

Relationship of crystal structure to interionic interactions in the lithium–manganese spinel oxides[☆]

P. Piszora^a, C.R.A. Catlow^b, S.M. Woodley^b, E. Wolska^{a,*}

^a Faculty of Chemistry, Laboratory of Magnetochemistry, Adam Mickiewicz University, 60-780 Poznań, Grunwaldzka 6, Poland

^b The Royal Institution of Great Britain, Davy–Faraday Research Laboratory, 21 Albemarle Street, London W1X 4BS, UK

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Abstract

Lithium manganese oxides in the form of cubic spinel phases (space group $Fd3m$) are formed in a $\text{Li}_x\text{Mn}_{3-x}\text{O}_4$ system for rather limited values of x . Structural investigations by X-ray powder diffraction, applied to the Li–Mn–O compounds, indicate the formation of a second crystalline phase, Li_2MnO_3 (space group $C2/m$), with the increasing lithium content. Total Li^+ content per unit cell and the cation distribution over a spinel lattice in $\text{Li}_x\text{Mn}_{3-x}\text{O}_4$ have been studied by measurements of integrated intensities of X-ray reflections, and by structure refinement using Rietveld profile analysis. In an attempt to understand the factors affecting cation distribution in the spinel lattice, we applied the computer modelling techniques and investigated the Li^+ , Mn^{3+} and Mn^{4+} ion distribution by calculating the lattice energy, combined with energy minimisation procedures, using the General Utility Lattice Program (GULP), a program designed for simulation of ionic and semi-ionic solids, based on interatomic potential models. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Lithium manganese oxides; Structure refinement; Cation distribution; Energy minimisation; Lattice energy.

1. Introduction

A large number of studies on the synthesis of spinel-type lithium manganese oxides have been carried out, since they are important as electrode materials for rechargeable lithium batteries (Winter et al., 1998).

Series of oxides $\text{Li}_x\text{Mn}_{3-x}\text{O}_4$ ($1 \leq x \leq 1.33$) can be obtained in a temperature range from 350 to 900°C (Koksang et al., 1996). The oxidation number of manganese and composition of the manganese oxides

are dependent on the reaction conditions, such as temperature, starting materials and atmosphere. The $\text{LiMn}^{\text{III}}\text{Mn}^{\text{IV}}\text{O}_4$ spinel is easily formed at temperatures above 700°C, and $\text{Li}_{1.33}\text{Mn}_{1.67}^{\text{IV}}\text{O}_4$ ($\text{Li}_4\text{Mn}_5\text{O}_{12}$) spinel under low temperature conditions, below 500°C (Feng et al., 1999). Studies on the lithium ions content and distribution in the spinel lattice reveal, however, the existence of other spinel stoichiometries, with either cation deficiency or cation excess (Strobel et al., 1996). It was shown that in Li-rich systems the monoclinic Li_2MnO_3 phase coexists with the spinel phases (Strobel and Lambert-Andron, 1988).

The precise determination of the spinel unit-cell content is rather complicated, because of uncertainty in the experimentally-determined oxidation degree of manganese ions. The discrepancy also appears in the precise determination of Li^+ content and distribution in a given sample, depending on the method used. The

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* Corresponding author. Tel.: +48-61-8658167; fax: +48-61-8658008.

E-mail address: emilia@main.amu.edu.pl (E. Wolska)

single peak intensity measurement method suggests a near-stoichiometric lithium content in the LiMn_2O_4 sample, while from Rietveld method, there appears to be an excess of Li^+ , which may be expressed by the formula $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$.

The present report deals with a combination of experimental and computational methods applied for the structure refinement, enabling a comparison of structure parameters determined by X-ray diffraction, with the data obtained from the interatomic potentials and lattice energy calculations.

2. Materials and methods

Series of Li–Mn–O compounds have been obtained by solid state reaction at 600°C of Li_2CO_3 with the tetragonal spinel precursors, hydrohausmannite, $\text{Mn}_{3-\delta}(\text{O},\text{OH})_4$ (Series I and III) and hausmannite, $\text{Mn}_{3-\delta}\text{O}_4$ (Series II), prepared by autoclaving $\text{Mn}(\text{OH})_2$ at 150°C and its dehydration at 500°C , respectively (Kaczmarek and Wolska, 1993a,b).

