



# The relationships between phases and structures of lithium manganese spinels

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## Abstract

Structures of the cubic lithium manganese spinels synthesized at 900°C, and the tetragonal spinel synthesized by quenching from 920°C into liquid N<sub>2</sub> were determined by time-of-flight (TOF) neutron powder diffraction. The ionic distribution was determined for the tetragonal spinel to be [Li<sub>1</sub>]<sub>tetra</sub>(Mn<sub>2</sub>)<sub>octa</sub>O<sub>3.86(3)</sub>. A small amount of oxygen vacancy was observed at the oxygen site. On the other hand, the structure of the cubic spinel determined at 325 K showed oxygen vacancy at 32e site with interstitial oxygen at 8b sites. The occupation parameters at the interstitial 8b site decreased with decreasing synthesis temperature from 900° to 750°C. On the basis of these findings a new oxygen vacancy cluster model is proposed. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Spinel; Cubic; Tetragonal

## 1. Introduction

Lithium manganese oxide spinels are a promising candidate as the cathodes in rechargeable lithium batteries because of their low cost and higher voltages than layered rock salt cathodes, LiMO<sub>2</sub> (M = Co, Ni) [1]. The capacity of the cells increases with decreasing *x* in Li<sub>1+x</sub>Mn<sub>2-x</sub>O<sub>4</sub> and the highest capacity of ~140 mA h/g has been obtained for the stoichiometric composition, LiMn<sub>2</sub>O<sub>4</sub>, while the cycling characteristics improve with decreasing *x* [2].

The structure of lithium manganese spinels varies with the synthesis conditions, and the structures of the phases prepared under various synthesis conditions are still not clear. Previously, the Jahn–Teller distortion [3,4] and the vacancy formations [5] have been reported and these structures are dependent on the synthesis conditions [6]. The

Jahn–Teller distortion in the spinel manganese oxides is caused by the cooperative interactions of the local distortions around Jahn–Teller ions, Mn<sup>3+</sup>, on the octahedral sites. Recently, a phase transition was reported for the cubic spinel, LiMn<sub>2</sub>O<sub>4</sub>, around room temperature accompanying a symmetry change from cubic to orthorhombic [7]. The tetragonal phase has also been reported for the lithium manganese spinel which was synthesized by quenching from 920°C [5].

Oxygen vacancy was reported to exist in these spinel structures [8]. In the cubic spinel, LiMn<sub>2</sub>O<sub>4</sub>, the oxygen vacancy can easily be introduced by the synthesis at higher temperatures, and the charge and discharge characteristics are significantly affected by the amount of oxygen vacancy. Two structural models were proposed for the oxygen deficient spinel with the nominal composition, LiMn<sub>2</sub>O<sub>4-δ</sub>; the oxygen deficient spinel with a composition, LiMn<sub>2</sub>O<sub>4-δ</sub> [9], and the spinel with interstitial cations at the 16c octahedral sites in *Fd* $\bar{3}m$  space group [10]. However, no structural data is available for the oxygen deficient spinels.

Since the ionic distribution in the host affects the charge–discharge characteristics, it is important to eluci-

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date the ionic distribution in these phases. Neutron diffraction is expected to be a powerful means to clarify structural details, because of the difference in the coherent scattering lengths of Li, Mn and O atoms ( $b_c(\text{Li}) = -0.1900 \times 10^{-14}$ ,  $b_c(\text{Mn}) = -0.3730 \times 10^{-14}$ ,  $b_c(\text{O}) = 0.5803 \times 10^{-14}$  fm).

In this study, the structure of the samples synthesized at various conditions in the system,  $\text{LiMn}_2\text{O}_4\text{--Li}_4\text{Mn}_5\text{O}_{12}\text{--Li}_2\text{Mn}_4\text{O}_9$ , were determined by neutron diffraction measurements. A new cluster model containing oxygen vacancy and interstitial oxygen ions is proposed for the sample synthesized at 900°C.

## 2. Experimental

The lithium manganese spinels were prepared by heating appropriate molar ratios of  $\text{Li}_2\text{CO}_3$  and  $\text{Mn}_2\text{O}_3$  ( $\text{Li}_2\text{CO}_3$ : High Purity Chemicals Laboratory, > 99.9% purity;  $\text{Mn}_2\text{O}_3$ : High Purity Chemicals Laboratory, > 99.9% purity). They were mixed, pelleted, and then heated at 750–1000°C in an oxygen atmosphere.

