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$LiMn_2O_4$: a spinel-related low-temperature modification

Kenji Tateishi,[a]* Katsumi Suda,[b] Douglas du Boulay,[c] Nobuo Ishizawa[c] and Shuji Oishi[d]

[a]Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta Midori, Yokohama 226-8502, Japan, [b]Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta Midori, Yokohama 226-8502, Japan, [c]Ceramics Research Laboratory, Nagoya Institute of Technology, Asahigaoka, Tajimi 507-0071, Japan, and [d]Department of Environmental Science and Technology, Faculty of Engineering, Shinshu University, Wakasato, Nagano 380-8553, Japan

Correspondence e-mail:
tateishi@r3401.msl.titech.ac.jp

Key indicators

Single-crystal synchrotron study
T = 297 K
Mean σ(Mn–O) = 0.003 Å
R factor = 0.038
wR factor = 0.038
Data-to-parameter ratio = 10.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Single-crystal synchrotron X-ray diffraction at 297 K revealed the spinel-related low-temperature orthorhombic form of black octahedrally shaped single crystals of lithium dimanganate, $LiMn_2O_4$, grown by the flux method. Three of five MnO_6 octahedra show typical Jahn–Teller distortions associated with Mn^{III} states. The bond valence sums indicate that these three sites are enriched with Mn^{III} and the other two with Mn^{IV}, though the charge distribution among these sites is still partially disordered.

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Comment

Lithium manganese spinels are attractive candidates for cathode materials of rechargeable lithium ion batteries. Stoichiometric $LiMn_2O_4$ is a mixed-valence compound comprised of distinct Mn^{III} and Mn^{IV} ions in equal proportions. Above the transition temperature T_t, Mn^{III} and Mn^{IV} ions are randomly distributed amongst the 16d sites of $Fd\overline{3}m$ symmetry, while they are localized on five independent sites in $Fddd$ symmetry below T_t. Li ion dynamics, which is very important from the viewpoint of practical applications, is also different in high (HT) and low temperature (LT) phases (Verhoeven *et al.*, 2001). Structural information about these two phases is therefore essential for a complete understanding of the processes involved. Powder X-ray and neutron diffraction experiments have been reported previously by

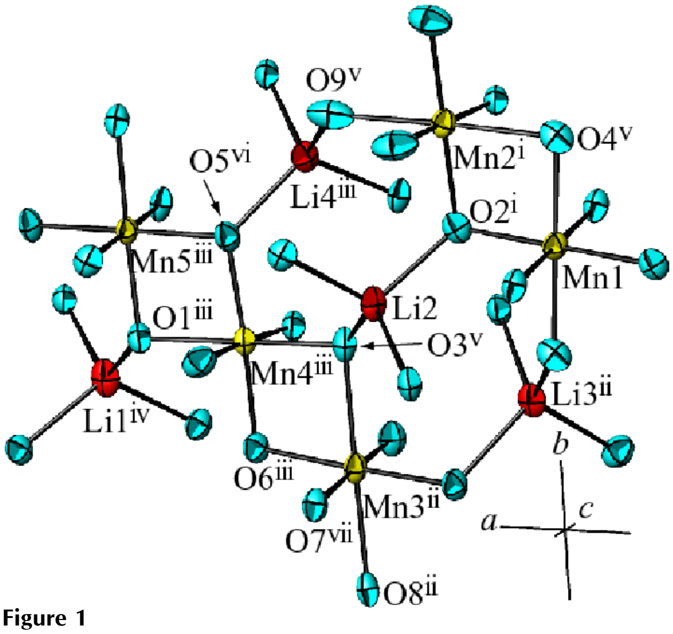

Figure 1
A view of $LiMn_2O_4$ with displacement ellipsoids drawn at the 90% probability level. [Symmetry codes: (i) $\frac{1}{4}+x, \frac{1}{4}+y, 1-z$; (ii) $\frac{1}{2}-x, y-\frac{1}{4}, \frac{1}{4}+z$; (iii) $\frac{3}{4}-x, y, \frac{3}{4}-z$; (iv) $\frac{1}{2}+x, y, \frac{1}{2}+z$; (v) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (vi) $\frac{1}{2}+x, \frac{1}{4}-y, \frac{3}{4}-z$; (vii) $\frac{1}{4}+z, y-\frac{1}{4}, \frac{1}{2}-z$.]

