder as a starting material, has been used for the purpose of refining its crystal structure.[9] However, $LiMn_2O_4$ crystals of a much larger size are difficult to prepare using the flux system because of the low solubility of γ-MnOOH and $LiMn_2O_4$, and decomposition of $LiMn_2O_4$ at temperatures above 800 °C in air.[10]

Evaporation of a chemical reagent or compound by heating has been reported to be useful for promoting crystal formation of ultrafine crystals such as Mg_2SiO_4, FeO, Fe_3O_4 and Cu_2O ultrafine crystals.[11,12] This method also results in the production of a crystal film on a substrate.[13] In this study, we are interested in the promotion of $LiMn_2O_4$ crystal growth by use of evaporation of $MnCl_2$–LiCl flux. Since $MnCl_2$ and LiCl melts evaporate at a temperature above their melting points (606 °C for LiCl and 650 °C for $MnCl_2$), the continuous evaporation supplies manganese and lithium sources to facilitate the growth of $LiMn_2O_4$ crystals. By use of this method, we succeeded in obtaining for the first time $LiMn_2O_4$ single crystals larger than 0.1 × 0.1 × 0.1 mm^3 in size. The formation reaction among vapor phases of $MnCl_2$, LiCl and atmospheric oxygen suggests a new route for preparation of spinel-type $LiMn_2O_4$.

$MnCl_2$ solution (2 mol·dm^{-3}) was added to LiCl (50 g) to prepare a mixture of LiCl and $MnCl_2$. The content of Mn in the mixture was adjusted to 4–18 mmol in 2 mmol steps. Each mixture was then dried at 180 °C for 3 h. After grinding, the mixture was placed in a pure alumina crucible (150 mL in volume), and then covered with a 40-g layer of LiCl to prevent sudden evaporation and oxidation of $MnCl_2$ during the heating process. The crucible with cap in place was set in a muffle electric furnace and heated at 750 °C for 58 h. Polyhedral $LiMn_2O_4$ crystals, black-colored with a glossy surface, were formed on the wall of the crucible above the LiCl melt (i.e., the crucible-wall/LiCl-melt/air interface), arranged as a band with a width of about 5 mm for all Mn contents. The melt was dissolved in distilled water, and the $LiMn_2O_4$ crystals were obtained after washing and filtering.

The X-ray diffraction (XRD) analyses of the product were carried out using a Rigaku type RINT2100VPC X-ray diffractometer with a vertically moveable gonio-axis. The SEM observation was carried out on JEOL type JSM-5310 scanning electron microscope. Lithium and manganese contents of the $LiMn_2O_4$ crystals were determined by atomic absorption spectrometry after dissolving the crystals in a mixed solution of HCl and H_2O_2. The available oxygen for $LiMn_2O_4$ crystals was determined by the standard oxalic method,[14] from which the mean oxidation number of manganese (Z_{Mn}) and oxygen content were calculated. The chemical formula was calculated from manganese and lithium contents and Z_{Mn}.

The crystal phase, shape, size and yield obtained for different Mn contents are summarized in Table 1. The XRD analysis of the products indicated sharp diffraction peaks of a single $LiMn_2O_4$ phase in the range of 8 to 12 mmol of Mn content. The chemical formula of $LiMn_2O_4$ obtained at 8 mmol of Mn content was $Li_{1.03}Mn_{1.97}O_4$ on the base of chemical analysis results, which is very close to the theoretical formula of $LiMn_2O_4$. The yield and size of the crystals increased with an increase of the Mn content. However, changing the Mn content ranges yielded some by-products. The crystal shape also changed with the Mn content. Octahedral $LiMn_2O_4$ single crystals were obtained at 4 and 6 mmol of Mn content; octahedral and rectangular $LiMn_2O_4$ single crystals at 8 to 12 mmol of Mn content. These crystals had smooth surfaces with sizes larger than 0.1 × 0.1 × 0.1 mm^3. The SEM photograph at the top of

Table 1. The crystal phase, shape, size and yield obtained at different Mn contents

Mn content /mmol	4	6	8	12	14	18
Crystal phase	$LiMn_2O_4$ + Li_2MnO_3		$LiMn_2O_4$		$LiMn_2O_4$ + Mn_2O_3	
Shape	octahedral		octahedral, rectangular		pillar polycrystal	
Size/mm^3	0.1x0.1x0.1		0.1x0.1x0.1		0.9x0.5x0.5	
Yield/g	0.10	0.15	0.18	0.26	0.31	0.39