X-ray diffraction studies were performed with a computerised TUR-61 (HZG-3) diffractometer employing the Mn-filtered $\text{FeK}\alpha$ radiation. For structural refinements the Rietveld program package GSAS was used (Larsen and Von Dreele, 1987).

Measurements of integral intensities of X-ray powder diffraction lines appear to be the most informative

about the distribution of Li^+ , Mn^{3+} and Mn^{4+} cations in the spinel structure of $\text{Li}_x\text{Mn}_{3-x}\text{O}_4$. The intensities, I_{hkl} , may be calculated for different models, assuming variable unit-cell content, based on the relation $I_{hkl} = |F_{hkl}|^2 \cdot p \cdot (L - P)$, where F_{hkl} stands for the structure factor ($F_{hkl} = \sum f_j \exp[2\pi i(hx_j + ky_j + lz_j)]$), p is the multiplicity number, $L - P$ the Lorentz-polarisation factor, f_j form factor (International Tables for X-Ray Crystallography, 1962). In particular, the spinel (Fd3m) X-ray pattern shows among other reflections whose intensities depend on tetrahedral (220, 422) or octahedral (222) cation positions. For example, a decrease in the 222-line intensity points out on the lithium for manganese substitution in the octahedral 16d Wyckoff positions (Wolska, 1996).

All calculations performed in this study employed the static lattice computer code, General Utility Lattice Program (GULP; Gale, 1996), which is based on the Born model of ionic lattice, and from which the structure and crystal properties may be calculated.

3. Results and discussion

X-ray diffraction patterns presented in Fig. 1 illustrate the composition of crystalline phases formed by the lithium ions insertion into spinel lattice during thermal treatment of a mixture of Li_2CO_3 and Mn_3O_4 . Our experiments show that the formation of single-

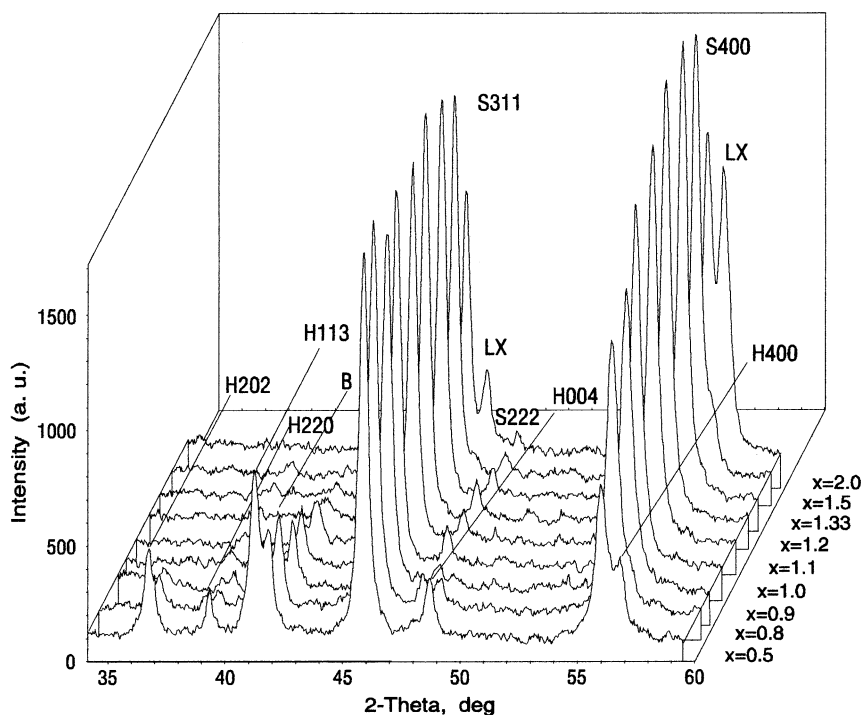


Fig. 1. X-ray powder diffraction patterns of samples with nominal composition $\text{Li}_x\text{Mn}_{3-x}\text{O}_4$ (Series II). S, spinel phase; H, hausmannite (Mn_3O_4); LX, Li_2MnO_3 ; B, bixbyite ($\alpha\text{-Mn}_2\text{O}_3$) phase.

