Charge ordering at low temperature in lithium manganese oxide spinel

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Abstract. Spinels lithium manganese oxide LiMn2O4-δ synthesized from mixtures of different raw materials were used to study the relationship between the synthesis method and properties of the spinel. The investigation was emphasized on phase transition in lithium manganese oxide spinel compound at low temperature studied by means of neutron powder diffraction. It is found that the cubic structure of LiMn2O4-δ, synthesized from Li2CO3, with space group Fd-3m at room temperature was distorted to orthorhombic symmetry with space group Fddd at 290K and become more obvious down to 10K, where the splitting indicates the structural transition close to tetragonal. The equal proportion of coexisted Mn3+ (Jahn-Teller) and Mn4+ ions is associated with partial charge ordering. It is also found that the sample synthesized from LiOH·H2O and MnOx does not show phase transition at low temperatures. The extent of orthorhombic distortion is related to oxygen vacancy, δ, which is affected by the synthesis method such as the choice of starting materials, mixing method and annealing temperature.

1. Introduction

Spinel lithium manganese oxide compound is widely applied for cathode material in Li-ion battery due to its relatively low toxicity, cheaper, easiness in preparation, better electrochemical performance etc. [1-10]. It is worth noting, however, that the preparation process of this material could determine the final product because its composition, particularly in relation to the average Mn valence, will affect the structure and finally, its electrochemical performance [11-17]. The complication in the structure occurs due to the cooperative interaction of local distortion around Jahn-Teller ions Mn3+ (t2g3-e-g1) in octahedral sites [18, 19], which is accompanied by asymmetry reduction from cubic. Non-Jahn-Teller ions of Mn4+ (t2g3-e-g0) and Mn2+ (t2g3-e-g2) suppress the distortion. Several spinel-type manganese oxides show tetragonal distortion c/an at room temperature as a function of average Mn valence. The c/a reaches the largest and lowest in oxides with average Mn valence of 3.0+ and 3.5+, respectively. The spinel LiMn2O4 has an average Mn valence of 3.5+, which is just a critical point, and will easily be interfered with even by a slight change in synthesis condition such as oxygen and lithium content, due to charge compensation [17].

Previous works suggested some factors responsible for phase transition in spinel LiMn2O4, such as Jahn-Teller distortion [20-29], partial charge ordering of Mn3+ and Mn4+ [30] nonstoichiometric lithium [31], and oxygen stoichiometry [32]. The absence of Jahn-Teller ordering is related to the stoichiometric spinel without phase transition at low temperature [33]. Another result showed that the
phase transition is closely related to the population of oxygen vacancies and its existence is the sole and necessary condition for the phase transition, not the synthesis temperature, nor the thermal treatment history [34]. It was proposed that in a strictly stoichiometric sample, this phase transition should not occur. Therefore, direct comparison between methods of synthesis, which include the choice of raw materials, mixing method, heating parameters etc., will be precious in order to understand the synthesis, phase relationship and physical properties of LiMn$_2$O$_4$.

In this work, the stoichiometry and the structural details of spinel LiMn$_{2,\delta}$O$_{4,\delta}$ were investigated in relation to the occurrence of phase transition. In order to determine accurately the site occupancies of light atoms such as lithium, or even oxygen, in the presence of manganese, and also to clarify structural details of spinel LiMn$_{2,\delta}$O$_{4,\delta}$, neutron diffraction (ND) was employed. ND is a powerful and suitable means in structure determination because of the difference in the coherent scattering lengths of atoms in LiMn$_2$O$_4$[32].

2. Experimental method

Spinels lithium manganese oxide LiMn$_{2,\delta}$O$_{4,\delta}$ were synthesized from mixtures of the stoichiometric amount of Li$_2$CO$_3$ (99.99%, Kojundo Chem. Lab.) and Mn$_2$O$_3$ (99.99%, Kojundo Chem. Lab.) and mixed by using an agate mortar for about 1 hour. The mixtures were then pressed into a pellet and heated at 1073.15 and 1173.15K in the air for 4 hrs and cooled down naturally. Spinels were also synthesized from LiOH·H$_2$O (>98%, Kojundo Chem. Lab.) and MnO$_3$ (Kojundo Chem. Lab.) and mixed by mechanical alloying (MA) method in a stainless steel (SS) jar using a planetary ball mill (RETSCH PM 200) with SS balls (10 mm dia.) for 6 hrs. The mixtures were then pressed into a pellet and heated at 1073.15K in oxygen for 4 hrs. Precise structure analyses of the spinel samples at low temperatures of 10K, 80K, 150K, 220K, 290K were determined at BL-08, SuperHRPD, at Materials and Life Science Facility (MLF), Japan-Proton Accelerator Research Complex (J-PARC). The structural parameters were refined with Z-Rietveld [35-37].

