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$(Li_{0.91}Mn_{0.09})Mn_2O_4$

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Lithium manganese oxide crystals with composition $(Li_{0.91}Mn_{0.09})Mn_2O_4$ were synthesized by a flux method. The crystals have a structure closely related to that of the cubic spinel $LiMn_2O_4$, but 9% of the lithium ions in the tetrahedral 4*a* site are substituted by Mn^{2+} ions. This substitution lowers the average Mn oxidation state below 3.5+, resulting in a Jahn–Teller distortion of the MnO_6 octahedron.

Comment

Lithium manganese oxides, in particular $LiMn_2O_4$ and $LiMnO_2$, are currently under intense investigation as possible cathode materials for Li-ion batteries (Thackeray, 1997). Structural information on these materials is crucial for a complete understanding of the lithium insertion/extraction process on electrochemical cycling. Powder XRD (X-ray diffraction) and neutron diffraction have previously been used to study the structures of these materials. Since lithium is a poor X-ray scatterer, powder XRD cannot give accurate information about the lithium content. On the other hand, both lithium and manganese are rather weak neutron scatterers and both have negative scattering lengths. Thus, neutron powder diffraction can also prove inadequate in revealing subtleties in the structure, such as the lithium site occupation. Single-crystal XRD can provide valuable supporting information.

Cubic $LiMn_2O_4$ ($Fd\bar{3}m$) has the spinel structure with a ccp (cubic close-packed) oxygen lattice. Mn ions occupy one half of the octahedral sites and Li ions one eighth of the tetrahedral sites. The average manganese oxidation state is 3.5+, *i.e.* there are equal numbers of Mn^{3+} and Mn^{4+} ions. Substitution of all of the lithium ions by Mn^{2+} ions gives hausmannite, Mn_3O_4 (Jarosch, 1987), which has the same spinel structure as cubic $LiMn_2O_4$, although the presence of Mn^{2+} ions on the tetrahedral site lowers the manganese oxidation state in the octahedral site to 3+ causing a Jahn–Teller (J–T) distortion since the d^4 electron configuration of manganese then becomes stabilized. The structure becomes tetragonal, $I4_1/amd$, with the MnO_6 octahedron distorted in the *c*-axis direction. Transforming this tetragonal phase to correspond to the cubic spinel gives a *c*/*a* ratio for hausmannite of 1.16. The *c*/*a* ratio is commonly used to describe the magnitude of the J–T distortion, which is directly coupled to the average manganese oxidation state.

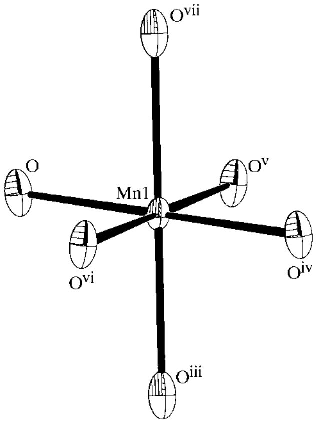

Figure 1
The structure of $(Li_{0.91}Mn_{0.09})Mn_2O_4$. Displacement ellipsoids are drawn at the 50% probability level.

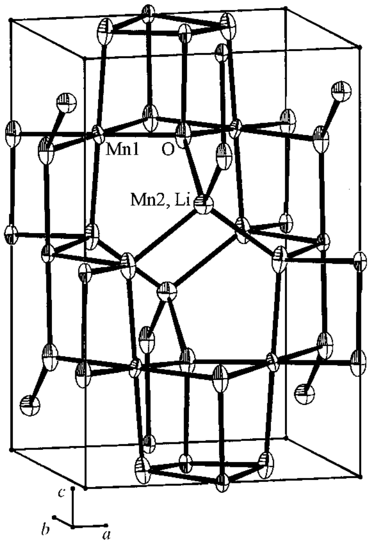

Figure 2
The MnO_6 octahedron with displacement ellipsoids drawn at the 50% probability level.