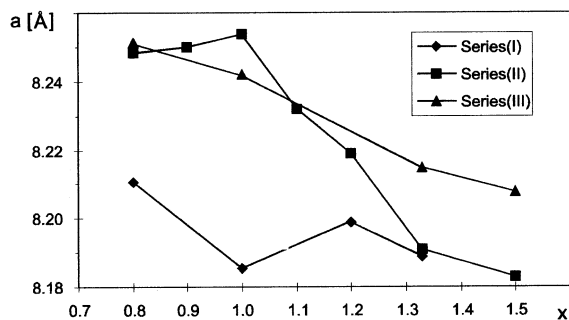


Fig. 2. Unit-cell parameter values, a , obtained for the spinel phases formed in Series I–III (see text). For standard deviations compare Table 2.

phase $\text{Li}_x\text{Mn}_{3-x}\text{O}_4$ spinel takes place for rather limited quantities of lithium. It appears that the stoichiometry of Li–Mn–O compounds also depends on the hydroxylation degree of the manganese oxide precursors.

Table 1
Lattice constants, a , of the cubic spinel unit cell ($Fd3m$)

	Unit cells		
	Series(I), a (Å)	Series(II), a (Å)	Series(III), a (Å)
$\text{Li}_{0.8}\text{Mn}_{2.2}\text{O}_4$	8.2106(4)	8.2482(15)	8.2510(14)
$\text{Li}_{0.9}\text{Mn}_{2.1}\text{O}_4$	–	8.2499(24)	–
$\text{Li}_{1.0}\text{Mn}_{2.0}\text{O}_4$	8.1854(5)	8.2536(9)	8.2422(13)
$\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$	–	8.2321(19)	–
$\text{Li}_{1.2}\text{Mn}_{1.8}\text{O}_4$	8.1987(5)	8.2189(5)	–
$\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$	8.1886(7)	8.1909(13)	8.2149(19)
$\text{Li}_{1.5}\text{Mn}_{1.5}\text{O}_4$	–	8.1828(10)	8.2076(27)

Table 2
Structural parameters for $\text{Li}_x\text{Mn}_{3-x}\text{O}_4$, with $x = 1.0$ (Li 1.0) and $x = 1.33$ (Li 1.33) from the Rietveld refinement in $Fd3m$ space group

Atom	Site	Coordinates ($x = y = z$)	Occupancy determined for sample	
			Li 1.0	Li 1.33
			$\text{Li}_{7.648}\text{Mn}_{16.35}\text{O}_{32}$	$\text{Li}_{8.392}\text{Mn}_{15.608}\text{O}_{32}$
Li(1)	$8a$	0	0.956(10)	0.989(9)
Mn2(1)	$8a$	0	0.044(10)	0.011(9)
Li(2)	$16d$	0.625	–	0.030(5)
Mn3(1)	$16d$	0.625	0.501(5)	0.420(5)
Mn4(1)	$16d$	0.625	0.499(5)	0.545(5)
$a(\text{Å})$			8.2579 (3)	8.1845(3)
u			0.3888(5)	0.3881(5)
R_{wp} (%)			6.45	6.97
R_{p} (%)			4.72	5.01
$B_{\text{iso}} (B_{\text{Li}} = B_{\text{Mn}} = B_{\text{Fe}} = B_{\text{O}})$			1.97 Å ²	

In the series with a nominal $\text{Li}_x\text{Mn}_{3-x}\text{O}_4$ stoichiometry, with $0.5 \leq x \leq 2.0$, the well crystallized cubic spinel phase was accompanied by the tetragonal hausmannite, Mn_3O_4 , and/or bixbyite, $\alpha\text{-Mn}_2\text{O}_3$, when $x < 1$, whereas the monoclinic Li_2MnO_3 phase was formed beside the spinel phase, for $x > 1.33$.

Results of accurate measurements of the spinel unit cell parameter, a , are shown in Fig. 2 and Table 1. The distinct dispersion of the lattice constant values obtained for the same nominal stoichiometries in series I, II and III, indicate the differences of both the lithium content and of the oxidation degree of manganese in the spinel structures.