3. Results and discussion

The structure of LiMn$_{2,\delta}$O$_{4,\delta}$ as a function of measurement temperature was studied by neutron diffraction measurements. The samples were synthesized from Li$_2$CO$_3$ and Mn$_2$O$_3$ followed by annealing at 1073.15 and 1173.15K. Figure 1.a. shows the neutron diffraction peak profile at room and low temperatures of the sample after annealed at 1173.15K (hereinafter referred to as sample A). Orthorhombic distortion appeared at 290K and is shown as shoulders flanking, for example the peak of (400), as shown in Figure 1.b. The distortion becomes more obvious from 220K down to 10K, where the splitting indicates the structural transition close to tetragonal [38, 39].

Figure 2a. and Figure 2b. shows that the extent of orthorhombic distortion is related to oxygen vacancy, $\delta$. After annealed at 1073.15 (hereinafter referred to as sample B) and 1173.15K (sample A) the $\delta$ values are 0.016 and 0.028, respectively. The diffraction pattern shows peak splitting, which corresponds to the orthorhombic symmetry. As for comparison, sample synthesized from LiOH·H$_2$O and MnO$_3$ by MA method for 6 hours and annealed at 1073.15K (hereinafter referred to as sample C) does not show any peak splitting, as shown in Figure 2.c. and oxygen site was found fully occupied ($\delta = 0$). Similar work and results of the structural study using laboratory XRD and reactor source neutron diffraction (HRPD) have been reported previously [40]. Figure 2.d. shows the diffraction pattern of the three samples measured at 150 K and shows that the orthorhombic distortion decreased with decreasing $\delta$ from 0.028 to 0.

The low-temperature structures of LiMn$_{2,\delta}$O$_{4,\delta}$ synthesized at 1173.15K and measured below 290K were determined using neutron diffraction and the data were refined by adopting an orthorhombic cell of space group Fddd similar to those reported earlier [30, 41]. The superlattice reflections were observed and indexed by the $3a\times3a\timesa$ cell based on the parent cubic cell of $a$. Tables 1 to 5 summarized the results from neutron diffraction measurement at 290, 220, 150, 80, and 10K, respectively. Lattice, structural parameters and final $R$ factors including their estimated standard deviation in parentheses are presented. In this analysis, the atomic displacement parameters were
treated isotropically and constrained to identical values for each chemical element. Anisotropic displacement parameter has also been tried, however, the results did not improve the $R$ values.

**Figure 1.** (a) Neutron diffraction patterns measured at room and low temperature of LiMn$_2$O$_{4-\delta}$ synthesized by conventional method from Li$_2$CO$_3$ and Mn$_2$O$_3$ and annealed at 1173.15K. (b) peak splitting of (400)$_c$ reflection around $d = 2.0 \sim 2.1$

**Figure 2.** Neutron diffraction patterns measured at room and low temperature of LiMn$_2$O$_{4-\delta}$ synthesized by conventional method from Li$_2$CO$_3$ and Mn$_2$O$_3$ and annealed at (a) 1173.15K, (b) 1073.15K and (c) by MA method for 6 hours from LiOH.H$_2$O and MnO$_x$ and annealed at 1073.15K. (d) comparison for the measurement at 150K.
### Table 1. Rietveld refinement results for neutron diffraction measurement at 10K of spinel LiMn$_2$O$_{4.5}$ synthesized by conventional method and annealed at 1173.15K in O$_2$.

