SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF DEFECT SPINELS IN THE LITHIUM-MANGANESE-OXIDE SYSTEM

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ABSTRACT

Lithium-manganese-oxides prepared at moderate temperatures are under investigation as insertion electrodes for rechargeable lithium batteries. The structures of two defect-spinel compounds synthesised by the reaction of $MnCO_3$ and Li_2CO_3 at 400°C are reported. The cation distributions in the structures were determined by neutron-diffraction to be $\{Li_{.85}\square_{.15}\}_{8a}[Mn_{1.74}Li_{.26}]_{16d}O_4$ and $\{Li_{.87}\square_{.13}\}_{8a}[Mn_{1.71}Li_{.29}]_{16d}O_4$, where 8a and 16d refer to the tetrahedral and octahedral sites of the prototypic spinel space group Fd3m, respectively. The structures are discussed in relation to the spinel system $Li_2O \cdot yMnO_2$ (y≥2.5).

MATERIALS INDEX: lithium, manganese, oxides, spinels

INTRODUCTION

Lithium-manganese-oxides with a spinel-type structure are of interest as insertion electrodes for rechargeable lithium battery applications [1,2]. The best-known material is $Li[Mn_2]O_4$ which has space group symmetry Fd3m; it is isostructural with the prototype mineral spinel $Mg[Al_2]O_4$. In $Li[Mn_2]O_4$ the lithium ions occupy the tetrahedral 8a sites and the manganese ions the octahedral 16d sites. The oxygen ions, which are cubic-close-packed, occupy the 32e positions. Lithium insertion into $Li[Mn_2]O_4$ causes a displacement of the Li^+ ions from the 8a positions into neighbouring interstitial 16c octahedral sites to yield $Li_2[Mn_2]O_4$ after the insertion of one lithium per spinel unit [3,4]. A neutron-diffraction analysis of $Li_2[Mn_2]O_4$ has shown that the Li^+ ions occupy both tetrahedral and octahedral sites [5]. Lithium extraction from $Li[Mn_2]O_4$ produces the defect spinel

λ-MnO$_2$ [6]. The [Mn$_2$]O$_4$ spinel framework remains intact during both lithium insertion and extraction; λ-MnO$_2$ retains the cubic symmetry of the parent compound whereas the onset of a Jahn-Teller distortion in Li$_{1+x}$[Mn$_2$]O$_4$ at x=0.08, when the average Mn valency is 3.46, reduces the crystal symmetry from cubic to tetragonal [3].

Electrochemical extraction of lithium from Li[Mn$_2$]O$_4$ occurs in two stages at approximately 4V, whereas lithium is inserted into Li[Mn$_2$]O$_4$ to a composition Li$_2$[Mn$_2$]O$_4$ at a constant voltage of 2.9V [3,7]. Although the reversibility of the higher voltage reaction is good, lithium cells show a significant capacity loss when cycled on the 2.9V plateau [1,8]. The loss in capacity is believed to be mainly a result of the Jahn-Teller distortion that causes a 16% increase in the c/a ratio of the unit cell during the insertion and extraction of lithium. Li[Mn$_2$]O$_4$ electrodes therefore have limited use in rechargeable 3V lithium cells.

It was recently reported that Li[Mn$_2$]O$_4$ could be oxidized to form an oxygen-rich, defect spinel LiMn$_2$O$_{4.5}$ (Li$_2$Mn$_4$O$_9$) [9]. Li$_2$Mn$_4$O$_9$ is an intermediate member of the Li$_2$O·yMnO$_2$ system (y≥2.5); it has y=4.0. The end members of the system are the stoichiometric spinel Li$_4$Mn$_5$O$_{12}$ (y=2.5) and the defect spinel λ-MnO$_2$ (y=∞). Of particular interest are the spinels that fall within the compositional range 2.5≤y≤4.0 because they operate far more effectively than Li[Mn$_2$]O$_4$ as electrodes in rechargeable 3V lithium cells [1]. They have the following attractive features:

1)   Li$_2$O·yMnO$_2$ compounds (2.5≤y≤4.0) can be synthesised within a few hours by reacting Li$_2$CO$_3$ (or LiOH) with MnCO$_3$ at 400°C,

2)   the theoretical capacities of these spinel electrodes (in which all the manganese ions are tetravalent), for example, Li$_2$Mn$_4$O$_9$ (213mAh/g) and Li$_4$Mn$_5$O$_{12}$ (163mAh/g) are higher than the capacity of Li[Mn$_2$]O$_4$ (148mAh/g), and

3)   Li/Li$_2$O·yMnO$_2$ cells are significantly more stable on cycling than Li/Li[Mn$_2$]O$_4$ cells. The superior cycling has been attributed to the fact that lithium is inserted into cubic Li$_2$O·yMnO$_2$ spinel structures with minimal increase in unit-cell volume and that the Jahn-Teller effect (tetragonal distortion) occurs late in the discharge reaction when the average valency of the manganese ions reaches approximately 3.5.

There is currently little information about the structures of Li$_2$O·yMnO$_2$ spinel products made by the solid state reaction of Li$_2$CO$_3$ and MnCO$_3$ at moderate temperatures. In this paper our attempts to prepare two single-phase spinel compounds within the range 2.5≤y≤4.0, namely Li$_4$Mn$_5$O$_{12}$ (y=2.5) and Li$_2$Mn$_3$O$_7$ (y=3) at 400°C are reported. The structures of the resulting products as determined by neutron diffraction are discussed in relation to Li$_2$Mn$_4$O$_9$ (y=4) and a standard λ-MnO$_2$ (y=∞) sample.

EXPERIMENTAL

A standard λ-MnO$_2$ sample (sample A) was prepared by Hunter's method by reacting LiMn$_2$O$_4$ in 2M H$_2$SO$_4$ at 20°C for 16 hours [6]. Two other spinel compounds, labelled sample B and sample C were prepared by the reaction of Li$_2$CO$_3$ and MnCO$_3$ powders. Li:Mn ratios of 2:3 and 4:5 were selected for samples B and C in anticipation of synthesising single-phase Li$_2$Mn$_3$O$_7$ and Li$_4$Mn$_5$O$_{12}$ products, respectively. The powders were thoroughly mixed, prior to firing, by ball-milling in hexane in sealed ceramic

containers for several days. After evaporating the hexane at room temperature, 30g samples were manually reground and fired at 400°C in air. Samples for neutron diffraction analysis were heated for 20 hours. Powder X-ray diffraction data were collected on samples that had been heated for only 5 hours to demonstrate the speed at which spinel compounds can be synthesised by solid state reactions at moderate temperature. The lithium and manganese concentrations in the fired samples were determined by atomic absorption methods. These analyses showed that there had been no loss of lithium during synthesis (Table 1); the lithium content in sample B was, in fact, slightly higher than expected.

TABLE 1
Li:Mn ratios of samples B and C before and after firing at 400°C as determined by atomic absorption spectroscopy.

| Sample	Li:Mn before firing	Li:Mn after firing
B	2.00:3.00	2.03:3.00
C	4.00:5.00	4.25:5.00

X-ray diffraction data of the samples were collected at the CSIR on an automated Rigaku diffractometer. The beam of $CuK\alpha$ radiation was monochromated with a graphite single crystal. Structures were determined by profile refinement of time-of-flight neutron-diffraction data collected on the Polaris diffractometer at the ISIS facility of the Rutherford Appleton Laboratory. Peak shape was defined by a double-decay exponential, convoluted with a Voigt function [10,11]. Neutron-scattering amplitudes used in the refinements were $b(Li)= -.203 \times 10^{-12}cm$, $b(Mn)= -.373 \times 10^{-12}cm$ and $b(O)= .5804 \times 10^{-12}cm$ [12]. In the refinements of the spinel structures the tetrahedral sites were assumed to be occupied by only lithium ions because Mn^{3+} (d^4) and Mn^{4+} (d^3) ions favour octahedral, not tetrahedral, coordination. Because both lithium and manganese ions can occupy the 16d octahedral sites of the spinel structure, the cation distribution was determined in accordance with the composition that was closest to the expected stoichiometry and that was consistent with the overall negative scattering from these sites.