We have undertaken a detailed investigation of the lithium ions distribution over the tetrahedral and octahedral sites of spinel lattice, and on the Li:Mn ratio limits, using the Rietveld structure refinement method on the X-ray powder diffraction line profiles. Although the changes in the manganese oxidation degree do influence, only slightly, the intensity of X-ray reflection

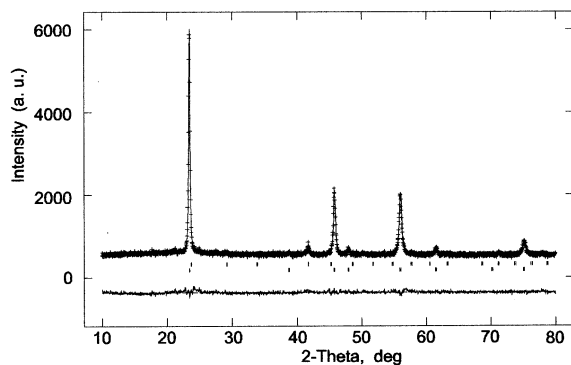


Fig. 3. Observed, calculated and difference profiles resulting from the Rietveld analysis of powder X-ray diffraction data collected in LiMn_2O_4 (space group $Fd3m$).

(form factors, f_p , differ by one electron), they can alter visibly the peak positions, because of different ionic radii of Mn^{3+} (0.645 Å) and Mn^{4+} (0.53 Å), changing the lattice parameter (Shannon, 1976). Structural parameters obtained after refinement in the $Fd3m$ space group, for X-ray patterns of samples with the LiMn_2O_4 and $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ stoichiometries (Series II) are presented in Table 2. Observed, calculated and difference

Table 3

Relative integrated intensities of the X-ray powder diffraction lines, observed and calculated, for samples $(\text{Li})_{\text{tet}}[\text{Mn}_2]_{\text{oct}}\text{O}_4$ and $(\text{Li})_{\text{tet}}[\text{Li}_{0.33}\text{Mn}_{1.67}]_{\text{oct}}\text{O}_4$

hkl	I_{hkl}/I_{311}			
	LiMn_2O_4		$\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$	
	Experimental	Model	Experimental	Model
111	237.87	208.83	261.86	221.69
311	100	100	100	100
222	8.73	18.83	3.18	11.16
400	112.54	121.11	129.61	134.83
331	11.95	21.65	11.22	18.30
511	28.77	39.58	36.77	44.99

Table 4

Lattice energy and the unit-cell parameters of $\text{Li}_x\text{Mn}_{3-x}\text{O}_4$ series, calculated with the aid of GULP

x	Total lattice energy (eV)	Unit-cell constant, a (Å)
1	−1725.80	8.26739
1.1	−1740.03	8.20548
1.2	−1754.84	8.14308
1.33	−1775.58	8.05923

profiles resulting from the Rietveld analysis of X-ray diffraction data collected on LiMn_2O_4 , are shown in Fig. 3. It has to be stressed, that the $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ patterns are very similar, which may cause the uncertainty in determination of the crystallographic positions of such light atoms as lithium, by X-ray diffraction techniques (Wolska et al., 1999).

Measurements of the integrated intensity ratios of the single X-ray reflections for the same samples, presented in Table 3, compared with the intensities calculated for $(\text{Li})_{\text{tet}}[\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}]_{\text{oct}}\text{O}_4$ and $(\text{Li})_{\text{tet}}[\text{Li}_{0.33}\text{Mn}^{\text{IV}}]_{\text{oct}}\text{O}_4$ models, confirm that the lithium ion limits in the $\text{Li}_x\text{Mn}_{3-x}\text{O}_4$ spinel structure is not easy to determine.

Application of modelling methods, based on the interatomic potentials independently derived for the relevant binary oxides (Lewis and Catlow, 1985; Catlow et al., 1994), enables the calculation of lattice energy and the refinement of crystal structure (Gale, 1996). Results presented in Table 4, indicate a slight increase of energy with the increasing lithium content in the spinel lattice $\text{Li}_x\text{Mn}_{3-x}\text{O}_4$, and the decrease of the unit cell constant, a , from 8.267 to 8.059 Å, for $x = 1$ and $x = 1.33$, respectively. These values should be compared to other results obtained, i.e. experimental: 8.2460 and 8.1900 (Hill et al., 1979), 8.232 and 8.162 (Thackeray and Rossouw, 1994), 8.2536(9) and 8.1908(3) Å (this study) and calculated on the basis of ionic radii and oxygen parameters: 8.2810 and 8.2277 Å (Shannon, 1976; Hill et al., 1979).

We believe that the progress in evaluation of interatomic potentials, by taking into consideration their strong dependence on the coordination number, will improve the consistency of calculations and experiments, and it will be possible to predict the lithium ion distribution over the spinel cationic positions (Woodley et al., in press).

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