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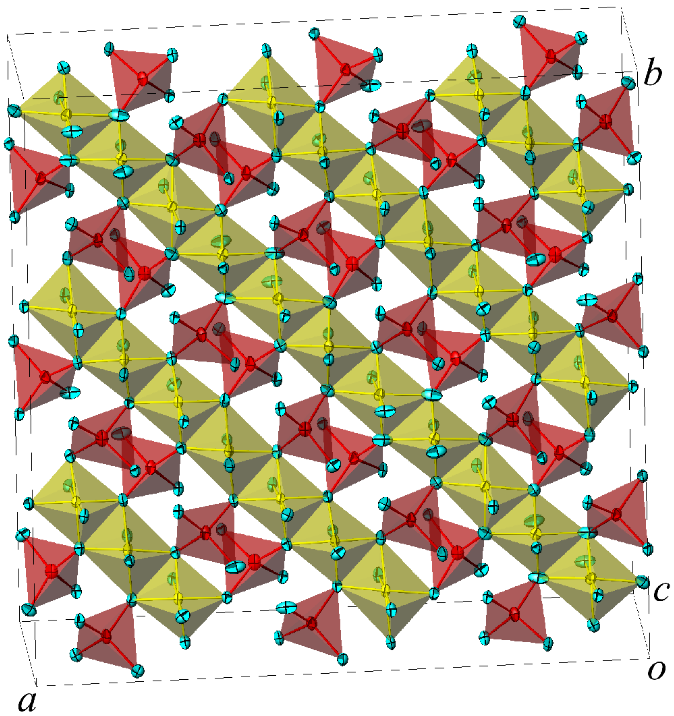

Figure 2
A slice of the unit cell, with displacement ellipsoids drawn at the 90% probability level. Key: Mn atoms are yellow, Li atoms are red and O atoms are light blue.

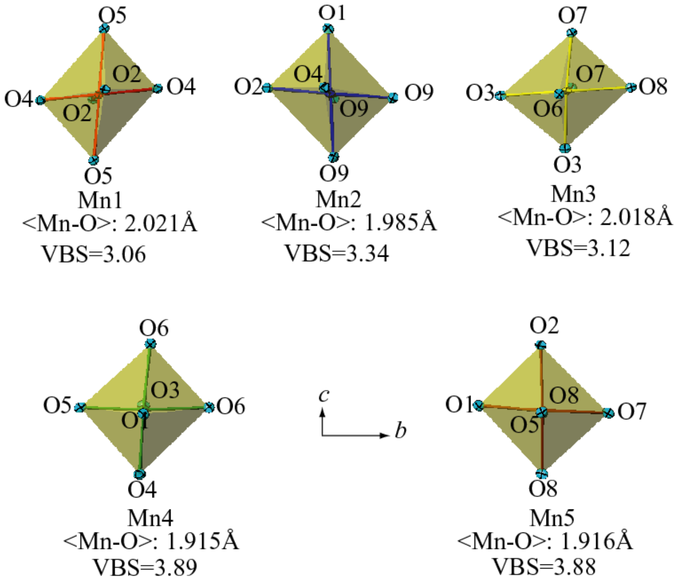

Figure 3
Distortion of the five independent MnO_6 octahedra projected down the *a* axis.