RESULTS AND DISCUSSION

The observed and calculated neutron-diffraction profiles of samples A, B and C are shown in Figs. 1(a-c). The refined cystallographic parameters of the three defect spinel structures are given in Tables 2(a-c).

Sample A: "λ-MnO$_2$"

An excellent fit between the observed and calculated data was obtained for the standard λ-MnO$_2$ sample (Fig. 1). The refinement was consistent with other reported refinements [4,6]; it showed, in particular, a small amount of scattering from residual lithium (5%) in the tetrahedral 8a sites and that the octahedral 16d sites were fully occupied by manganese. The refined composition of this phase, in spinel notation, $\{Li_{0.05}\square_{0.95}\}_{8a}[Mn_2]_{16d}O_4$, gave an average valency of 3.975 for the manganese ions. The lattice parameter $a=8.0445(1)$Å is marginally larger than values reported for other "λ-MnO$_2$" samples, for example, $a=8.03$Å [6] and $a=8.029$Å [4].
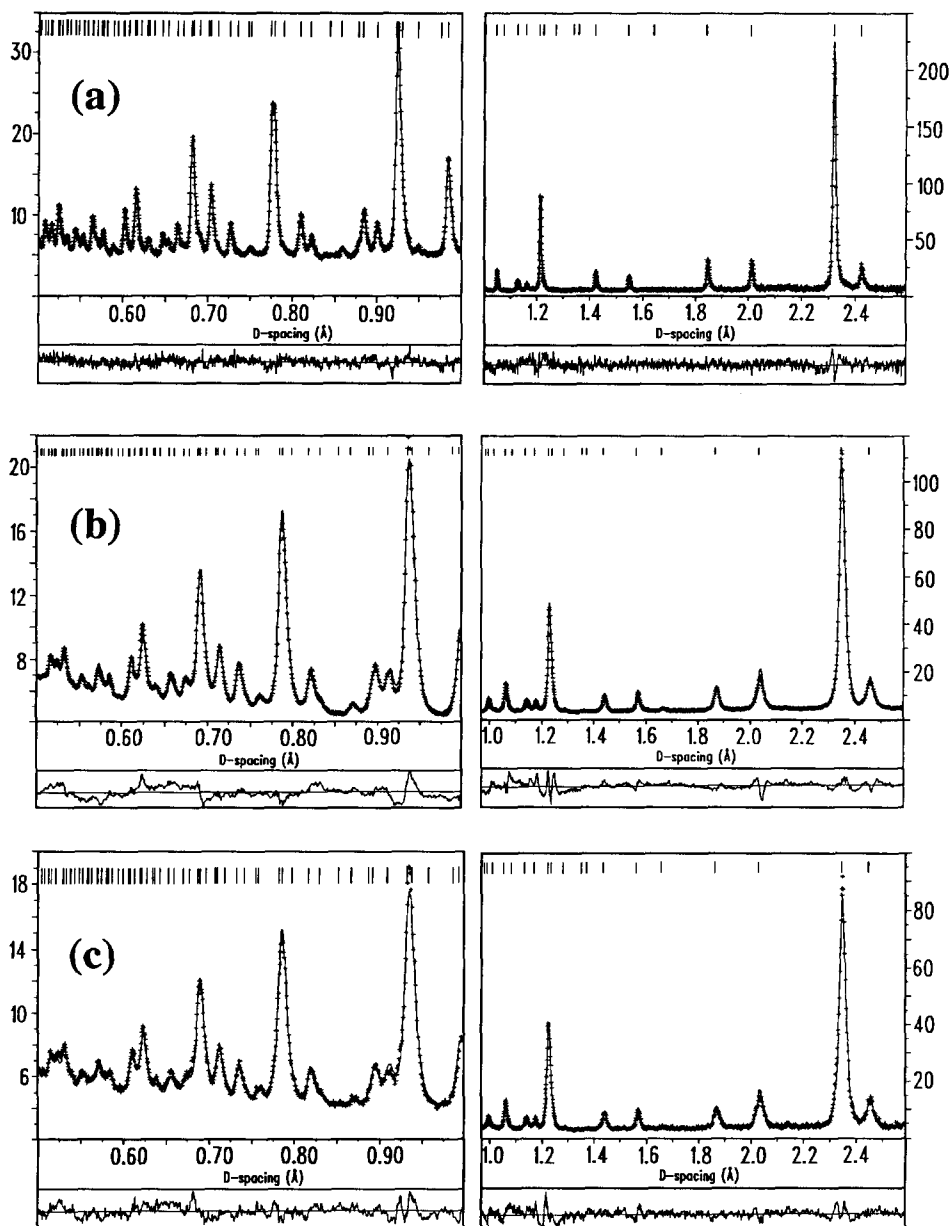
FIG. 1

