Spinel-to-CaFe$_2$O$_4$-Type Structural Transformation in LiMn$_2$O$_4$ under High Pressure

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Abstract: A new form of LiMn$_2$O$_4$ is reported. The structure is the CaFe$_2$O$_4$-type and 6% denser than the spinel. The structure transformation was achieved by heating at 6 GPa. Analysis of the neutron diffraction pattern confirmed an average of the structure; the unit cell was orthorhombic at $a = 8.8336(5)$ Å, $b = 2.83387(18)$ Å, and $c = 10.6535(7)$ Å (Pnma). Electron diffraction patterns indicated an order of superstructure $3a \times b \times c$, which might be initiated by Li vacancies. The exact composition is estimated from the structure analysis and quantity of intercalated Li. The polycrystalline CaFe$_2$O$_4$-type compound showed semiconducting-like characters over the studied range above 5 K. The activation energy was reduced to $\sim 0.27$ eV from $\sim 0.40$ eV at the spinel form, suggesting a possible enhancement of hopping mobility. Magnetic and specific-heat data indicated a magnetically glassy transition at $\sim 10$ K. As the CaFe$_2$O$_4$-type transition was observed for the mineral MgAl$_2$O$_4$, hence the new form of the lithium manganese oxide would provide valuable opportunities to study not only the magnetism of strongly correlated electrons but also the thermodynamics of the phase transition in the mantle.

Introduction

LiMn$_2$O$_4$ spinel is a geometrically frustrated antiferromagnetic material. Recent research progress indicates that the magnetic property is accompanied by a degree of charge segregation.1–5 The association might result in the complicated magnetic ground state: neutron scattering detected substantial diffuse reflections remaining far below the magnetic transition temperature $\sim 60$ K,5 while neutron polarization analysis revealed nearly half of spins are ordered.1 The magnetic properties are highly sensitive to the material stoichiometry probably due to the relation to the charge segregation:2 the magnetic nature is indeed profoundly influenced by the electrochemical method.3 Due to the rather complicated magnetic properties further investigations including magnetic and structural studies would be required to establish a solid picture of the unusual magnetic state.

Here we report the discovery of a structure transformation in the compound. The spinel structure was found transforming to another under high pressure, 6 GPa, during heating at 1100 °C or above. The high-pressure (HP) form was identified as the CaFe$_2$O$_4$ (calcium ferrite)-type,6–8 which is approximately 6% more dense than the spinel. As one of the key materials of geological science, “Spinel” MgAl$_2$O$_4$ shows the calcium ferrite-type transition;9–11 hence it would be of value to study the structure thermodynamics in LiMn$_2$O$_4$, because the transition appears in a rather moderate pressure range than in the mantle. Very recently, CuRh$_2$O$_4$ was found to show a corresponding structure transition under high pressure.12

In the calcium ferrite-type structure, all manganese ions are in a 6-fold coordinated environment by oxygen as well as in the perovskite manganese oxides, which show a broad range

1 ANML, National Institute for Materials Science.
2 National Institute of Standards and Technology.
3 NMC, National Institute for Materials Science.
4 ANCC, National Institute for Materials Science.
5 MAS, National Institute for Materials Science.
6 Ni MMA, National Institute for Materials Science.
of magnetic and electrical properties. Furthermore, the MnO₃ forms a double chain-type unit, in which magnetic anisotropy is inherent. We then expect the new form of LiMn₂O₄ would be valuable also for studies to expand understanding of the correlated electron nature of the perovskite manganese oxides.

In this study, the structure transformation was investigated by neutron, X-ray, and electron diffraction, and the magnetic properties of the new form of LiMn₂O₄ are reported.