other authors but high precision single-crystal X-ray diffraction experiments, in principle, can provide more accurate three-dimensional information about the electron density. Akimoto *et al.* (2000) have already revealed details of single-crystal studies of the HT phase, so here we report the LT structure determined *via* single-crystal synchrotron X-ray diffraction. The structure of the LT phase was first determined in a powder neutron diffraction experiment (Rodríguez-Carvajal *et al.*, 1998). In that analysis, the atomic displacement parameters (ADPs) were treated isotropically and constrained to identical values for each chemical element. In the current study, the greater experimental precision of the single-crystal experiment permitted refinement of anisotropic ADPs for all atom sites, with more precise positional parameters (Fig. 1 and 2). Our study confirms the *Fddd* symmetry adopted by Rodríguez-Carvajal *et al.*, but the atomic positions differ somewhat from their results. The atomic positions directly affect the interatomic bond lengths and these, in turn, are strongly correlated with constituent atomic valences. Bond valence sums (BVS; Brown & Altermatt, 1985) determined for each Mn site are 3.06 for Mn1, 3.34 for Mn2, 3.12 for Mn3, 3.89 for Mn4, and 3.88 for Mn5, averaging to 3.50 over the unit cell. The average is, therefore, perfectly consistent with the $LiMn_2O_4$ composition. The evidence suggests that the Mn4 and Mn5 sites include some Mn^{III} component, whereas Rodríguez-Carvajal *et al.* concluded that they were well defined Mn^{IV} sites. BVS also indicate that Mn1, Mn2 and Mn3 strongly include the contribution of Mn^{III}. Fig. 3 shows five independent MnO_6 octahedra projected down the *a* axis. The bond lengths of Mn1—O5 (2.155 Å) are about 10% longer than those of Mn1—O4 (1.939 Å) and Mn1—O2 (1.967 Å), arising from the typical Jahn–Teller effect of high-spin Mn^{III} ions. The same arguments also apply to both the $Mn2O_6$ and $Mn3O_6$ octahedra and they have longer Mn—O bond length along the *a* and *b* axes, respectively. On the other hand, these tendencies do not appear at Mn4 and Mn5, whose BVS are close to 4.00.

A tetragonal modification of $(Li_{0.91}Mn_{0.09})Mn_2O_4$ with a = 5.7502 (9) Å and c = 8.637 (3) Å has been reported by Björk *et al.* (2001). Their unit cell has an approximate geometrical relation with the present orthorhombic structure; $a_o \sim b_o \sim 3\sqrt{2}\, a_t$ and $c_o \sim c_t$, though the difference in the *c* length is more than 0.4 Å. In addition, tetragonality of the present compound was rejected from the viewpoint of the merge statistics of equivalent reflections and a small but clear difference in the *a* and *b* lengths. A possible contamination of Mn atoms at Li sites was also examined by the population analysis, but in vain. Details are presented in the *Experimental* section.

Experimental

Single crystals of $LiMn_2O_4$ were synthesized using a Li_2MoO_4 flux. Reagent grade Li_2CO_3 and $MnCO_3$ were weighed and combined together to form a nominal 7 mol% $LiMn_2O_4$ mixture. Approximately 31.7 g of the mixture was placed in a platinum crucible and heated to 1373 K at a rate of 45 K h^{-1} under an air atmosphere. The peak temperature was maintained for 10 h, and then reduced to 723 K at 5 K h^{-1} before discharge. The flux was rinsed out with warm water. The crystals were black and octahedrally shaped, with a maximum size of about 0.1 × 0.1 × 0.1 mm along the edge. Transition temperatures were revealed by the existence of superlattice reflections using a Rigaku RAPID imaging plate diffractometer with a cryostat using nitrogen gas flow. This compound showed a first order phase transition at 294 (1) K on cooling and at 310 (1) K on heating.