X-ray diffraction patterns of the powdered samples were obtained with an X-ray diffractometer (Rigaku RAD-C, 12 kW) with Cu  $K\alpha$  radiation. The diffraction data were collected at each 0.02° step width over a  $2\theta$  range from 20° to 110°. Differential scanning calorimetry (DSC) was measured by a TAS-200 (Rigaku) between 150 and 360 K at a heating and cooling rate of 10 K/min.

Neutron diffraction data for the cubic and the tetragonal spinels were taken at 325 K and 300 K, respectively, on a time-of-flight (TOF) neutron powder diffractometer, VEGA, at the KENS pulsed spallation neutron source at

the National Laboratory for High Energy Physics (KEK). The specimen (ca. 10 g) was contained in a cylindrical vanadium cell of dimensions 5 mm in radius, 55 mm in height, and 200  $\mu\text{m}$  in thickness. The structural parameters were refined with RIETAN [11].

## 3. Results and discussion

### 3.1. Tetragonal $\text{LiMn}_2\text{O}_4$ at 300 K

The tetragonal  $\text{LiMn}_2\text{O}_4$  was synthesized at 920°C and quenched using liquid  $\text{N}_2$ . The X-ray diffraction measurements of the samples synthesized from the initial composition of a Li/Mn ratio of 0.500 indicated an impurity phase  $\text{Li}_2\text{MnO}_3$ . The sample for the neutron diffraction measurements was synthesized with a starting composition of Li/Mn = 0.475. The amount of the phase  $\text{Li}_2\text{MnO}_3$  was about 5%, as determined by Rietveld refinement results.

Intensity data for interplanar spacings between 0.5 and 2.6 Å were used for Rietveld analysis. We refined the structure parameters of  $\text{LiMn}_2\text{O}_4$  with space group  $I4_1/amd$  using the structural model: Li at  $4a$  (0, 3/4, 1/8), Mn at  $8d$  (0, 0, 1/2), O at  $16h$  (0,  $y$ ,  $z$ ) with  $y \approx 0.5$  and  $z \approx 0.25$ . During the refinement, vacancy at  $4a$  lithium site,  $8d$  manganese site, and  $16h$  oxygen site was considered. In the lithium  $4a$  and the manganese  $8d$  sites, no significant deviation from  $g = 1.00$  was observed, while in the oxygen  $16h$  site, a value of  $g = 0.963(11)$  was obtained. Finally, anisotropic thermal parameters were assigned for the O  $16h$  site. Table 1 lists final  $R$  factors, lattice and structural parameters with their estimated standard deviations in parentheses. In the difference Fourier

Table 1

(a) Rietveld refinement results for the tetragonal lithium manganese spinel synthesized with an initial composition, Li/Mn = 0.495 at 920°C

Atom	Site	$g$	$x$	$y$	$z$	$B$ (Å <sup>2</sup> )
Li(1)	$4a$	1	0	3/4	1/8	0.26(12)
Mn(1)	$8d$	1	0	0	1/2	0.30(6)
O(1)	$16h$	0.964(9)	0	0.4734(3)	0.2644(2)	0.698 <sup>a</sup>
Atom	$U_{11}$ (Å <sup>2</sup> ) <sup>b</sup>	$U_{22}$ (Å <sup>2</sup> )	$U_{33}$ (Å <sup>2</sup> )	$U_{12}$ (Å <sup>2</sup> )	$U_{13}$ (Å <sup>2</sup> )	$U_{23}$ (Å <sup>2</sup> )
O(1)	0.020(6)	0.015(4)	0.054(4)	0	0	0.021(3)

Space group  $I4_1/amd$ ,  $a = 5.7356(3)$  Å,  $c = 8.6464(5)$  Å,  $R_{wp} = 7.96$ ,  $R_p = 5.78$ ,  $S = R_{wp}/R_e = 1.34$ ,  $R_1 = 3.49$ ,  $R_F = 1.94$ .

