Structural Phase Transition of $\text{Li}_2\text{MnSiO}_4$ Noriaki Nakayama, Takanobu Itoyama, Keiko Fujiwara,
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The orthorhombic $Pmn\bar{b}$ phase of $\text{Li}_2\text{MnSiO}_4$ has been prepared by solid state reaction of Li_2CO_3 , $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, and highly dispersed SiO_2 at 800 °C and the subsequent slow cooling in Ar gas stream. The crystal structure was refined by the Rietveld method based on the model structure without disorder in the site occupancies, although some anomaly was observed for Mn sites. The DTA curve shows peaks at around 680 and 770 °C on heating and at around 510 °C on cooling indicating a reversible structural phase transition. From the *in-situ* XRD patterns at high temperature, the first order phase transition from $Pmn\bar{b}$ to a distorted orthorhombic wurzite-type structure with the random arrangement of Li, Si, and Mn.

keywords: order-disorder, wurzite-type structure, DTA, high temperature powder XRD

1. INTRODUCTION

Lithium transition metal silicates, Li_2MSiO_4 (M: Mn, Fe, Co), have been investigated extensively in this decade as a new class of positive electrode materials for lithium ion batteries.¹⁻⁴⁾ In these silicates, oxide ions form a pseudo-hexagonal closed packed (hcp) structure. The cations occupy a half of its tetrahedral sites and show several kinds of ordered arrangements depending on the transition metals species and the heat treatments during the sample preparation.^{5,6)} The homogeneity of the ordered structure may have significant effect on the electrode properties. Several investigations on the details of polymorphism have been reported⁷⁻¹³⁾, mainly for the hydro-thermally prepared and heat-treated samples. However, the phase relations among polymorphs and the microstructures are still unclear. The mutual phase relationships above polymorphs are of interests to obtain the single-phase materials and to clarify the electrochemical properties. In this paper, the structural phase transition of $\text{Li}_2\text{MnSiO}_4$ was investigated using TG-DTA and powder XRD at high temperature.

Polymorphism of $\text{Li}_2\text{MnSiO}_4$

$\text{Li}_2\text{MnSiO}_4$ was reported for the first time by P. Tart and T. Cahay in 1970 as a member of the compounds Li_2MXO_4 (M: Mg, Zn, Cd, Mn, Fe, Co; X: Si, Ge) with the crystal structures analogous to those of Li_3PO_4 .¹⁴⁾ However, the detailed crystal structure of $\text{Li}_2\text{MnSiO}_4$ had remained unclear until recently. In 2006, Dominko et al. reported the crystal structure of orthorhombic $Pmn2_1$ phase prepared by the sol-gel method. The arrangements of cations refined by powder XRD are somewhat disordered.¹⁵⁾ In 2007, Politaev et al. reported the crystal structure of monoclinic $P2_1/n$ phase prepared by solid state reaction at 1150°C.¹⁶⁾ The monoclinic phases with $P2_1/n$ symmetry have been often reported as high temperature phases of many Li_2MSiO_4 compounds. They

also pointed out the small site mixing of Li and Mn atoms and the off-stoichiometry from $\text{Li}_2\text{MnSiO}_4$.

In 2010, Mali et al. reported the structural analysis by using powder XRD and Li NMR of three polymorphs; $Pmn2_1$ phase prepared by hydrothermal method, $Pmn\bar{b}$ phase obtained by heating $Pmn2_1$ phase at 900°C and subsequent slow cooling to the room temperature, and $P2_1/n$ phase obtained by heating $Pmn2_1$ phase at 900°C and subsequent rapid cooling to the room temperature. The difference of crystal structures of these three polymorphs viewed along the [100] directions of $Pmn2_1$ phase and the corresponding directions of other two phases were illustrated in Fig. 1. In $Pmn2_1$ phase, the layers of LiO_4 tetrahedra and those of $\text{MnO}_4/\text{SiO}_4$ tetrahedra stacked alternately along b axis and all the coordination tetrahedra are aligned to the [001] directions. Mn and Si atoms are ordered in each layer. Using the hexagonal lattice parameters of fundamental wurzite-type structure (a_h and c_h), the unit cell parameters are expressed as $a = 2a_h$, $b = \sqrt{3}a_h$, and $c = c_h$. In the $Pmn\bar{b}$ phase iso-structural to $\text{Li}_2\text{CdSiO}_4$ ¹⁷⁾, the arrangement of $\text{MnO}_4/\text{SiO}_4$ tetrahedra in the b-plane is similar to that in $Pmn2_1$ phase but their direction in two neighboring layers are opposite. The lattice parameter b was doubled and some of two LiO_4 tetrahedra share their edge. However, the refined structural parameters of $Pmn\bar{b}$ phase have not been reported yet. In the $P2_1/n$ phase, $\text{MnO}_4/\text{SiO}_4$ tetrahedra form a complex ordered arrangement other than layered type one.