Crystal data

$LiMn_2O_4$
$M_r = 180.82$
Orthorhombic, *Fddd*
$a = 24.7550$ (9) Å
$b = 24.8832$ (9) Å
$c = 8.2003$ (3) Å
$V = 5051.3$ (3) Å^3
$Z = 72$
$D_x = 4.28$ Mg m^{-3}

Synchrotron radiation
Cell parameters from 24 reflections
$\theta = 85.5–86.1°$
$\mu = 10.00$ mm^{-1}
$T = 297$ K
Octahedron, black
$0.05 \times 0.05 \times 0.05$ mm

Data collection

Tsukuba BL-14A diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical (*Xtal*3.7 *ABSORB*; Hall *et al.*, 2000)
$T_{\rm min} = 0.693$, $T_{\rm max} = 0.720$
10732 measured reflections
2642 independent reflections
1557 reflections with $F > 3\sigma(F)$

$R_{\rm int} = 0.025$
$\theta_{\rm max} = 36.5°$
$h = -39 \rightarrow 39$
$k = -39 \rightarrow 0$
$l = -12 \rightarrow 12$
6 standard reflections every 194 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.038$
$wR = 0.038$
$S = 3.20$
1549 reflections

146 parameters
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 3.05$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.65$ e Å^{-3}

Table 1
Selected geometric parameters (Å).

Mn1^{i}—O2^{ii}	1.967 (3)	Mn4^{i}—O6^{ix}	1.931 (3)
Mn1^{i}—O4^{i}	1.939 (3)	Mn5^{i}—O1^{i}	1.913 (3)
Mn1^{i}—O5^{ii}	2.155 (3)	Mn5^{i}—O2^{ii}	1.936 (3)
Mn1^{i}—O2^{iii}	1.967 (3)	Mn5^{i}—O5^{ii}	1.907 (3)
Mn1^{i}—O4^{iv}	1.939 (3)	Mn5^{i}—O7^{i}	1.970 (3)
Mn1^{i}—O5^{iii}	2.155 (3)	Mn5^{i}—O8^{i}	1.890 (3)
Mn2^{ii}—O1^{i}	1.966 (3)	Mn5^{i}—O8^{x}	1.884 (3)
Mn2^{ii}—O2^{ii}	1.933 (3)	Li1^{i}—O1^{i}	1.971 (3)
Mn2^{ii}—O4^{i}	2.085 (4)	Li1^{i}—O1^{ii}	1.971 (3)
Mn2^{ii}—O9^{i}	2.108 (5)	Li1^{i}—O1^{ix}	1.971 (3)
Mn2^{ii}—O9^{ii}	1.904 (3)	Li1^{i}—O1^{x}	1.971 (3)
Mn2^{ii}—O9^{v}	1.915 (3)	Li2^{iv}—O2^{ii}	2.000 (6)
Mn3^{vi}—O3^{vii}	2.194 (4)	Li2^{iv}—O3^{v}	1.978 (6)
Mn3^{vi}—O6^{i}	1.947 (4)	Li2^{iv}—O3^{i}	1.978 (6)
Mn3^{vi}—O7^{viii}	1.936 (3)	Li2^{iv}—O2^{xi}	2.000 (6)
Mn3^{vi}—O3^{vi}	1.908 (3)	Li3^{iv}—O4^{i}	1.984 (6)
Mn3^{vi}—O7^{vi}	1.961 (4)	Li3^{iv}—O7^{iv}	2.024 (6)
Mn3^{vi}—O8^{vi}	2.160 (3)	Li3^{iv}—O7^{viii}	2.024 (6)
Mn4^{i}—O1^{i}	1.962 (3)	Li3^{iv}—O4^{xi}	1.984 (6)
Mn4^{i}—O3^{vii}	1.871 (4)	Li4^{i}—O5^{ii}	1.955 (9)
Mn4^{i}—O4^{i}	1.903 (3)	Li4^{i}—O6^{xii}	1.968 (8)
Mn4^{i}—O5^{ii}	1.888 (3)	Li4^{i}—O8^{vii}	1.931 (8)
Mn4^{i}—O6^{i}	1.938 (3)	Li4^{i}—O9^{vii}	1.938 (8)