The neutron-diffraction profiles of (a) "λ-MnO_2" (sample A), (b) "$Li_2Mn_3O_7$" (sample B) and (c) "$Li_4Mn_5O_{12}$" (sample C) for the d-spacing range 0.5Å to 2.6Å. The difference between the observed and calculated pattern is plotted below each profile on the same scale.

TABLE 2
Crystallographic parameters of (a) Sample A ("λ-MnO₂")
(b) Sample B ("Li₂Mn₃O₇") and (c) Sample C ("Li₄Mn₅O₁₂") as determined
by neutron-diffraction analysis.

(a) Sample A: "λ-MnO$_2$" a = 8.0445(1)Å   Space Group = Fd3m

Atom	Position	x	y	z	B_{11}	B_{12}	n
Li	8a	.125	.125	.125	.39(1)	-	.05(1)
Mn	16d	.5	.5	.5	.39(1)	-	1.0
O	32e	.2631(1)	.2631(1)	.2631(1)	.45(1)	.03(1)	1.0

R_p=5.22; R_{wp}=4.12; R_E=2.76.
χ^2=2.23 for 3754 observations and 19 basic variables.

(b) Sample B: "Li$_2$Mn$_3$O$_7$" a=8.1605(1)Å   Space Group = Fd3m

Atom	Position	x	y	z	B_{11}	B_{12}	n
Li(1)	8a	.125	.125	.125	.62(12)	-	.85(3)
Li(2)	16d	.5	.5	.5	.37(3)	-	.13(1)
Mn	16d	.5	.5	.5	.37(3)	-	.87(1)
O	32e	.2629(1)	.2629(1)	.2629(1)	.94(2)	-	1.0

R_p=3.82; R_{wp}=3.58; R_E=0.69.
χ^2=26.6 for 1675 observations and 21 basic variables.

(c) Sample C: "Li$_4$Mn$_5$O$_{12}$" a=8.1430(1)Å   Space Group = Fd3m

Atom	Position	x	y	z	B_{11}	B_{12}	n
Li(1)	8a	.125	.125	.125	.99(21)	-	.82(5)
Li(2)	16d	.5	.5	.5	.35(5)	-	.15(2)
Mn	16d	.5	.5	.5	.35(5)	-	.85(2)
O	32e	.2625(1)	.2625(1)	.2625(1)	.89(3)	-.27(2)	1.0

R_p=5.51; R_{wp}=4.95; R_E=1.96.
χ^2= 6.39 for 1675 observations and 21 basic variables.