| Atom  | site | $g$ | $x$    | $y$       | $z$    | $B$/Å$^2$ |
|-------|------|-----|--------|-----------|--------|-----------|
| Li(1) | 8a   | 1   | 1/8    | 1/8       | 1/8    | 0.186(22) |
| Li(2) | 16f  | 1   | 3/8    | 0.2113(5) | 3/8    | =Li1(B)   |
| Li(3) | 16e  | 1   | 0.2065(5) | 3/8       | 3/8    | =Li1(B)   |
| Li(4) | 32h  | 1   | 0.2913(4) | 0.2953(3) | 0.1255(8) | =Li1(B) |
| Mn(1) | 16d  | 1   | 1/4    | 1/4       | 1/2    | 0.01      |
| Mn(2) | 32h  | 1   | 0.0829(2) | 0.0848(1) | 0.5011(4) | =Mn1(B) |
| Mn(3) | 32h  | 1   | 0.0835(2) | 0.3301(1) | 0.2493(8) | =Mn1(B) |
| Mn(4) | 32h  | 1   | 0.2524(1) | 0.1680(1) | 0.2484(6) | =Mn1(B) |
| Mn(5) | 32h  | 1   | 0.1662(1) | 0.2463(1) | 0.2496(6) | =Mn1(B) |
| O(1)  | 32h  | 0.998(5) | 0.1744(1) | 0.1687(1) | 0.2586(3) | 0.066(4) |
| O(2)  | 32h  | 0.991(6) | 0.0796(1) | 0.00731(1) | 0.4816(4) | =O1(B)   |
| O(3)  | 32h  | 1   | 0.0789(1) | 0.3317(1) | 0.4811(4) | =O1(B)   |
| O(4)  | 32h  | 1   | 0.2517(1) | 0.1730(1) | 0.4775(4) | =O1(B)   |
| O(5)  | 32h  | 0.995(5) | 0.0060(1) | 0.0079(1) | 0.2444(2) | =O1(B)   |
| O(6)  | 32h  | 1   | 0.2564(1) | 0.0894(1) | 0.2393(4) | =O1(B)   |
| O(7)  | 32h  | 0.931(5) | 0.16271(1) | 0.3235(1) | 0.2376(5) | =O1(B)   |
| O(8)  | 32h  | 1   | 0.0904(1) | 0.2441(1) | 0.2335(4) | =O1(B)   |
| O(9)  | 32h  | 0.941(4) | 0.0853(1) | 0.1621(1) | 0.5146(3) | =O1(B)   |

Space group Fdd2, $a = 24.73987(4)$ Å, $b = 24.79315(4)$ Å, $c = 8.19544(1)$ Å
$R_{wp} = 5.87$, $R_p = 4.44$, $R_e = 2.62$, $S = R_{wp}/R_e = 2.24$, $R_B = 3.09$, $R_f = 4.15$

### Table 2. Rietveld refinement results for neutron diffraction measurement at 80K of spinel LiMn$_2$O$_{4.5}$ synthesized by conventional method and annealed at 1173.15K in O$_2$.

| Atom  | site | $g$ | $x$    | $y$       | $z$    | $B$/Å$^2$ |
|-------|------|-----|--------|-----------|--------|-----------|
| Li(1) | 8a   | 1   | 1/8    | 1/8       | 1/8    | 0.095(21) |
| Li(2) | 16f  | 1   | 3/8    | 0.2117(4) | 3/8    | =Li1(B)   |
| Li(3) | 16e  | 1   | 0.2072(4) | 3/8       | 3/8    | =Li1(B)   |
| Li(4) | 32h  | 1   | 0.2911(4) | 0.2961(3) | 0.1278(7) | =Li1(B) |
| Mn(1) | 16d  | 1   | 1/4    | 1/4       | 1/2    | 0.001     |
| Mn(2) | 32h  | 1   | 0.0828(1) | 0.0847(1) | 0.5011(3) | =Mn1(B) |
| Mn(3) | 32h  | 1   | 0.0841(1) | 0.3299(1) | 0.2493(6) | =Mn1(B) |
| Mn(4) | 32h  | 1   | 0.2524(1) | 0.1683(1) | 0.2484(5) | =Mn1(B) |
| Mn(5) | 32h  | 1   | 0.1666(1) | 0.2462(1) | 0.2493(5) | =Mn1(B) |
| O(1)  | 32h  | 1   | 0.1737(1) | 0.1688(1) | 0.2597(3) | 0.147(4)  |
| O(2)  | 32h  | 1   | 0.0794(1) | 0.0074(1) | 0.4835(4) | =O1(B)   |
| O(3)  | 32h  | 0.987(5) | 0.0788(1) | 0.3310(1) | 0.4808(4) | =O1(B)   |
| O(4)  | 32h  | 0.988(6) | 0.2512(1) | 0.1728(1) | 0.4781(4) | =O1(B)   |
Table 3. Rietveld refinement results for neutron diffraction measurement at 150K of spinel LiMn$_2$O$_4$-$\delta$ synthesized by conventional method and annealed at 1173.15K in O$_2$.

