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Single crystal growth of the spinel-type $LiMn_2O_4$

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Abstract

Single crystals of the spinel-type $LiMn_2O_4$ have been successfully grown by a solvent evaporation flux method at 1173 K. The maximum size of the octahedral-shaped single crystal is $0.09 \times 0.09 \times 0.09\,mm^3$ along the octahedral edges. The single-crystal X-ray diffraction study confirmed the cubic $Fd\bar{3}m$ space group and the lattice parameter of $a = 8.2483(6)$ Å of the as-grown single crystal at 297 K. The preliminary single-crystal low temperature X-ray diffraction experiments confirmed the cubic–orthorhombic structure transition around 285 K on the cooling process. The tripled periodicity toward the *a*- and *b*-axis directions of the low temperature form has been also confirmed.

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1. Introduction

Lithium manganese oxide, $LiMn_2O_4$, has the cubic spinel structure. An increasing interest has developed around the Li–Mn–O spinels due to their potential use as positive electrode materials in lithium ion rechargeable batteries [1]. The vast majority of the studies devoted to these compounds deal with their electrochemical characteristics, but, only very recently, their structural and physical properties have also been investigated using polycrystalline samples [2].

The stoichiometric compound $LiMn_2O_4$ presents a first order structural transition close to room temperature [3]. In the case of manganese perovskite oxides, structural phase transitions accompanied by sharp modifications of electronic and magnetic properties have been attributed to charge ordering [4]. However, the mechanism of the structural transition has not been clarified yet in the case of the spinel-type $LiMn_2O_4$.

The crystal structure of the low temperature form has been investigated using neutron and synchrotron radiation X-ray powder diffraction methods. Rousse and her co-workers [2,5,6] and Massarotti et al. [7] reported an orthorhombic $\sim 3a \times 3a \times a$ superstructure of the basic cubic spinel structure, induced by a partial charge ordering on the manganese sites [2]. The powder technique, however, does not fully solve the problem, because it only provides a structure refinement using the starting model structure.

To clarify the true crystal symmetry, the precise crystal structure, the mechanism of the structural transition, and the physical properties of

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$LiMn_2O_4$, sizable, well-characterized single crystal specimens are highly desired, as in the study of Fe_3O_4 magnetite [8], but the corresponding single crystals with good quality have not yet been synthesized. In the present study, we report the single crystal growth, chemical characterization of the spinel-type $LiMn_2O_4$, and the preliminary results of single-crystal X-ray diffraction experiments below room temperature.

2. Experimental procedure

Single crystals were grown by a solvent evaporation flux method. Starting $LiMn_2O_4$ powder samples were supplied by Nippon Chemical Industrial Co., Ltd., Japan. In order to find the best conditions to grow single crystals, we examined some flux materials, e.g., LiCl (3N), Li_2O_2 (3N), Li_2CO_3 (4N), and Li metal (2Nup). They were mixed with $LiMn_2O_4$ in various ratios and fired at several temperatures in gold crucibles. The produced single crystals were easily separated from the frozen flux materials by rinsing the gold tube in water for several minutes.

The products were observed by using an optical microscope and a scanning electron microscope (SEM: JEOL JSM-5400). Chemical compositions for single crystal specimens were analyzed by SEM-EDX and inductively coupled plasma (ICP) spectroscopy.

Single crystals were carefully examined with an X-ray precession camera (MoKα radiation) in order to check on crystal quality and to determine the lattice parameters, systematic extinctions, and possible superstructures. The intensity data of the cubic spinel structure were collected by the $2\theta-\omega$ scan mode with a scan rate of 1°/min at 297 K on a four-circle diffractometer (Rigaku AFC-7R, operating conditions: 50 kV, 180 mA) using graphite-monochromatized MoKα radiation ($\lambda = 0.71073$ Å).

Temperature dependence of the structure between 230 and 330 K was investigated on the four-circle diffractometer using a nitrogen gas flow cryostat. The temperature was stable at 0.5 K. Single-crystal X-ray diffraction peak profiles were measured after equilibrium of the crystal specimen for 30 min at a given temperature.