Experimental Section

Sample Preparation. Polycrystalline spinel LiMn₂O₄ was prepared from fine powders Li₂CO₃ (4N) and Mn₂O₃ (4N). The Mn₂O₃ powder was preheated in air at 650 °C for 18 h. To test an effect of possible Li volatility on the sample quality, stoichiometric (Li:Mn = 1/2) and 6% Li-excess (1.06:2) mixtures were heated simultaneously. At first, those were heated in air at 700 °C for 18 h in an alumina crucible with a cap, followed by cooling and grinding. The heating was then repeated at 800 °C for 12 h and then at 850 °C for 60 h. The products were examined by powder X-ray diffraction method (Cu Kα, RIGAKU RINT2000), and we confirmed both samples were of high quality and qualitatively equivalent. More specifically, the cubic lattice constant was a = 8.251(1) Å and 8.252(1) Å for the Li/Mn = 1/2 and 1.06/2 samples, respectively, which are in good accord with what was reported elsewhere. The X-ray result suggested both samples were nearly stoichiometric, regardless of the nominal composition.

The spinel powder prepared at the Li/Mn = 1/2 composition was employed for the next round of synthesis. The powder was placed in a gold capsule, and the capsule was installed in a high-pressure apparatus. The powder was polished carefully on a fine alumina (0.3 mm) and after the sample, respectively. The calibrated neutron wavelength was 0.190, 0.375, and 0.581 (×10⁻¹² cm) for Li, Mn, and O, respectively.

A part of the sample was studied by electron diffraction (ED) on a Hitachi H-1500 electron microscope, in which the electrons were accelerated at 820 kV.

Physical Property Measurements. Parts of the sample were subjected for electrical and magnetic measurements. The sample pellet as made in the high-pressure furnace was cut into a bar shape and wired for the four-terminal resistivity measurement. The study was conducted between 5 K and 390 K in a commercial apparatus (Quantum design, PPMS). The ac-gage current was 0.1 mA, and the ac-frequency was 30 Hz. The specific heat of the sample was measured in the PPMS apparatus by a time-relaxation method between 1.8 K and 60 K.

Magnetic susceptibility was measured in magnetic fields of 50 Oe and 70 kOe. The sample was cooled to 1.8 K without the field, and then the magnetic field was applied, followed by heating to 350 K (zero-field cooling, ZFC) and cooling again to 1.8 K (field-cooling, FC) in a commercial apparatus (Quantum design, MPMS). The magnetization study was conducted in the apparatus at 2 K, 20 K, 30 K, and 50 K within the field range ±70 kOe.

Lithium Intercalation. Li ions were intercalated into the sample in a two-electrode electrochemical cell between 1.0 V and 4.5 V. The working electrode consisted of the sample (20 mg) and conductive binder (8 mg of poly(tetrafluoroethylene) and 4 mg of acetylene black), which was pressed on a titanium mesh at 300 kg/cm² and then dried in argon at room temperature for 48 h. A lithium foil was used as the counter electrode. The electrolyte solution was a mixture of ethylene carbonate and diethyl carbonate with a volume ratio of 1/1 containing 1 M LiPF₆ as a supporting salt. The cathodic current was 20 mA/g (0.22 mA/cm²).

Results and Discussion

X-ray powder diffraction patterns for the samples prepared under the high-pressure condition are shown in Figure 1. For easy comparison the pattern of the starting spinel is shown as well. Each number at the left side indicates the heating temperature. The patterns clearly indicate a formation of another structure under the synthesis conditions at 1100 °C or above. To identify the structure, several structure models were tested on the peak distribution, and we found the CaFe₂O₄-type was most likely. The peak positions were well characterized by assuming the CaFe₂O₄-type orthorhombic unit cell with lattice constants a = 8.836(1) Å, b = 2.834(1) Å, and c = 10.65(1) Å (Pnma for the 1100 °C profile). The compound is probably isostructural with NaRh₂O₄, NaRu₂O₄, and NaMn₂O₄, which were recently studied, and the results thus suggest the spinel-type LiMn₂O₄ goes into the CaFe₂O₄-type under the high-pressure condition. To confirm the transformation, we considered a neutron diffraction study, as the X-ray patterns may have limited information about oxygen and lithium. We then tried to improve the sample quality by optimizing the synthesis conditions in order to gain reliability of the neutron structure analysis.