| Atom | site | g | x   | y   | z   | B/Å$^2$ |
|------|------|---|-----|-----|-----|---------|
| Li(1) | 8a   | 1 | 1/8 | 1/8 | 1/8 | 0.153(21) |
| Li(2)  | 16f  | 1 | 3/8 | 0.2102(4) | 3/8 | =Li1(B) |
| Li(3)  | 16e  | 1 | 0.2072(4) | 3/8 | 3/8 | =Li1(B) |
| Li(4)  | 32h  | 1 | 0.2913(3) | 0.2962(3) | 0.1258(6) | =Li1(B) |
| Mn(1)  | 16d  | 1 | 1/4 | 1/4 | 1/2 | 0.1 |
| Mn(2)  | 32h  | 1 | 0.0827(1) | 0.0841(1) | 0.5012(3) | =Mn1(B) |
| Mn(3)  | 32h  | 1 | 0.0840(2) | 0.3298(1) | 0.2490(6) | =Mn1(B) |
| Mn(4)  | 32h  | 1 | 0.2524(1) | 0.1687(1) | 0.2484(5) | =Mn1(B) |
| Mn(5)  | 32h  | 1 | 0.1667(1) | 0.2460(1) | 0.2492(5) | =Mn1(B) |
| O(1)   | 32h  | 1 | 0.1734(1) | 0.1687(1) | 0.2596(3) | 0.164(3) |
| O(2)   | 32h  | 1 | 0.0792(1) | 0.0074(1) | 0.4833(4) | =O1(B) |
| O(3)   | 32h  | 0.963(4) | 0.0791(1) | 0.3311(1) | 0.4806(3) | =O1(B) |
| O(4)   | 32h  | 1 | 0.2510(1) | 0.1726(1) | 0.4782(4) | =O1(B) |
| O(5)   | 32h  | 1 | 0.0058(1) | 0.0071(1) | 0.2448(2) | =O1(B) |
| O(6)   | 32h  | 1 | 0.2564(1) | 0.0895(1) | 0.2378(4) | =O1(B) |
| O(7)   | 32h  | 0.984(4) | 0.1622(1) | 0.3227(1) | 0.2393(4) | =O1(B) |
| O(8)   | 32h  | 1 | 0.0899(1) | 0.2446(1) | 0.2338(4) | =O1(B) |
| O(9)   | 32h  | 0.876(4) | 0.0852(1) | 0.1616(1) | 0.5147(3) | =O1(B) |

Space group Fddd, $a = 24.73179(3)$ Å, $b = 24.82818(4)$ Å, $c = 8.19496(1)$ Å $R_{wp} = 3.58$, $R_p = 3.19$, $R_e = 2.53$, $S = R_{wp}/R_e = 2.0$, $R_B = 3.37$, $R_f = 4.16$

Table 4. Rietveld refinement results for neutron diffraction measurement at 220K of spinel LiMn$_2$O$_4$-$\delta$ synthesized by conventional method and annealed at 1173.15K in O$_2$.

| Atom | site | g | x   | y   | z   | B/Å$^2$ |
|------|------|---|-----|-----|-----|---------|
| Li(1) | 8a   | 1 | 1/8 | 1/8 | 1/8 | 0.249(24) |
| Li(2)  | 16f  | 1 | 3/8 | 0.2126(4) | 3/8 | =Li1(B) |
| Li(3)  | 16e  | 1 | 0.2077(5) | 3/8 | 3/8 | =Li1(B) |
| Li(4)  | 32h  | 1 | 0.2913(4) | 0.2965(3) | 0.1252(7) | =Li1(B) |
Table 5. Rietveld refinement results for neutron diffraction measurement at 290K of spinel LiMn$_2$O$_{4.8}$ synthesized by conventional method and annealed at 1173.15K in O$_2$.