Sample B: "Li$_2$Mn$_3$O$_7$"

The refined composition of Sample B, was determined to be, in spinel notation, $\{Li_{0.85}\square_{0.15}\}_{8a}[Mn_{1.74}Li_{0.26}]_{16d}O_4$. This composition, which is equivalent to $Li_{1.94}Mn_{3.04}O_7$ (or $Li_2O \cdot 3.13MnO_{1.985}$), is in reasonably good agreement with the expected formula $Li_2Mn_3O_7$ (or $Li_2O \cdot 3.0MnO_2$). The model showed unequivocally that the spinel product was lithium-deficient with vacancies on the tetrahedral 8a sites. It also showed that the manganese ions were not quite fully oxidized ($n^+_{Mn}=3.97$). The small amount of surplus lithia (or unreacted Li_2CO_3) that was present in the sample could not be detected as a second phase in the neutron-diffraction pattern. The 16d octahedral sites were completely filled with lithium and manganese. It should be noted that it is possible to account for the total negative scattering from the octahedral sites by increasing the manganese to lithium ratio and introducing vacancies in these sites. However, because such calculations move the composition of the spinel phase further away from the expected stoichiometry, the preferred composition of sample B was deemed to be $Li_{1.94}Mn_{3.04}O_7$.

Sample C: "Li$_4$Mn$_5$O$_{12}$"

The refinement of sample C yielded the spinel composition $\{Li_{0.82}\square_{0.18}\}_{8a}[Mn_{1.70}Li_{0.30}]O_4$, or alternatively, $Li_{3.36}Mn_{5.10}O_{12}$. The refinement demonstrated that this spinel phase, like sample B, was lithium-deficient with vacancies on the tetrahedral 8a sites; the octahedral sites were completely filled with lithium and manganese. However, in this model the average valency of each manganese ion is 4.04 which marginally exceeds the fully-oxidized state of 4.0. The excess charge on the manganese can be compensated for by increasing, within the allowed limits of experimental error, the lithium content in the tetrahedral 8a sites and the manganese to lithium ratio in the octahedral 16d sites. The composition of the spinel phase, in which the manganese ions are exactly tetravalent, which most closely approximates that of $Li_4Mn_5O_{12}$ is $Li_{3.48}Mn_{5.13}O_{12}$, or in spinel notation, $\{Li_{0.87}\square_{0.13}\}_{8a}[Mn_{1.71}Li_{0.29}]_{16d}O_4$. (The possibility that sample C, like sample B, may be very slightly oxygen deficient, cannot be entirely discounted). It is of interest to note that $Li_{3.48}Mn_{5.13}O_4$ can also be represented as $Li_2O \cdot 2.95MnO_2$ which, coincidently, is close to the composition that was anticipated for sample B, had the reaction gone to completion. The data at hand therefore show that, despite extremely well-mixed samples, the formation of single-phase $Li_4Mn_5O_{12}$ at moderate temperatures is hindered by the rapid decomposition and complete oxidation of $MnCO_3$ while only partly reacting with the Li_2O component of Li_2CO_3. It is anticipated that with longer reaction times a single-phase stoichiometric $Li_4Mn_5O_{12}$ product would be generated; the second stage of the reaction is expected to occur relatively slowly because it necessitates the physical incorporation of Li_2O into an already fully-oxidized lithium-manganese-oxide structure.

The cation distribution in the four spinel phases of the $Li_2O \cdot yMnO_2$ system that have been characterized thus far by neutron diffraction are listed in Table 3. In the two end members of this system, λ-MnO_2 and $Li_4Mn_5O_{12}$, the octahedral 16d sites are completely filled; in λ-MnO_2 the tetrahedral sites are empty whereas in $Li_4Mn_5O_{12}$ they are filled with lithium. In $Li_2Mn_4O_9$ (y=4), vacancies exist on both the tetrahedral and octahedral sites of the structure [9]. As y decreases towards 2.5 it is evident that the octahedral sites are preferentially filled by lithium and that vacancies are retained on the tetrahedral sites. It has not been possible to synthesise defect spinels with y>4 by reaction of Li_2CO_3

and $MnCO_3$ at 400°C because of the thermal instability of these phases. However, there are indications that these structures can be synthesised at room temperature by the removal of Li_2O from $Li_2O \cdot yMnO_2$ spinels ($2.5 \leq y \leq 4.0$) with acid [13]. It is anticipated from the trends in Table 3 that fully-oxidized $Li_2O \cdot yMnO_2$ spinels with compositions between $Li_2Mn_4O_9$ and λ-MnO_2 will have vacancies, like $Li_2Mn_4O_9$, on both tetrahedral and octahedral sites.