The samples heated at 1100 °C or above were found to contain a small amount of impurity as marked by stars "**" in Figure 1. The impurity was identified as Li₂MnO₃ from the X-ray pattern and the EPMA result. The presence of the impurity in the final product suggests that Li deficiency in the main compound might be a possible Li source of the impurity. To get rid of the possible Li source, a Li-reduced mixture (nominal
composition was Li/Mn = 0.9/2, if the starting powders are stoichiometric) was heated at 6 GPa and 1500 °C for 1 h in the same synthesis manner, and we found that the amount of Li₂MnO₃ was indeed reduced in the final product. Many Li-reduced mixtures (Li/Mn = 0.8/2, 0.75/2, and 0.5/2) were also tested. However, the product quality was poor; other impurities appeared, unfortunately.

Apart from the consideration about the possible Li deficiency, other various nominal compositions, including Li excess (the maximum Li content was 1.2 mol per the formula unit) and oxygen excess (the maximum oxygen content was 4.2 per the formula unit), were tested over the heating range between 1100 °C and 1500 °C at 6 GPa. However, no indications of sample quality improvement were seen, and then we decided to take the sample at the Li/Mn = 0.9/2 composition for the neutron diffraction study.

We had another problem in the sample preparation. In each high-pressure run, approximately 0.8 g sample was produced, and we found it was too little for the neutron diffraction study. We therefore needed to repeat the synthesis run 8 times to increase the sample mass. All products were examined by the X-ray diffraction method, and all were found equivalent in quality. Six products were subjected to the neutron diffraction study, and the other two were reserved for the other chemical and magnetic studies. The X-ray diffraction pattern of the mixture of the six products is shown in Figure 2.

The neutron diffraction study was conducted in the NIST center for neutron research. The obtained pattern at room temperature was analyzed with the GSAS software. The initial parameters were employed from the structure of NaMn₂O₄ (Space group: Pnma, a = 8.9055(18) Å, b = 2.8524(5) Å, and c = 11.0825(22) Å). Preliminary fits to the neutron diffraction pattern suggested it was much more reasonable than the other structure models, such as CaMn₂O₄ (Space group: Pbcm, a = 3.1492(6) Å, b = 9.98(2) Å, and c = 9.66(2) Å) and CaTi₂O₄ (Space group: Bbmm, a = 9.718(4) Å, b = 9.9960(4) Å, and c = 3.140(2) Å). Perhaps, if the largest and the next largest

Figure 1. X-ray diffraction profiles of the lithium manganese oxides before (top) and after the high-pressure heating. The number of each pattern indicates heating temperature (°C) at 6 GPa. Asterisks (*) indicate the Li₂MnO₃ peaks.

Figure 2. Powder neutron diffraction profile (main panel) and X-ray diffraction profile (small panel) of the selected sample. Observed (+) and calculated (solid lines) intensities and differences between those (bottom) are shown. Vertical small bars indicate reflection positions for Li₂MnO₃ (upper) and Li₀.₉₂Mn₂O₄ (lower). Asterisks (*) indicate X-ray peaks for Li₂MnO₃. The sample was at room temperature.
lattice constants are much closer, either the Pbcm or the Bbmm model might be more likely than the Pnma structure model of the compound.

To complete the structure analysis, we needed to investigate the probable Li deficiency. In the ED patterns, we found extra spots indicating a superstructure, which might be initiated by the Li vacancies. Representative patterns are shown in Figure 3a–c. Those clearly indicate not only the primary spots (the orthorhombic unit cell) but also small extra reflections along a*.

Neither a diffuse nor a sharp anomaly was seen in the other directions. The order of the superstructure is then concluded to be $3a \times b \times c$, where $a \times b \times c$ denotes the orthorhombic unit cell. The observed extinction order indicated the space group Pnma for the 3a-type superstructure as well as the average structure.

More specifically, the (200) index in Figure 3c seems not to match with the other spots in Figure 3b. It was, however, confirmed, due to double diffraction, as the same order of spots that appeared during the sample analysis was tilted somewhat along the a-axis. Additional ED patterns are available in the Supporting Information.

The 3a-type superstructure is probably due to ordering of Li vacancies and the local modification in the vicinity of the vacancy. In Figure 4, a sketch of the 3a-type superstructure model is shown. Solid and dotted lines indicate the 3a-type and the average unit cell, respectively. One of three Li sites is assumed having a vacancy per the large unit cell.