(b) Rietveld refinement results for the cubic lithium manganese spinel synthesized with an initial composition, Li/Mn = 0.5 at 900°C

Li(1)	$8a$	1	1/8	1/8	1/8	1.36(6)
Mn(1)	$16d$	1	1/2	1/2	1/2	0.645 <sup>a</sup>
O(1)	$32e$	0.967(3)	0.26296(3)	$=_x(\text{O}(1))$	$=_x(\text{O}(1))$	1.176 <sup>a</sup>
O(2)	$8b$	0.028(2)	3/8	3/8	3/8	1.10
Atom	$U_{11}$ (Å <sup>2</sup> ) <sup>b</sup>	$U_{22}$ (Å <sup>2</sup> )	$U_{33}$ (Å <sup>2</sup> )	$U_{12}$ (Å <sup>2</sup> )	$U_{13}$ (Å <sup>2</sup> )	$U_{23}$ (Å <sup>2</sup> )
Mn(1)	0.0080(2)	$= U_{11}$	$= U_{11}$	-0.0019(2)	$= U_{12}$	$= U_{12}$
O(1)	0.0149(2)	$= U_{11}$	$= U_{11}$	-0.00401(13)	$= U_{12}$	$= U_{12}$

Space group  $Fd\bar{3}m$ ,  $a = 8.24609(17)$  Å,  $R_{wp} = 6.49$ ,  $R_p = 4.92$ ,  $S = R_{wp}/R_e = 1.0860$ ,  $R_1 = 2.15$ ,  $R_F = 2.67$ .

<sup>a</sup>Equivalent isotropic thermal parameter,  $B_{eq}$ .

<sup>b</sup>The form of the anisotropic temperature factor is  $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^{*}b^{*}U_{11} + 2hla^{*}c^{*}U_{13} + 2klb^{*}c^{*}U_{23})]$ .

map, no residual peaks at the interstitial sites were observed. Fig. 1 illustrates the profile fit and difference pattern for  $\text{LiMn}_2\text{O}_4$ ; the calculated pattern fits the observed one fairly well. Table 2 gives interatomic distances and bond angles calculated with ORFFE [12]. The composition of the tetragonal spinel was  $\text{LiMn}_2\text{O}_{3.86(3)}$ , which gives a manganese valence of +3.36.

### 3.2. Cubic $\text{LiMn}_2\text{O}_4$ at 325 K

The cubic  $\text{LiMn}_2\text{O}_4$  was synthesized at  $900^\circ\text{C}$  in  $\text{O}_2$  and was slowly cooled to room temperature. The X-ray

diffraction measurements indicated a single-phase sample with the cubic spinel structure. However, the X-ray diffraction patterns of the samples stored for several weeks indicated peak splittings with small reflections due to superlattice reflections. These splittings were indexed by an orthorhombic cell with the lattice parameters,  $a = 8.2861(4)$ ,  $b = 8.2008(4)$ , and  $c = 8.2469(4)$  Å. This distortion has been reported previously by Oikawa et al. [7]. No impurity phase such as  $\text{Li}_2\text{MnO}_3$  was observed. DSC measurements of the sample between 360 and 150 K indicated an endothermic peak at 298 K and an exothermic peak at 311 K for the cooling and heating processes