By thermal dissociation of cubic $LiMn_2O_4$, Tarascon *et al.* (1994) have synthesized a phase with the same cell parameters and the same space group ($I4_1/amd$) as obtained in this work with a *c*/*a* ratio of 1.06. Thermogravimetric analysis showed a weight loss of 1.5% compared with the starting cubic phase. This was attributed to oxygen loss and is equivalent to 0.16 oxygen per unit formula, giving a phase composition of $LiMn_2O_{3.86}$. These results were confirmed by Yamada *et al.* (1995).

The present structure $(Li_{0.91}Mn_{0.09})Mn_2O_4$ (space group $I4_1/amd$, origin choice 2) is closely related to cubic $LiMn_2O_4$ and tetragonal hausmannite, Mn_3O_4. Both structures can be described as a cubic close-packing of O atoms, with manganese in octahedral positions and either lithium or divalent manganese (Nabrotski & Kleppa, 1967) in tetrahedral positions. An intermediate compound, where a fraction of the lithium ions were substituted for manganese, was reported by Thackeray *et al.* (1996). In the present structure, 9% of the lithium ions were found to be substituted by manganese ions, presumably Mn^{2+}. Substitution of Mn^{2+} ions into the Li site lowers the average oxidation state of manganese in the octahedral site to 3.45+, compared with 3.5+ for the cubic spinel. The slight excess of Mn^{3+} ions causes a J–T distortion of the MnO_6 octahedron, where the Mn—O bond in the *c*-axis direction is elongated by 7% compared with the Mn—O bonds in the *ab* plane (Fig. 2); this gives a *c*/*a* ratio of 1.06. Recent results from Paulsen & Dahn (1999) support our finding, *i.e.* lithium substitution and no oxygen deficiency in this phase.

Experimental

Crystals were grown by a flux technique using a 1:1 ratio of LiCl (BDH, 99%) and $LiBO_2$ (Alfa, 99%). A mixture of MnO (Aesar, 99.5%) and MnO_2 (Baker, 99.5%) was used to maintain the Mn^{3+}/Mn^{4+} balance. The starting materials were mixed and heated in a platinum crucible to 1253 K. The mixture was held at this temperature for 2 h and then cooled slowly to 1123 K at a rate of 0.7 K h^{-1}. Crystals could then be separated from the flux by a hot-pouring process. Several crystals were examined by X-ray diffraction, all of which exhibited multi-phase properties. The crystals were thus cut into smaller pieces, and a suitable piece was selected and mounted on a glass fibre.

Crystal data

$(Li_{0.91}Mn_{0.09})Mn_2O_4$
$M_r = 185.13$
Tetragonal, $I4_1/amd$
$a = 5.7502\ (9)$ Å
$c = 8.637\ (3)$ Å
$V = 285.58\ (11)$ Å^3
$Z = 4$
$D_x = 4.304$ Mg m^{-3}
Mo $K\alpha_1$ radiation
Cell parameters from 25 reflections
$\theta = 19–20°$
$\mu = 8.78$ mm^{-1}
$T = 293$ K
Octahedral, black
0.3 × 0.3 × 0.2 mm

Data collection

Stoe IPDS diffractometer
ω scans
Absorption correction: numerical (*JANA*'98; Petriček & Dušek, 1997)
$T_{min} = 0.182$, $T_{max} = 0.377$
1225 measured reflections
103 independent reflections
1225 reflections with $I_{net} > 15\sigma(I_{net})$
$R_{int} = 0.049$
$\theta_{max} = 28.0°$
$h = -7 \rightarrow 7$
$k = -7 \rightarrow 7$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R(F) = 0.038$
$wR(F^2) = 0.083$
$S = 3.94$
1225 reflections
14 parameters
$w = 1/[\sigma^2(F)^2 + 0.01F^2]$
$(\Delta/\sigma)_{max} = 0.1$
$\Delta\rho_{max} = 0.52$ e Å^{-3}
$\Delta\rho_{min} = -0.55$ e Å^{-3}
Extinction correction: Becker & Coppens (1974), isotropic type 2
Extinction coefficient: 0.8 (1) × 10^3