3. Results and discussion

Single crystals of $LiMn_2O_4$ were obtained only when LiCl was used as a flux (the nominal weight ratio of $LiMn_2O_4$: LiCl = 1 : 8) and heated typically at 1173 K for 10 days in a covered gold crucible. It should be noted that a control of the evaporation speed of the LiCl flux at high temperatures is very important to grow the single crystals in the present experiment.

The crystals are black in color and, as seen in Fig. 1, octahedral-shaped with typical dimensions of about $0.05 \times 0.05 \times 0.05\,mm^3$. Fig. 2 shows the

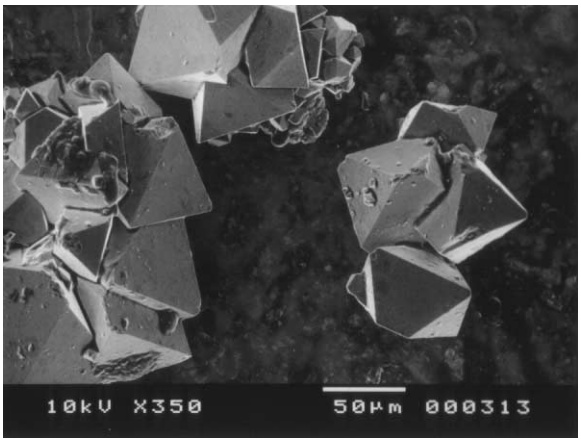

Fig. 1. Scanning electron microphotograph of typical as-grown single crystals of $LiMn_2O_4$.

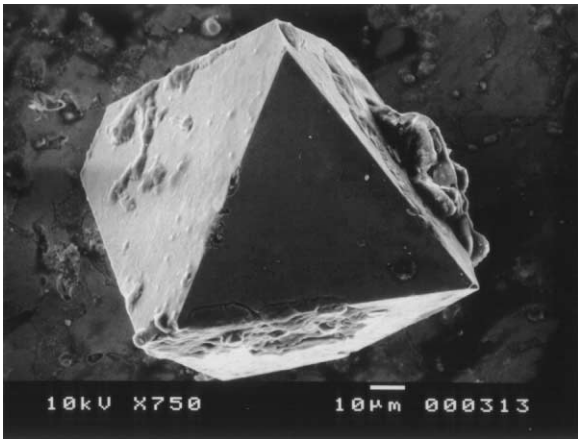

Fig. 2. Scanning electron microphotograph of an octahedral-shaped single crystal of $LiMn_2O_4$.

largest single crystal of $0.09 \times 0.09 \times 0.09\,mm^3$ along the octahedral edges. The triangular plane was determined to be of the cubic {1 1 1} plane by the X-ray precession photographs.

SEM-EDX analysis showed that the crystals were free from gold contamination from the crucible. The chemical analysis by ICP spectroscopy using the pulverized crystals confirmed the stoichiometric chemical composition.

The cubic spinel structure with $Fd\bar{3}m$ space group has been confirmed by X-ray precession photographs taken at 298 K using MoKα radiation. The structural parameters were refined using a four-circle X-ray diffraction data taken at 297 K and reported elsewhere [9]. A summary of the crystallographic data is given in Table 1. The refined lattice parameter and the oxygen parameter x are in good agreement with the previous results for the stoichiometric $LiMn_2O_4$ using neutron powder diffraction data [10,11]. The oxygen occupation was refined to the nominal value within the experimental error.

Fig. 3 shows the temperature dependence of single-crystal X-ray diffraction peak profiles of the cubic (4 0 0) reflection from 300 to 230 K. The peak intensity starts to decrease at 285 K, and the peak splits into three components at lower temperatures. This fact suggests the structural phase transition takes place at about 285 K on the cooling process.

The tripled periodicity toward the a- and b-axis directions of the low temperature form has also been confirmed. The additional $(\frac{2}{3}\,\frac{10}{3}\,0)$ superlattice reflection can be clearly observed below the transition temperature, as shown in Fig. 4. Accordingly, the $\sim 3a \times 3a \times a$ orthorhombic lattice parameters were determined by the single-crystal X-ray diffraction method to be $a = 24.752(11)$ Å, $b = 24.842(11)$ Å, and $c = 8.209(4)$ Å at 270 K.