The Li-O and Mn-O bond lengths in the defect spinel structures are consistent with those reported for structures with close-packed-oxygen arrays (Table 4). For the three $Li_2O \cdot yMnO_2$ spinels in the range $2.5 < y \leq 4.0$ there is no variation in the octahedral Mn(Li)-O bond distance (1.940Å) whereas the tetrahedral Li-O distance decreases

TABLE 3
The cation distribution, in spinel notation, in spinel phases from
the $Li_2O \cdot yMnO_2$ system.

Compound	y	Spinel notation
λ-MnO_2 (ideal)	∞	$\{\square_{1.0}\}_{8a}[Mn_2]_{16d}O_4$
$Li_{0.05}Mn_2O_4$ (sample A)*	80	$\{Li_{0.05}\square_{0.95}\}_{8a}[Mn_2]_{16d}O_4$
$Li_2Mn_4O_9$ [9]	4.0	$\{Li_{0.89}\square_{0.11}\}_{8a}[Mn_{1.78}\square_{0.22}]_{16d}O_4$
$Li_{1.94}Mn_{3.04}O_7$ (sample B)*	3.13	$\{Li_{0.85}\square_{0.15}\}_{8a}[Mn_{1.74}Li_{0.26}]_{16d}O_4$
$Li_{3.48}Mn_{5.13}O_{12}$ (sample C)	2.95	$\{Li_{0.87}\square_{0.13}\}_{8a}[Mn_{1.71}Li_{0.29}]_{16d}O_4$
$Li_4Mn_5O_{12}$ (ideal)	2.50	$\{Li_{1.00}\}_{8a}[Mn_{1.67}Li_{0.33}]_{16d}O_4$

* Note: Samples A and B are slightly oxygen-deficient; they can be represented
by $Li_2O.yMnO_{2-\delta}$ where δ = 0.025 and 0.015, respectively.

TABLE 4
Variation of Li-O and Mn-O bond distances (Å) in $Li_2O \cdot yMnO_2$ defect spinels with
respect to the lattice parameter a(Å) and the oxygen positional coordinate
(spinel "u parameter" [14]).

	$Li_{0.05}Mn_2O_4$* (Sample A)	$Li_2Mn_4O_9$ ([9])	$Li_{1.94}Mn_{3.04}O_7$* (Sample B)	$Li_{3.48}Mn_{5.13}O_4$ (Sample C)
y	80	4	3.13	2.95
a (Å)	8.0445	8.174	8.1605	8.1430
u	.2631	.2634	.2629	.2625
Li-O (Å) (tetrahedral)	1.924	1.959	1.950	1.939
Mn(Li)-O (Å) (octahedral)	1.912	1.940	1.940	1.940

* see footnote in Table 3.

significantly with y. The bond distances in these cubic structures are dependent on several factors: 1) the lattice parameter a, 2) the oxygen positional coordinate (in spinels this is often referred to as the "u parameter" [14]), 3) the distribution of Li^+ and Mn^{4+} cations in the octahedral sites, and 4) the concentration of vacancies on tetrahedral and octahedral sites. For example, in $Li_{0.05}[Mn_2]O_4$ (sample A) the significantly short Mn-O (1.912Å) and Li-O (1.924Å) distances can be attributed predominantly to strong Mn-O bonding that results from the total occupation of the 16d octahedral sites by manganese. In $Li_2Mn_4O_9$ (1.959Å), the relatively large tetrahedral Li-O distance can be attributed to the existence of vacancies on both the tetrahedral and octahedral sites of the structure and the relatively large values of a and u.