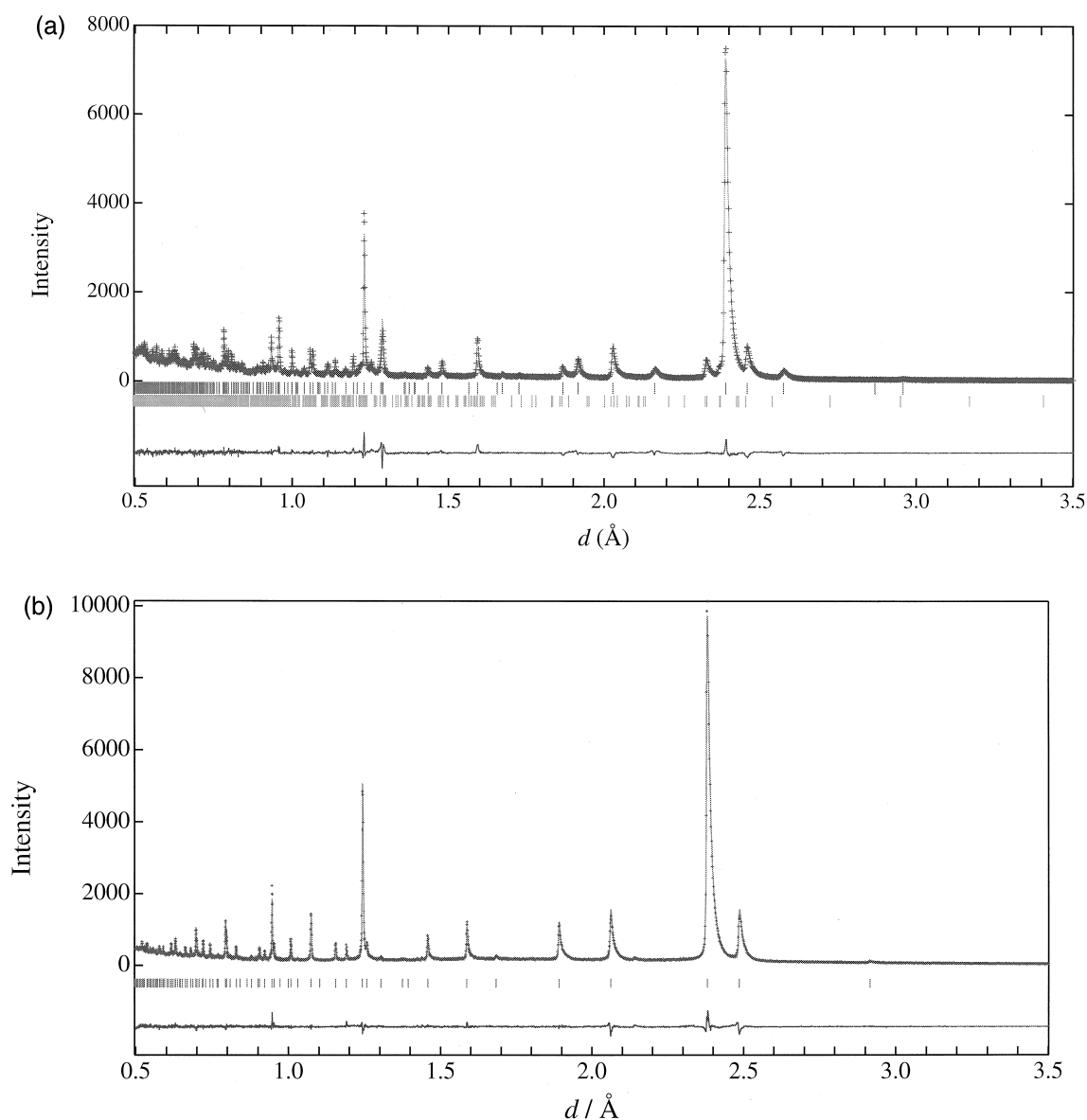


Fig. 1. Observed, calculated and difference plots for the tetragonal lithium manganese spinel synthesized with an initial composition,  $\text{Li}/\text{Mn} = 0.495$  at  $920^\circ\text{C}$  (a), and the cubic lithium manganese spinel synthesized with an initial composition,  $\text{Li}/\text{Mn} = 0.5$  at  $900^\circ\text{C}$  (b). The solid lines are calculated intensities, plus (+) overlying them indicates observed intensities, and  $\Delta y_i$  is the difference between observed and calculated intensities.

Table 2

(a) Interatomic distances (Å), bond angles (°) and interlayer distances (Å)

LiMn <sub>2</sub> O <sub>4</sub>		
Interatomic distances	Li–O(1)	1.9704(4)×4
	Mn–O <sup>a</sup> (1)	1.9605(2)×6
	Mn–O(2)	1.7853
Bond angles	O(1)–Li–O <sup>b</sup> (1)	109.4712×4
	O <sup>a</sup> (1)–Mn–O <sup>c</sup> (1)	85.589(16)×2
	O <sup>a</sup> (1)–Mn–O <sup>d</sup> (1)	96.411(16)×2
	Mn–O(2)–Mn <sup>a</sup>	83.59(15)×6

Symmetry codes: <sup>a</sup>3/4–y, 3/4–x, z; <sup>b</sup>1/4–y, 1/4–x, z; <sup>c</sup>3/4–y, x, 3/4–z.