Symmetry codes: (i) $\frac{3}{4}-x, \frac{3}{4}-y, z$; (ii) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (iii) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (iv) $\frac{1}{4}+x, \frac{1}{4}+y, 1-z$; (v) $\frac{1}{2}+x, \frac{3}{4}-y, \frac{5}{4}-z$; (vi) $\frac{1}{2}-x, 1-y, \frac{1}{2}-z$; (vii) $\frac{1}{2}-x, \frac{1}{4}+y, z-\frac{1}{4}$; (viii) $\frac{1}{4}+x, 1-y, \frac{1}{4}+z$; (ix) $\frac{3}{4}-x, \frac{1}{2}+y, \frac{1}{4}-z$; (x) $\frac{1}{2}+x, \frac{3}{4}-y, \frac{1}{4}-z$; (xi) $\frac{3}{4}-x, \frac{1}{2}+y, \frac{5}{4}-z$; (xii) $\frac{1}{4}+x, \frac{1}{2}-y, z-\frac{1}{4}$.

Single-crystal diffraction data were measured using a horizontal-type four-circle diffractometer at beamline 14A of the Photon Factory, Tsukuba, Japan (Satow & Iitaka, 1989). An eight-channel avalanche photodiode detector was used for photon counting (Kishimoto *et al.*, 1998). The 0.75044 (5) Å wavelength used was calibrated using a spherically ground Si standard reference crystal. Crystals of $LiMn_2O_4$ were mounted on tapered glass capillaries and preprocessed at low temperatures before the synchrotron diffraction experiment. Cell dimensions were determined using 24 reflections from around $2\theta \simeq 86°$. A half sphere of diffraction data to $2\theta = 73°$ was measured at 297 (1) K, using an octahedrally shaped crystal of size 0.05 mm along the edge. Because no reflections violating the F lattice-centering conditions were observed in the sphere of $2\theta < 15°$, only the F-centred reflections were measured up to $2\theta = 73°$. Moreover, the measured reflections also satisfied the conditions $h00$: $h = 4n$, $0k0$: $k = 4n$ and $00l$: $l = 4n$, which are conditions of *Fddd* symmetry. The direct-methods phasing algorithms of the *SHELXS*97 (Sheldrick, 1997) package provided an initial solution assuming *Fddd* symmetry. The structure was essentially the same as that given by the neutron diffraction study (Rodríguez-Carvajal *et al.*, 1998). The structural parameters were then refined using *Xtal*3.7 (Hall *et al.*, 2000). The merging R factor reduced from 2.7 to 2.5% after applying an analytical absorption correction (de Meulenaer & Tompa, 1965). Dispersion and absorption coefficients were determined from the tables of Sasaki (1990) and the final least-squares R factor reduced to $R(F) = 0.038$. The populations of individual chemical elements were refined with all other parameters fixed at values obtained in the final cycle. They ranged from 1.12 (3) to 1.13 (4) for independent four Li atoms, from 0.991 (3) to 0.996 (3) for five Mn atoms, and from 0.992 (6) to 1.002 (7) for nine O atoms. Given that the excess values at the Li sites was only 0.39 (12) electrons at the most, the degree of contamination of Mn atoms at Li sites seemed marginal. Thus, a stoichiometric composition was assumed for the present crystal. The maximum positive residual density of 3.0 e Å^{-3} was found at 0.71 Å from Mn3 and the minimum negative residual density of -0.7 e Å^{-3} at 1.65 Å from Li2.

The IUCr *checkCIF* software suggested the possibility of pseudosymmetry $I4_1/amd$ for the final positional parameters. However, the merge R factor was 0.107 after transforming the unit cell from orthorhombic to tetragonal. In addition, the difference between the a and b cell dimensions was 0.128 (1) Å, being 100 times larger than the esu. The tetragonality of the crystal was thus rejected in the present study.

Data collection: *Diff14A Software* (Vaalsta & Hester, 1997); cell refinement: *Xtal*3.7 (Hall *et al.*, 2000); data reduction: *Xtal*3.7; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *Xtal*3.7; molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *Xtal*3.7.

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