The powder X-ray diffraction patterns of $Li[Mn_2]O_4$, $Li_{0.05}[Mn_2]O_4$ ("λ-MnO_2"), $Li_2Mn_4O_9$, $Li_{1.94}Mn_{3.04}O_7$ and $Li_{3.48}Mn_{5.13}O_{12}$ are shown in Fig. 2(a-e). Despite the strong similarity in the relative intensities of the five patterns, it is possible to distinguish these
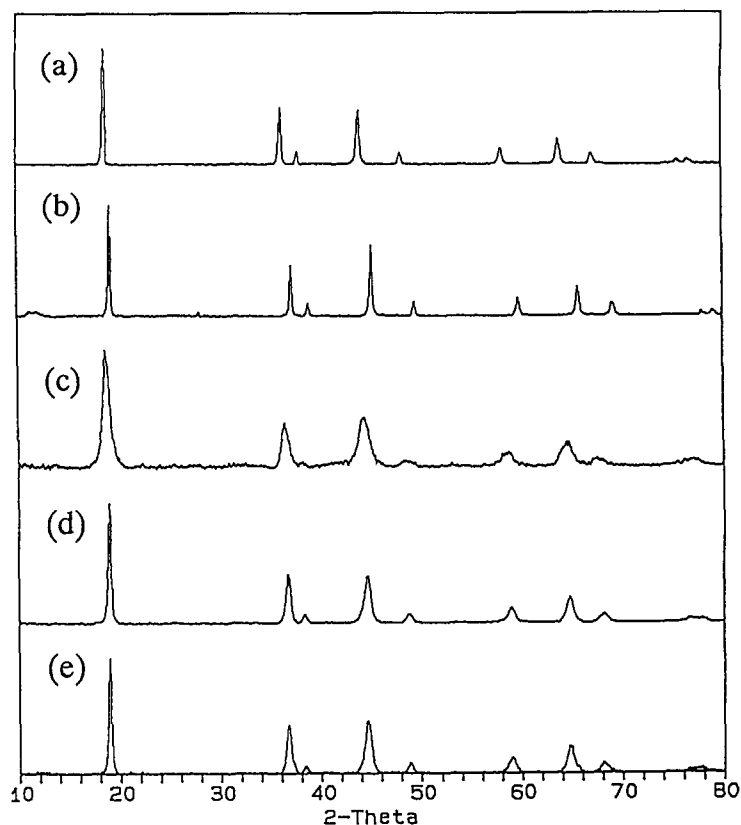
FIG. 2

Powder X-ray diffraction patterns of
(a) $Li[Mn_2]O_4$ (b) $Li_{0.05}[Mn_2]O_4$ (sample A)
(c) $Li_2Mn_4O_9$ [9]   (d) $Li_{1.94}Mn_{3.04}O_7$ (sample B)
(e) $Li_{3.48}Mn_{5.13}O_{12}$ (sample C).

spinel phases from one another by their lattice parameter values. However, there exist an infinite number of spinel compositions within the $LiMn_2O_4$-$Li_4Mn_5O_{12}$-MnO_2 tie-triangle of the Li-Mn-O phase diagram [1] with lattice parameters that vary between 8.03Å and 8.25Å. It is therefore impossible, in principle, to use only a lattice parameter value, or a visual inspection of an X-ray- or neutron-diffraction pattern to identify a specific spinel phase in the Li-Mn-O system.

CONCLUSIONS

This study has demonstrated that lithium-manganese-oxide spinel compounds synthesised by the reaction of $MnCO_3$ and Li_2CO_3 at 400°C tend to be lithium deficient. Although it has been possible with neutron-diffraction data to identify and determine the site occupancy of lithium on the tetrahedral 8a sites, the data cannot distinguish unambiguously between lithium and manganese on the octahedral 16d sites. Compositions of the spinel products were therefore determined from structural refinements that provide the closest fit to the expected stoichiometries. The refined compositions, the distribution of the manganese and lithium cations on the octahedral 16d sites, and the Li-O and Mn-O bond distances within the structures are consistent with the expected trends in the $Li_2O \cdot yMnO_2$ spinel system. Ideally, refinements of these structures should be undertaken in combination with high-quality X-ray data from which the site occupancy of the manganese ions on the 16d sites would be obtained with greater reliability because lithium is an extremely weak scatterer of X-rays.

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