Figure 3. Electron diffraction patterns of the CaFe$_2$O$_4$-type Li$_{0.92}$Mn$_2$O$_4$ taken at room temperature. The zone axis was (a) [100], (b) [010], and (c) [001].

Figure 4. Sketch of the 3a $\times$ b $\times$ c superstructure model. Solid and dotted lines indicate the 3a-type and the average unit cell, respectively. One of three Li sites is assumed having a vacancy per the large unit cell.
was tested, and we found the solutions became unstable; thermal displacement factors of Mn1 and Mn2 fell into an unreasonably small level, below 0.1 Å² (100U iso), and the Li occupancy factor was then fixed at 0.9167 (0.08). Although the 3a-type superstructure. The Li-site occupancy was then fixed at 0.9167 (0.08), as 1/12 mol of Li per the formula unit were assumed absent (see the sketch in Figure 4). Shortly afterward, we could reach a much improved solution; the R factors wR p and R p were 6.68% and 5.13%, respectively. Alternative possibilities, such as mixing of Li and Mn, were tested, and no improvement was achieved.

The refinement result is shown in the main panel of Figure 2, the average structure parameters are listed in Tables 1 and 2, and the crystal structure is outlined from the solutions in Figure 5. The thermal displacement parameter of Li is remarkably large, decreases with the increasing amount of intercalated Li ions, y in Li0.92Mn2O4, and then sharply dropped at y = 0.08-0.09, indicating the intercalation limit of the structure. The quantity matches well with the expectation from the 3a-type superstructure model. In addition, a scanning electron image of the sample is shown in Figure 8, in which the morphology and the size of particles are seen. The observation was intended to investigate possible factors, which might affect the intercalation; however, we did not see any of the possibilities.

Details of the local structure around the manganese ion is outlined in Figure 9 from the average structure data and compared with that of related compounds. The average bond distance to coordinated oxygen is 1.93(7) Å and 1.95(9) Å for Mn1 and Mn2, respectively, and a distortion factor of the Mn−O octahedra (defined as the ratio of the longest to the shortest bond distance) is 8.7% and 9.9% for Mn1−Oy and Mn2−Oy, respectively. The result seems intermediate between that of the spinel LiMn2O4, in which no distortion was reported, and that of NaMn2O4, in which a significant distortion 17% (Mn1−Oy) was found. Although a small distortion was detected, the local...
environments of the two manganese sites are comparable. This fact would suggest that Mn\(^{3+}\) and Mn\(^{4+}\) are likely distributed randomly to a certain degree rather than separated crystallographically.

To check the self-consistency of the structure solutions, the bond valence sum was calculated; +3.78 (Mn1) and +3.65 (Mn2).\(^{26}\) The estimation is consistent with the rather mixed picture of Mn\(^{3+}\) and Mn\(^{4+}\), however, slightly higher than the expected value +3.54. The bond valence sum of the \(3\alpha\)-type structure solutions was also calculated: +3.75 (the distortion factor was 19%), +3.93 (17%), +3.75 (16%), +3.34 (16%).

+3.37 (4%), and +3.64 (16%), for Mn11, Mn12, Mn13, Mn21, Mn22, and Mn23, respectively. The outcome would suggest Mn$^{3+}$ ions are preferred in Mn21 and Mn22 sites. The average of all the sums is +3.63, much better than the result of the average model analysis. However, Mn23–O6 has a much smaller degree of distortion, while the Jahn–Teller element Mn$^{3+}$ is supposed to be dominant at the site. The fact may suggest that even the large unit cell does not match perfectly with the structure of the compound. Again, we stress that further improvement of sample quality and focused studies on the local structure are needed to make clear the issue. Those are left for future work.