West and Glasser have reported DTA and high temperature powder XRD studies on the structural phase transitions of several Li_2MXO_4 phases.⁵⁾ However, as for $\text{Li}_2\text{MnSiO}_4$, DTA and powder XRD measurements at high temperatures to clarify the phase relations of these three polymorphs have not been reported yet. In this paper, their preliminary results are presented.

Fig.1 Crystal structures of three polymorphs for $\text{Li}_2\text{MnSiO}_4$ viewed along $[100]$ directions. Hatched, black (or grey), and white tetrahedra show SiO_4 , MnO_4 , and LiO_4 tetrahedra, respectively. LiO_4 tetrahedra in (c) were not drawn for simplicity.

2. EXPERIMENTAL

Samples were prepared by solid-state reaction in an Ar gas stream. The starting reagents were Li_2CO_3 (Kojundo Chemical Lab. Co. LTD), $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (Wako Chemical Co. LTD), and highly dispersed amorphous SiO_2 with the specific surface area of $200 \text{ m}^2/\text{g}$ (Merk Co. LTD). The samples were heat treated at 800°C for 1 day and then slowly cooled to room temperature with the rate of about $1^\circ\text{C}/\text{min}$.

Samples were characterized by powder XRD method using $\text{CuK}\alpha$ radiation. The diffraction patterns were obtained in a Bragg-Brentano geometry with a diffracted beam Graphite monochromator. The powder XRD measurements at high temperatures were performed for samples sealed in an evacuated fused silica tube with a diameter of 1.5 mm. Rietveld refinement was performed using Rietan-FP program¹⁸⁾. DTA analyses were performed using a MacScience TG-DTA 2020S apparatus equipped with the infrared arc-image furnace.

3. RESULTS AND DISCUSSION

3.1 Powder XRD patterns of as-prepared samples

The powder XRD patterns of the obtained samples could be indexed as a $Pmnb$ phase although very weak 200/110 and 111 peaks of Li_2SiO_3 phase were detected. The peak intensities of $Pmnb$ phase with odd index k , such as 011, 031, 211 and 231 peaks, due to the doubled b -axis compared to $Pmn2_1$ phase showed fairly high intensity. Figure 1 and Table I-III show the results of powder XRD Rietveld refinement. Atomic positions are set similarly to those in the refined structure of $\text{Li}_2\text{CdSiO}_4$ ¹⁷⁾; Li in (8a), Mn in (4a), Si in (4a), O1 in (4a) and O2 in (8a), and O3 in (4a) sites, respectively. The isotropic thermal parameter B_{iso} for Li atoms was fixed to be $1.5 \text{ \AA}^2$ and those for O atoms in the 3 sites are constrained to be equal. Without assuming cation mixing (all g was set to be 1), fairly good R -values were obtained as summarized in Table I ($R_{\text{wp}} = 12.93$, $R_{\text{e}} = 9.98$, $S = R_{\text{wp}}/R_{\text{e}} = 1.295$). The lattice parameters are $a = 6.3071(2) \text{ \AA}$, $b = 10.7595(3) \text{ \AA}$, and $c = 5.0118(2) \text{ \AA}$, which almost agree with the previously reported values by Mali et al.¹³⁾; $a = 6.3148(2) \text{ \AA}$, $b = 10.7742(3) \text{ \AA}$, and $c = 5.0138(2) \text{ \AA}$. The atomic positions and isotropic

Fig.2 Final observed (crosses), calculated (solid upper line) and difference (solid lower line) powder XRD pattern for $Pmnb$ phase of $\text{Li}_2\text{MnSiO}_4$. Vertical bars indicate Bragg positions. The inset shows peaks due to doubled b -axis.