(b) Interatomic distances (Å), bond angles (°) and interlayer distances (Å)

Interatomic distances	Li–O <sup>e</sup>	1.9752(17)×4
	Mn–O <sup>f</sup>	1.9257(19)×4
	Mn–O <sup>g</sup>	2.0709(10)×2
Bond angles	O <sup>e</sup> –Li–O <sup>h</sup>	110.80(5)×4
	O <sup>f</sup> –Mn–O <sup>i</sup>	96.54(7)×4
	O <sup>f</sup> –Mn–O <sup>g</sup>	96.00(7)×2

Symmetry codes: <sup>e</sup>3/4–y, 3/4+x, 1/4–z; <sup>f</sup>1/4–y, –1/4–x, 1/4+z; <sup>g</sup>x, 1/2–y, z; <sup>h</sup>–3/4+y, 3/4+x, 1/4–z; <sup>i</sup>1/4–y, 1/4–x, 3/4–z.

respectively. The aim of the neutron diffraction measurements in the present study was to determine the ionic distribution at each site including the oxygen site. The diffraction data was taken at the temperature 325 K where the cubic spinel structure appears.

We refined the structure parameters of LiMn<sub>2</sub>O<sub>4</sub> with space group *Fd* $\bar{3}$ *m* using the model: Li at 8*a* (1/8, 1/8, 1/8), Mn at 16*d* (1/2, 1/2, 1/2), O at 32*e* (*x*, *x*, *x*) with *x* ≈ 0.25. During the refinements, several models were considered; vacancy at 8*a* lithium site, 16*d* manganese site, and 32*e* oxygen site, cations in the interstitial 16*c* site, disordering at the manganese and lithium sites. However, no significant deviation from the stoichiometric composition was observed at the lithium 8*a* and manganese 16*d* sites, and no cations were found to be present at the interstitial 16*c* sites. In the oxygen 32*e* site, a small amount of vacancy was observed with a value of occupation parameter, *g* = 0.967(11). The difference Fourier map indicated the presence of interstitial ions near the 8*b* site, while in the tetragonal LiMn<sub>2</sub>O<sub>4</sub>, no peaks were found at this site. The refinement therefore proceeded with a structural model in which oxygen partially occupies the 8*b* interstitial site, with oxygen vacancy at 32*e* site. Finally, anisotropic thermal parameters were assigned for the Mn 16*d* and O(1) 32*e* sites.

Table 1(b) lists final *R* factors, lattice and structural parameters with their estimated standard deviations in parentheses. Fig. 1(b) illustrates the profile fit and difference pattern for LiMn<sub>2</sub>O<sub>4</sub>; the calculated pattern fits the observed one fairly well. Table 2(b) gives interatomic distances and bond angles calculated with ORFFE [12].

The composition of the tetragonal spinel was LiMn<sub>2</sub>O<sub>3.90</sub>, which indicates a manganese valence of +3.40.

The refinement results indicated about 2.8(2)% of oxygen at 8*b* site with a similar amount of oxygen vacancy of 3.3(3)% at 32*e* site. The ratio of vacancy/interstitial oxygen ions is thus about 4/1. Fig. 2 shows the structure of the cubic spinel. Since the 8*b* site was surrounded by four oxygen ions at 32*e* site and four manganese ions at 16*b* site, it is rather difficult for it to be occupied by any ions. However, it is plausible that the 8*b* site might be occupied when the four 32*e* oxygen sites are vacant. The neutron refinement results indicated both the oxygen vacancy and the interstitial oxygen at the 32*e* and 8*b* sites, respectively, which might suggest a formation of oxygen vacancy-interstitial clustering. Fig. 2(b) shows the cluster model proposed in the present study. In this model, one 8*b* site is connected to four manganese ions at 16*d* site, and