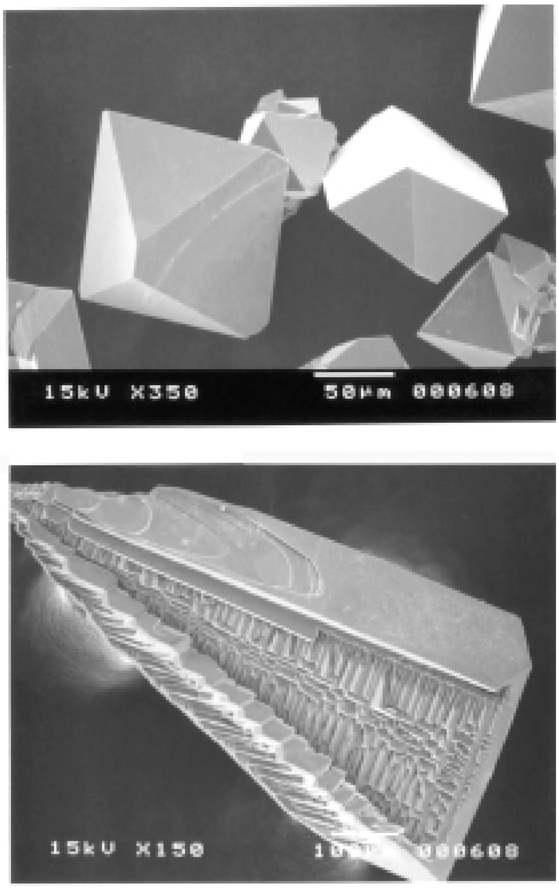

Figure 1. SEM images of $LiMn_2O_4$ crystals obtained at 8 mmol (top) and 18 mmol (bottom) of Mn contents.

Figure 1 shows the crystals obtained at 8 mmol of Mn content. Some crystal combinations were larger than 0.9 × 0.5 × 0.5 mm^3 for 18 mmol of Mn content, but consisted of some arrangement of single crystals, as shown at the bottom of Figure 1.

The formation of the $LiMn_2O_4$ crystals on the wall of the crucible above the LiCl melt can be explained by characterizing the evaporation of the $MnCl_2$–LiCl melt. The evaporation of LiCl and $MnCl_2$ throughout the covered LiCl layer at 750 °C supplies sources of vapor phases of manganese and lithium in the space of the crucible. The reaction, whereby $LiMn_2O_4$ forms from LiCl and $MnCl_2$ vapor phases, can be written as follows:

$$LiCl(g) + 2MnCl_2(g) + 2O_2(g) \rightarrow LiMn_2O_4(s) + 5/2Cl_2(g) \quad (1)$$

where the notations (g) and (s) refer to the species in the gas and solid phases, respectively. The reaction implies that oxygen in the atmosphere is need to oxidize Mn^{2+} to Mn^{3+} and Mn^{4+} and to form the spinel phase by reduction of chloride ions. This suggests a new route for preparing spinel-type $LiMn_2O_4$ crystals. This route may be also expected to produce ultrafine $LiMn_2O_4$ powder and crystal thin film by selecting the reaction field.

Reaction (1) shows that the formation of $LiMn_2O_4$ corresponds to partial pressure of LiCl, $MnCl_2$ vapor and atmospheric oxygen. In the present case, the formation of $LiMn_2O_4$ by reaction (1) is sensitive to changes in the partial pressure of $MnCl_2$, P_{Mn}, and atmospheric oxygen only because a great excess of LiCl flux makes the LiCl partial pressure almost constant. As shown in Table 1, a pure $LiMn_2O_4$ crystal phase could be obtained at P_{Mn} to some extent in the crucible space, where the P_{Mn} was controlled by the content of $MnCl_2$ (8–12 mmol) in the batch. At low Mn contents of 4 and 6 mmol, a low P_{Mn} facilitates the nucleation and growth of Li_2MnO_3 crystal through the reaction, $2LiCl + MnCl_2 + 3/2O_2 \rightarrow Li_2MnO_3 + 2Cl_2$; whereas at high P_{Mn} (when $MnCl_2$ content ranges from 14 to 18 mmol), the nucleation and growth of Mn_2O_3 are promoted through the reaction, $2MnCl_2 + 3/2O_2 \rightarrow Mn_2O_3 + 2Cl_2$.

The growth of $LiMn_2O_4$ located on the crucible-wall/LiCl-melt/air interface can be explained by the easy heterogeneous nucleation of $LiMn_2O_4$ on the solid/melt/air interface,[15] similar to the growth of Li_2MnO_3 plate crystals we have previously reported.[7] The evaporation of LiCl and $MnCl_2$ continuously supplies a source of manganese and lithium, which facilitates the growth of $LiMn_2O_4$ crystals, accompanied by the oxidation of Mn^{2+} to Mn^{3+} and Mn^{4+} by atmospheric oxygen.

In conclusion, the evaporation of $MnCl_2$–LiCl flux is suitable for the preparation and growth of large spinel-type $LiMn_2O_4$ single crystals. The partial pressures of $MnCl_2$ and atmospheric oxygen in the space of the crucible play an important role in the formation and growth of the $LiMn_2O_4$ crystals.

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