| Atom | site | g  | x   | y   | z   | B/Å$^2$ |
|------|------|----|-----|-----|-----|---------|
| Li(1)| 8a   | 1  | 1/8 | 1/8 | 1/8 | 0.708(26) |
| Li(2)| 16f  | 1  | 3/8 | 0.2117(6) | 3/8 | =Li1(B) |
| Li(3)| 16e  | 1  | 0.2037(5) | 3/8 | 3/8 | =Li1(B) |
| Li(4)| 32h  | 1  | 0.2952(4) | 0.2900(4) | 0.1189(9) | =Li1(B) |
| Mn(1)| 16d  | 1  | 1/4 | 1/4 | 1/2 | 0.234(6) |
| Mn(2)| 32h  | 1  | 0.0859(2) | 0.0835(2) | 0.4981(8) | =Mn1(B) |
| Mn(3)| 32h  | 1  | 0.0849(2) | 0.3320(2) | 0.2558(6) | =Mn1(B) |
| Mn(4)| 32h  | 1  | 0.2540(2) | 0.1651(2) | 0.2557(7) | =Mn1(B) |
| Mn(5)| 32h  | 1  | 0.1670(1) | 0.2506(2) | 0.2481(6) | =Mn1(B) |
| O(1) | 32h  | 1  | 0.1722(1) | 0.1679(2) | 0.2631(5) | 0.487(4) |
| O(2) | 32h  | 1  | 0.0779(1) | 0.0052(1) | 0.4750(5) | =O1(B) |
| O(3) | 32h  | 1  | 0.0766(1) | 0.3400(1) | 0.5023(3) | =O1(B) |
| O(4) | 32h  | 1  | 0.2485(1) | 0.1713(1) | 0.4814(5) | =O1(B) |
| O(5) | 32h  | 1  | 0.0047(1) | 0.0051(2) | 0.2672(4) | =O1(B) |
| O(6) | 32h  | 1  | 0.2528(1) | 0.0891(1) | 0.2361(6) | =O1(B) |
| O(7) | 32h  | 1  | 0.1681(1) | 0.3271(2) | 0.2295(4) | =O1(B) |
| O(8) | 32h  | 0.984(7) | 0.0899(1) | 0.2500(1) | 0.2335(4) | =O1(B) |
| O(9) | 32h  | 0.990(9) | 0.0828(1) | 0.1611(1) | 0.5247(5) | =O1(B) |

Space group Fddd, $a = 24.73724(4)$ Å, $b = 24.84622(4)$ Å, $c = 8.19759(1)$ Å
$R_{wp} = 5.27$, $R_p = 3.92$, $R_o = 2.56$, $S = R_{wp}/R_o = 2.06$, $R_B = 3.17$, $R_f = 4.05$
Space group $Fd\bar{d}d$, $a = 24.73288(12)$ Å, $b = 24.72116(7)$ Å, $c = 8.24676(3)$ Å

$R_{wp} = 8.00$, $R_p = 5.67$, $R_e = 2.56$, $S = R_{wp}/R_e = 3.12$, $R_B = 3.96$, $R_F = 7.39$

Figure 3 shows the Rietveld refinement patterns of neutron diffraction data for sample A measured at 290, 220, 150, 80, and 10K. The calculated patterns fit the observed one fairly well. At low temperatures, each one of Li, Mn, and O sites split to 4, 5 and 9, respectively. The 72 lithium atoms are distributed over four crystallographic sites of different multiplicity ($8a$, $16e$, $16f$, and $32h$); the 144 manganese atoms are distributed over five crystallographic sites ($1 \times 16d$ and $4 \times 32h$); and the 288 oxygen atoms are distributed over nine crystallographic sites ($9 \times 32h$). This result is in agreement with previous work [42], which lead to the conclusion that a total charge ordering between equal amounts of Mn$^{3+}$ and Mn$^{4+}$ is impossible by this arrangement.

Figure 4 shows the temperature dependence of lattice parameters of sample A. The orthorhombic distortion decreased with decreasing measurement temperature and $a$ and $b$ axes become closer as the structure further change towards tetragonal and are corresponds to the anti-ferromagnetic transition as indicated previously [38, 39].

Figure 5a shows that by using the adopted model for refinement, two sets of Mn–O bond distance was deduced. One set consists of three Mn sites [Mn(1), Mn(2), and Mn(3)] with longer average Mn–O distance (2.000 Å) and corresponds to lower valence state Mn$^{3+}$ ions. According to the previous result [30], these three Mn sites are not pure Mn$^{3+}$ ions since the average Mn–O distance is slightly smaller than what is expected for pure Mn$^{3+}$ (2.02 Å). Another set consists of two Mn sites [Mn(4) and Mn(5)] with shorter average Mn–O distance (1.915 Å) and corresponds to well-defined higher valence state Mn$^{4+}$ ions. This result is consistent with one previously reported by J. Rodriguez-Carvajal et.al. [30] but different in Mn–O distances order reported by other groups [40, 43]. Figure 5.b. shows that Jahn-Teller elongated Mn–O bonds are divided into long axes and short axes. The elongated bond lengths of Mn1–O5 (2.104 Å) ordered along the $z$-axis are about 7% longer than those of Mn1–O4 (1.93 Å) and Mn1–O2 (1.972 Å) due to the typical Jahn-Teller effect of high-spin Mn$^{3+}$. The same cases also found in both Mn2O6 octahedra (6%; longer along the $x$-axis) and Mn3O6 octahedra (10%; longer along the $y$-axis). On the other hand, this case is not found in Mn4O6 and Mn5O6, where both Mn ions have BVS of 4+. This result explains the order of Mn$^{3+}$–O bond length in figure 5a.