In Figure 10, electrical conductivity data are shown, which were obtained with and without the applied magnetic field of 70 kOe. The temperature vs resistivity plot (inset) clearly shows a semiconducting-like feature. The poor conductivity was found not to recover on cooling to 5 K, and there was very little magnetic field dependence. An Arrhenius plot (main panel) indicates the activation energy $(E_h)$ is 0.27 eV, assuming the hopping conduction picture. The analytic formula employed here was $\sigma = (A/T) \exp\left(\frac{-E_h}{k_B T}\right)$, where $A$ is a constant, and $k_B$ is the Boltzmann constant.\(^\text{(27)}\)\(^\text{(28)}\) It is nearly two-thirds of that of the spinel ($E_h = 0.40$ eV),\(^\text{(27)}\) suggesting a possible enhancement of hopping mobility due to a certain degree of structure change. Comparison between the two forms of the band structure would be of interest.

Magnetic susceptibility data are shown in Figure 11. The data were measured in the fields of 50 Oe (small panel) and 70 kOe (main panel). In the main panel, a small thermal hysteresis was seen below approximately 10 K, suggesting a magnetically glassy transition as was found in the spinel form.\(^\text{(1)}\)\(^\text{–}\)\(^\text{4}\) A small kink at ~40 K was seen in the weak field ZFC curve (small panel) with a thermal hysteresis, suggesting another magnetic ordering. Alternatively, the impurity Li$_2$MnO$_3$ might have a responsibility for the 40 K anomaly because it is antiferromagnetic below 36.5 K.\(^\text{18}\)


Figure 9. Expanded view of the average structure of the CaFe$_2$O$_4$-type Li$_{0.92}$Mn$_2$O$_4$. The number indicates bond distance (Å). The bond angles are in Table 2.

Figure 10. Temperature dependence of the electrical conductivity of the polycrystalline Li$_{0.92}$Mn$_2$O$_4$, crystallizing into the CaFe$_2$O$_4$-type structure (O), and the data measured in the magnetic field 70 kOe (●). The dashed line is a fit to the hopping conduction model.

Figure 11. Magnetic susceptibility of the CaFe$_2$O$_4$-type Li$_{0.92}$Mn$_2$O$_4$. Zero-field cooling (ZFC) and field-cooling (FC) data are shown as open and closed symbols, respectively. The data were measured at 70 kOe (main panel) and 50 Oe (top panel). The solid line indicates a Curie–Weiss law fit to the data. The arrow indicates a small kink in the ZFC curve.

In the $1/\chi$ vs $T$ plot of the 70 kOe data, a linear feature appeared, and we applied the Curie–Weiss (CW) law to the
linear part by a least-squares method: 
\[
\frac{1}{\chi(T)} = [C/(T - \Theta_W)] + \chi_0 \quad \varepsilon \,
\]
where \( \chi_0 \) is the temperature-independent susceptibility, \( C \) denotes the Curie constant, and \( \Theta_W \) is the Weiss temperature. The analyzed range was between 150 K and 350 K, and the result is indicated by the solid line. The CW parameters \( \mu_{\text{eff}} = 3.90(3) \mu_B \), \( \Theta_W = -180(3) \) K, and \( \chi_0 = 2.8(4) \times 10^{-4} \) emu/mol of Mn were obtained. The effective Bohr magneton (\( \mu_{\text{eff}} \)) was calculated from the Curie constant in relation to \( C = N_A \mu_{\text{eff}}^2 / 3 \Gamma \), where \( N_A \) is Avogadro’s constant. The \( \mu_{\text{eff}} \) is rather close to the spin value \( 3.87 \mu_B \) of Mn\(^{4+}\) (\( S = \frac{3}{2} \)) vs the simple expectation, \( 4.38 \mu_B \), for Mn\(^{3.54+}\) (the composition Li\(_{0.92}\)Mn\(_2\)O\(_4\) was assumed), calculated by the formula \( \mu_{\text{cal}} = \sqrt{1 - \chi_{S=\frac{3}{2}} + \chi_{S=\frac{3}{2}}^2} \), where \( \mu_S = 2\sqrt{S(S+1)} \mu_B \) and \( x = 0.54 \). Perhaps, the coexistence of Mn\(^{4+}\) compound Li\(_{0.92}\)Mn\(_2\)O\(_4\) and possible other Mn-rich impurities might be involved somewhat in the origin of the underestimation of \( \mu_{\text{eff}} \). The Weiss temperature is substantially lower than that of the spinel form (\( \Theta_W = -266 \) K), reflecting the change of the magnetic basis.