The cell parameters were obtained by least-squares refinement of setting angles from a Rigaku AFC-6*R* diffractometer. In the low-angle region, overlapping peaks were found that could not be attributed to the obtained cell. The crystal was transferred to a Stoe Image Plate Diffraction System (IPDS) and data were collected in the range 3.8–56.3° in 2θ. During the integration and indexing of the raw data, a number of weak reflections were found which did not conform to the chosen unit cell. These were expected to derive from an impurity phase and were thus not included in the final data set. The structure was refined using the atomic coordinates of $Li_2Mn_2O_4$ (Goodenough *et al.*, 1985).

Table 1
Selected geometric parameters (Å, °).

Mn1—O	1.9322 (10)	Mn2^{ii}—O	1.9800 (15)
Mn1—O^{i}	2.0619 (16)	Li^{ii}—O	1.9800 (15)
O—Mn1—O^{iii}	96.17 (6)	O^{viii}—Mn2—O^{ix}	110.90 (4)
O—Mn1—O^{iv}	180.0	O^{viii}—Mn2—O^{x}	106.66 (9)
O—Mn1—O^{v}	83.53 (6)	O^{viii}—Li—O^{ix}	110.90 (4)
O—Mn1—O^{vi}	96.47 (6)	O^{viii}—Li—O^{x}	106.66 (9)
O—Mn1—O^{vii}	83.83 (6)		

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

Data collection: *Image Plate Diffraction System* (Stoe & Cie, 1987); cell refinement: *Rigaku AFC*-6*R Software* (Rigaku, 1991); data reduction: *X-RED* and *X-SHAPE* (Stoe & Cie, 1996); program(s) used to refine structure: *DUPALS* (Lundgren, 1983); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *DISTAN* (Lundgren, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1365). Services for accessing these data are described at the back of the journal.

References

Becker, P. J. & Coppens, P. (1974). *Acta Cryst.* A**30**, 129–147.
Goodenough, J. B., Thackeray, M. M., David, W. I. F. & Bruce, P. G. (1984). *Rev. Chim. Miner.* pp. 435–455.
Jarosch, D. (1987). *Mineral. Petrol.* **37**, 15–23.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Lundgren, J.-O. (1983). *Crystallographic Computing Programs*. Report UUIC-B13-405. Institute of Chemistry, University of Uppsala, Sweden.
Nabrotsky, A. & Kleppa, O. J. (1967). *J. Inorg. Nucl. Chem.* **29**, 2701–2714.
Paulsen, J. M. & Dahn, J. R. (1999). *Chem. Mater.* **11**, 3065–3079.
Petriçek, V. & Dušek, M. (1997). *JANA*'98. Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic.
Rigaku (1991). *Rigaku AFC-6R Software*. Rigaku Corporation, Tokyo, Japan.
Stoe & Cie (1987). *Image Plate Diffraction System*. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1996). *X-RED* and *X-SHAPE*. Stoe & Cie, Darmstadt, Germany.
Tarascon, J. M., McKinnon, W. R., Coowar, F., Bowmer, T. N., Amatucci, G. & Guyomard, D. (1994). *J. Electrochem. Soc.* **141**, 1421–1431.
Thackeray, M. M. (1997). *Prog. Solid State Chem.* **25**, 1–71.
Thackeray, M. M., Mansuetto, M. F., Dees, D. W. & Vissers, D. R. (1996). *Mater. Res. Bull.* **31**, 133–140.
Yamada, A., Miura, K., Hinokuma, K. & Tanaka, M. (1995). *J. Electrochem. Soc.* **142**, 2149–2156.