Table I Crystallographic data, powder XRD data collection and the goodness of fit for Rietveld refinement

Crystal system	Orthorhombic	2θ range / $^\circ$	5 - 120
Space group	$Pmnb$ (62 setting2)	data points	11501
Lattice constants:		reflections	566
$a / \text{\AA}$	6.3071 (2)	parameters	50
$b / \text{\AA}$	10.7595 (3)		
$c / \text{\AA}$	5.0118 (2)	goodness of fit	
Cell volume / $\text{\AA}^3$	340.10(2)	$R_p / \%$	9.18
Formula weight	160.90	$R_{\text{wp}} / \%$	12.93
Density / (g/cm^3)	3.1424(3)	$R_e / \%$	9.98
Z	4	$S (= R_{\text{wp}}/R_e)$	1.295

Table II Refined atomic positions and temperature factors.

atom	Wyckoff symbol	g	x	y	z	B_{iso}
Li	8b	1	0.511(1)	0.913(1)	0.315(1)	1.5
Mn	4a	1	0.25	0.1653(1)	0.1897(2)	1.16(4)
Si	4a	1	0.25	0.3390(2)	0.6763(4)	0.52(5)
O(1)	4a	1	0.25	0.3425(3)	0.3467(7)	0.73(5)
O(2)	8b	1	-0.0385(3)	0.0916(2)	0.2820(5)	0.73
O(3)	4a	1	0.25	0.1951(3)	0.7602(7)	0.73

Table III Interatomic Distances in $\text{Li}_2\text{MnSiO}_4$.

MnO ₄	Mn-O(1)	2.063(4) $\text{\AA}$
	Mn-O(2) (x2)	2.038(2) $\text{\AA}$
	Mn-O(3)	2.176(4) $\text{\AA}$
	average	2.094(4) $\text{\AA}$
	distortion	7.6×10^{-4}
SiO ₄	Si-O(1)	1.653(4) $\text{\AA}$
	Si-O(2) (x2)	1.618(2) $\text{\AA}$
	Si-O(3)	1.604(3) $\text{\AA}$
	average	1.623(4) $\text{\AA}$
	distortion	1.2×10^{-4}
LiO ₄	Li-O(1)	1.983(4) $\text{\AA}$
	Li-O(2)	1.938(6) $\text{\AA}$
	Li-O(2)'	2.042(8) $\text{\AA}$
	Li-O(3)	1.944(4) $\text{\AA}$
	average	1.977(4) $\text{\AA}$
	distortion	4.5×10^{-4}

As for the distortion see text.

temperature factors B are listed in Table II. The selected atomic distances are listed in Table III.

It is noted that the B_{iso} for Mn is fairly larger than those of Si and O atoms. The observed Mn-O atomic distances indicate some peculiarity of MnO_4 polyhedra. The observed average Mn-O distance 2.094(4) Å is a little bit larger than the simple sum 2.04 Å of ionic radii; 0.66 Å for 4-coordinated HS Mn^{2+} and 1.38 Å for 4-coordinated O^{2-} . However, the average Si-O and Li-O distances, 1.623(4) and 1.977(4) Å, agree with the simple sums of corresponding ionic radii; 1.64 and 1.97 Å, respectively. The distortion parameter calculated as

$$\Delta = \sum (d_i - \langle d \rangle)^2 / \langle d \rangle^2,$$

where d_i is the length of the bond i , $\langle d \rangle$ is the average bond length, and the summation is from $i = 1$ to 4. The Δ of MnO_4 tetrahedra larger than those of SiO_4 and LiO_4 tetrahedra, as listed in Table III. The above results seem to be originated from some defects in the prepared crystallites. Actually TEM observation indicates that some crystallites show diffuse streaks in their electron diffraction patterns. The details will be reported elsewhere.

3.2 DTA curves and XRD patterns of quenched samples

Figure 3 shows DTA curves of $\text{Li}_2\text{MnSiO}_4$ $Pmnb$ phase measured up to 800°C and then down to 50°C with the heating and cooling rates of 10 K/min. It shows two endo-thermic peaks at 680 and 770 °C on heating. On cooling, it shows a broader exo-thermic peak at around 510K. Peak widths (FWHM: Full width at half maximum) estimated assuming a modified Lorentian peak profile function, $A(1+k^2x^2)^{-\alpha}$, were 35, 32, and 44 K, respectively. The temperature and width of exo-thermic peaks on cooling are dependent on the highest temperature of DTA measurements. When measured up to 900°C, a peak appears at 450°C. When measured up to 1000°C, two peaks appeared at 440 and 500 °C.