Magnetization was measured at 2 K, 20 K, 30 K, and 50 K, and the data are shown in Figure 12. Neither magnetic hysteresis nor spontaneous magnetization was seen in the data at 20 K and above. At 2 K an expected hysteresis from the magnetically glassy transition was found; however the experimental window was too narrow to correctly measure it. We were then able to see only the virgin curve at 2 K. There was no remarkable change in magnetization below and above the magnetic anomaly at \( \sim 40 \) K, which was suggested by the ZFC susceptibility measurement at 50 Oe.

In Figure 13a, specific heat data are shown. A small peak was found at 35 K in both the 70 kOe and the zero-field data. The peak is likely associated with the anomaly found in the weak-field susceptibility data. As the CW analysis to the 70 kOe susceptibility data indicated a substantial antiferromagnetic interaction, the peak is therefore likely due to an antiferromagnetic ordering. To investigate the magnetic contribution further, the lattice contribution is subtracted from the data in the following way.

The reference material CaSc\(_2\)O\(_4\) was prepared in the high-pressure furnace from CaO and Sc\(_2\)O\(_3\) by heating at 6 GPa and 1300 °C for 1 h.\(^{(30)}\) The data for CaSc\(_2\)O\(_4\) approximates the lattice contribution. (b) Magnetic part of the specific heat and (c) the magnetic entropy of the CaFe\(_2\)O\(_4\)-type Li\(_{0.92}\)Mn\(_2\)O\(_4\). The data for CaSc\(_2\)O\(_4\), which roughly approximates the lattice contribution, is shown by the dotted curve in Figure 13a, as it is nonmagnetic, isostructural, and has a comparable molecular weight (\( \sim 7\% \) larger). The magnetic contribution was then separated from the lattice contribution (Figure 13b), and the magnetic entropy was estimated in Figure 13c.

Overviews of the specific heat data are just reminiscent of what were observed for the spinel form, in which a small magnetic peak and substantial magnetic contribution remaining below the peak temperature were found.\(^{(2)}\) Due to the broad comparability of the specific heat features (see the small magnetic entropy at the peak and the large entropy loss at low temperature) and the results of the magnetic susceptibility measurements,\(^{(1-5)}\) magnetic coexistence of the long-range antiferromagnetic order with the glassy state is likely also in the CaFe\(_2\)O\(_4\)-type form. However, the possibility of the impurity contribution to the small peak (Li\(_{0.92}\)Mn\(_2\)O\(_4\) is antiferromagnetic


below 36.5 K\(^{18}\)) is not excluded. Further studies intended to figure out the magnetic ground state by neutron scattering in addition to the sample quality improvement would be needed.

In summary, we found the spinel-to-CaFe\(_2\)O\(_4\)-type transformation in the lithium manganese oxide, which was induced by heating at 6 GPa. As far as we know there were few studies on the phase transition after the work on the “Spinel” MgAl\(_2\)O\(_4\) over 15 years ago\(^{11}\). It could be interesting to study the transformation further because LiMn\(_2\)O\(_4\) may share the same structure thermodynamics with MgAl\(_2\)O\(_4\).

The magnetic susceptibility data and the specific heat data of the CaFe\(_2\)O\(_4\)-type form suggested the magnetically glassy state at low temperature. Further work, including development of sample quality and growth of single crystals, would be advantageous in exploration of possible magnetic anisotropy and in revealing details of the magnetic ground state.

The spinel-type LiMn\(_2\)O\(_4\) is ideal as a high-capacity battery material because of its low toxicity, low cost, and the high natural abundance of manganese. Recently, much attention has been focused on it and its related compounds to provoke a high electrochemical performance for future rechargeable lithium batteries. The dense version of the compound, reported here, could be significant in deepening the understanding of the nature of the compound and may help to provide valuable opportunities to invent advanced battery technology.

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**Supporting Information Available:** Additional ED patterns and crystallographic information file of the calcium ferrite-type Li\(_{0.92}\)Mn\(_2\)O\(_4\). These materials are available free of charge via the Internet at http://pubs.acs.org.

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