Table 1
Crystallographic data for $LiMn_2O_4$ at 297 K

Structural formula	$LiMn_2O_4$
Crystal system	Cubic
Space group	$Fd\bar{3}m$
a (Å)	8.2483(6)
V (Å^3)	561.16(13)
x for O at 32e site	0.2632(2)

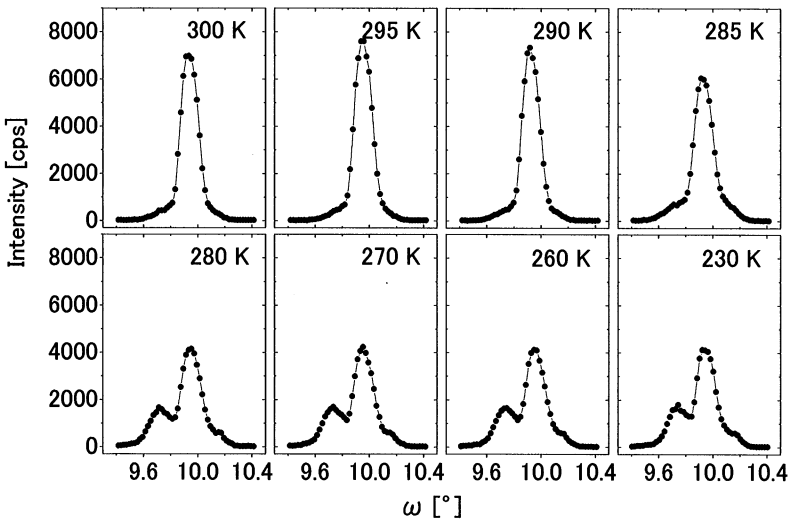

Fig. 3. Temperature dependence of the single-crystal X-ray diffraction peak profiles of the cubic (4 0 0) reflection from 300 to 230 K. The profiles were examined in the $2\theta-\omega$ scan mode with a step scan interval of 0.02° and the counting time of 2 s.

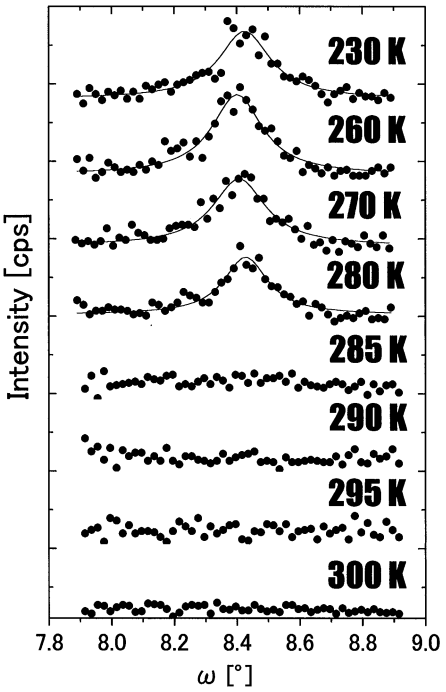

Fig. 4. Single-crystal X-ray diffraction peak profiles of the $(\frac{2}{3}\frac{10}{3}0)$ superlattice reflection at low temperatures.

4. Conclusion

Single crystals of the spinel-type $LiMn_2O_4$ have been successfully grown by a solvent evaporation flux method at 1173 K. The maximum size of the octahedral-shaped single crystal is $0.09 \times 0.09 \times 0.09\,mm^3$ along the octahedral edges. From the results of chemical and structural analyses, it is concluded that the stoichiometric single crystals of $LiMn_2O_4$ with ideal spinel structure, having the cubic $Fd\bar{3}m$ space group and the lattice parameter of $a = 8.2483(6)\,\text{Å}$, and with high crystallinity are obtained in the present study. The preliminary single-crystal X-ray diffraction experiments revealed the $\sim 3a \times 3a \times a$-type orthorhombic structure of the low temperature form.

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