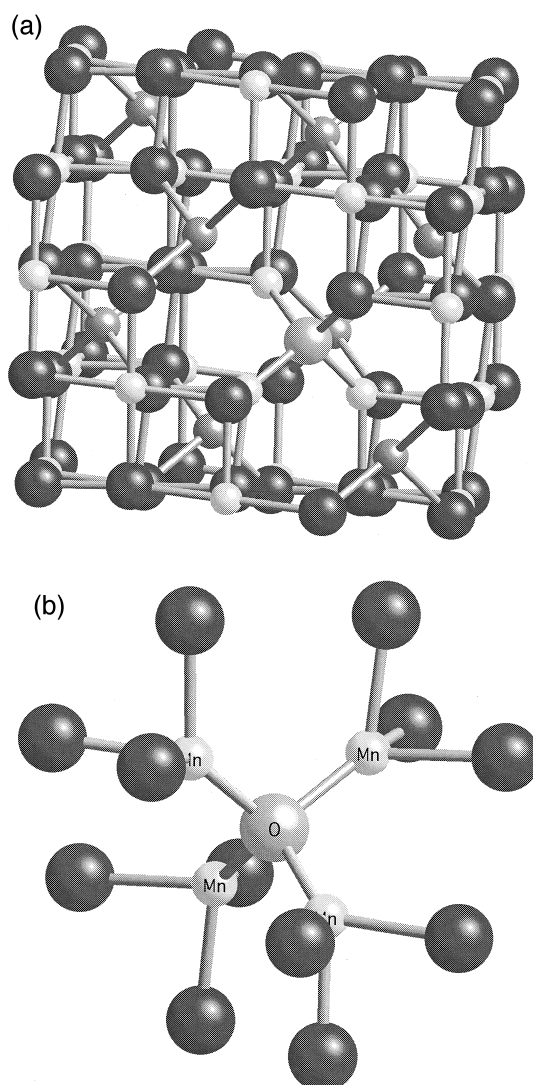


Fig. 2. Structure of the cubic spinel (a) and the oxygen vacancy-interstitial cluster model in the spinel structure (b).

Table 3

Selected Rietveld refinement results for the lithium manganese spinel synthesized in the present study

Synthesis temperature	Li/Mn ratio	$g(O1)$ at $32e$	$g(O2)$ at $8b$	$a$ (Å)	$c$ (Å)	Reference
900	0.5	0.967(3)	0.028(2)	8.2461(1)		this study
800	0.5	0.980(3)	0.022(3)	8.2418(2)		[13]
750	0.5	0.979(3)	0.021(3)	8.2401(2)		[13]
920Q <sup>a</sup>	0.495	0.963(11)	0	5.7356(3)	8.6464(5)	this study

<sup>a</sup>The tetragonal lithium manganese spinel synthesized at 920°C and quenched with liquid N<sub>2</sub>.

the octahedral coordination of the manganese ions changes to tetrahedral. Four tetrahedra are connected with each other by sharing a corner of the interstitial  $8b$  oxygen.

Table 3 summarizes the neutron diffraction data of the samples synthesized in the present study [13]. The neutron diffraction data for the samples synthesized at 800° and 750°C were also refined using the same cubic structure model of the sample synthesized at 900°C. The amount of oxygen vacancy at the  $32e$  site decreases from 0.033(3) to 0.021(3) and the interstitial oxygen at the  $8b$  site decreases from 0.028(2) to 0.018(2) when the synthesis temperature is decreased from 900° to 750°C. The vacancy-interstitial oxygen cluster might decrease with decreasing synthesis temperature, and this corresponds to the degradation of the charge–discharge characteristics with increasing synthesis temperature. In order to improve the charge–discharge capacity, the vacancy-interstitial oxygen should be avoided.

#### 4. Conclusion

The structure of the cubic lithium manganese spinels synthesized at 900°C and the tetragonal spinel synthesized by quenching from 920°C into liquid N<sub>2</sub> have been determined. A new cluster model is proposed for the cubic spinel which is composed of oxygen vacancy and interstitial oxygen ions. A small amount of interstitial oxygen was found around  $8b$  sites for the cubic spinel, while no interstitial oxygen was found in the tetragonal spinel. The cluster model proposed contains MnO<sub>4</sub> tetrahedra which are connected to each other by corner sharing at the  $8b$  oxygen ions. However, further structural studies to confirm the cluster model will be necessary.

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