Fig.3 DTA curves of orthorhombic $Pmnb$ phase. The heating and cooling rates were 10°C/min. The results of curve fitting to evaluate peak temperatures and widths are shown in (b)

Fig.4 XRD patterns of rapidly cooled samples from 700 and 800 °C (200 K/min). Marks * mean peaks of Li_2SiO_3 .

To clarify the phase relations, two samples heated up to 800 and 700 °C, respectively, were rapidly cooled with the rate of 200 K/min. Their XRD patterns at room temperature are shown in Fig. 4. The sample cooled from 700 °C shows the XRD pattern that can be indexed as a $Pmn2_1$ phase. The 011, 031, and 211 peaks of $Pmnb$ phase almost disappear and the 002 peak shifts to the higher angles. The lattice parameters are $a = 6.3094(2)$, $b = 5.3856(2)$, and $c = 4.9717(1)$ Å. The sample cooled from 800 °C showed an XRD pattern that can be indexed as a $P2_1/n$ phase. The increase of the 120 and 101 peak intensity, the splitting of 021 and 111 peaks, and the shift of 002 peak to the lower angle are typical for the diffraction pattern of $P2_1/n$ phase. The lattice parameters are $a = 6.3316(5)$, $b = 10.906(1)$, $c = 5.0644(2)$ Å, and $\beta = 91.06(1)^\circ$. This diffraction pattern shows two peaks of Li_2SiO_3 as marked by asterisk in the figure.

The above results may indicate that the first peak at 680 °C in the DTA curve is due to the transformation to $Pmn2_1$ phase and the second peak at 770 °C is due to the transformation to $P2_1/n$ phase. However, the *in-situ* XRD measurements at high temperatures revealed rather different results from those expected from this assumption.

3.3 XRD patterns measured at high temperatures

As shown in Fig. 5, powder XRD patterns at high temperatures show drastic changes above 676 °C. The intense 021 and 200/121 peaks of $Pmnb$ phase at room temperature almost disappear above 770 °C, although the rapidly cooled samples from 700 and 800 °C showed fairly high intensity of these peaks. However, 220/400 and 002 peaks keep their intensity at high temperatures. These two peaks correspond to the 10.1 and 00.2 peaks of the fundamental wurtzite-type structure, respectively. Therefore, it is well assumed that the arrangements of Li, Si, and Mn atoms are almost disordered above 770 °C, corresponding to the second peak in DTA curve on

Fig. 5 In-situ XRD patterns at high temperatures

Fig. 6 Lattice parameters, unit-cell volume at high temperatures.

heating. The splitting of fundamental 10.1 peaks indicate the crystal symmetry is still orthorhombic above 770 °C. The diffraction patterns at 676 and 725 °C, particularly at around 002 peak, indicate that two phases at low and high temperatures are coexist at temperatures in between two peaks of DTA curve. On cooling, the 021 and 200/121 peaks recover their intensity at 529°C. This temperature corresponds to the DTA peak on cooling. The intensity of 031 and 211 peaks characteristic for *Pmnb* phase is also recovered. Some peaks of Li_2SiO_3 appear similarly to the diffraction pattern of the sample rapidly cooled from 800°C.

Above results strongly indicates that the *Pmnb* phase of $\text{Li}_2\text{MnSiO}_4$ transforms a orthorhombic disordered wurtzite-type structures. The lattice parameters at high temperatures assuming orthorhombic unit cell of *Pmnb*

phase are shown in Fig. 6, which reveals the first-order nature of the phase transition. All lattice parameters show large expansion due to the phase transformation. The ratio of expansion of *a*, *b*, *c*, and unit cell volume are roughly +1, +1, +2, +4%, respectively. The thermal hysteresis of the phase transformation is about 100 K.

4. SUMMARY

The first order phase transition of $\text{Li}_2\text{MnSiO}_4$ from low temperature *Pmnb* phase to the high temperature disordered orthorhombic wurtzite-type structure was revealed for the first time. The characteristics of this phase transformation may be similar to those of the martensitic phase transition, as pointed out for the $\text{Li}_2\text{ZnSiO}_4$ by M. E. Villafuerte-Castrejon and A. R. West¹⁹⁾. The investigation of structural details on $\text{Li}_2\text{MnSiO}_4$ at high temperatures is in progress.

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