![Figure 3. Rietveld refinement patterns of low temperature neutron diffraction data for spinel LiMn$_2$O$_{4-\delta}$ synthesized by conventional method from starting materials Li$_2$CO$_3$ and Mn$_2$O$_3$ and annealed at 1173.15K.](image-url)
Figure 6 shows the distorted structure of sample A measured at 150K, around five different manganese sites due to Jahn-Teller distortion. The elongated Jahn-Teller bond formed by trivalent manganese ions octahedrally coordinated Mn-O₆, i.e. Mn1–O, Mn2–O and Mn3–O, are ordered along z, x and y direction, respectively. Mn4–O and Mn5–O is not showing any elongated bond because these two manganese ions are in 4+ states. The BVS (Bond Valence Sum) of all five Mn–O bonds are calculated by using the following equation [44].
where \( BVS = s_{ij} \) is bond valence sum, \( d_0 \) is the parameter for the bond taken from [44], \( d_{ij} \) is the distance of the bond and \( B \) is a constant and set fixed at 0.37. The calculated BVS of Mn1, Mn2, Mn3, Mn4 and Mn5 are 2.997, 3.002, 2.998, 4.001 and 4.003, respectively, and give an average of 3.400 over the unit cell. These BVSs are equal to the formal oxidation state of the manganese ions.

Figure 7 shows the crystal structure of sample A along [001] of the Mn and Li sites within a unit cell. The surfaces containing all Mn\(^{4+}\) ions (Mn4 and Mn5) are hole-rich regions and they wrap electron-rich regions containing Mn\(^{3+}\) ion, which distinguished by the presence of Li ions (solid circle; yellow rectangle) or the absence of Li ions (dashed circle; green rectangle). Mn1 occupied the special position (16d) is shown in the space between the circles. Previous results [30] indicated the equal number of holes (Mn\(^{4+}\)) in the \( e_g \) band to the number of electrons (Mn\(^{3+}\)) available for hopping. The crystal structure as shown in Figure 7. indicated that there are 32 Mn4 and 32 Mn5 (both in 32h position) forming 64 out of 72 localized holes on the tetravalent Mn sites (32h \( \times \) 2) per unit cell. Thus, the remaining 8 holes more per unit cell are expected to be distributed over nearly trivalent Mn1, Mn2 and Mn3 sites and lead to a certain electron hopping towards the eight holes per cell below the transition temperature. In agreement with previous work by J. Rodríguez-Carvajal et.al. [30] and G. Rouse et.al. [42], the transition to a totally charge-ordered should not be disregarded.
Figure 6. Five manganese sites showing elongated Mn-O bonds (bold bond).

Mn4
Ave. Mn-O: 1.918 Å
BVS: 4.001+

Mn5
Ave. Mn-O: 1.917 Å
BVS: 4.003+

Figure 7. Schematic projection of the superstructure LiMn$_2$O$_{4+δ}$ along [001] with partial charge-ordered structure.
4. Conclusion
The phase transition in spinel LiMn$_2$O$_4$ at low temperature has been studied by means of neutron powder diffraction. The existence of phase transition in this material is closely related to the synthesis conditions, which include the choice of starting material, mixing method and annealing temperature. The sample synthesized from a mixture of Li$_2$CO$_3$ and Mn$_2$O$_3$ by conventional method showed phase transition at low temperature. The phase transition is unequivocally from cubic (SG. Fd-3m) to orthorhombic (SG. Fddd) and started from around 290K down to 10K. The orthorhombic structure showed the coexistence of Mn$^{3+}$ (Jahn-Teller) and Mn$^{4+}$ ions. The equal proportion of both ions is associated with partial charge ordering.

Acknowledgment
T.Y.S.P.P. is grateful for all support kindly provided by MEXT Japan. The neutron diffraction experiment was supported by the S-type project of KEK with the proposal No. 2009S05 and is greatly acknowledged. Valuable discussions and suggestions from the members of Powder Diffraction Group associated with partial charge ordering.

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