Z. Kristallogr. Suppl. **26** (2007) 477-482

# Synchrotron X-ray diffraction study on the cation distribution in quaternary Li-Fe-Mn spinel oxides

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**Keywords**: Lithium-iron-manganese oxides, x-ray diffraction, crystal structure refinement, spinel structure

**Abstract.** Single phase spinel solid solutions of $Li_xMn_{3-x-y}Fe_yO_4$ series with range of $0.5 \le x \le 1.0$ and $0.2 \le y \le 1.0$, have been synthesized by a solid state reaction. By refining the high-resolution X-ray diffraction patterns with Rietveld profile analysis, the lattice parameters, interatomic distances and cation distribution were determined. The Fe-for-Mn substitution increases the spinel unit cell constant from ***a*** = 8.27Å to ***a*** = 8.38Å, for the *Fe/(Fe+Mn)* mole ratio of 0.1 and 0.472, respectively. Evidence is given that the lithium ions occupy the tetrahedral sites exclusively, for the molar ratio $0 \le Fe/(Mn+Fe) \le 0.3$.

## Introduction

Spinel compounds are important minerals and industrial materials. The spinel structure is based on a cubic close-packed array of oxide ions (32e), with ½ of the octahedral sites (16d) and ¼ of tetrahedral sites (8a) occupied by cations. The general chemical formula is $AB_2O_4$, and there are two ideal structures with different cation ordering schemes: $(A)_{8a}[B_2]_{16d}O_4$ (*normal spinel*) and $(B)_{8a}[AB]_{16d}O_4$ (*inverse spinel*). Stoichiometric normal spinel $LiMn_2O_4$ has the $Li^+$ ions occupying the tetrahedral sites, and a 1:1 mixture of $Mn^{3+}$ and $Mn^{4+}$ ions randomly distributed over the octahedral positions in the spinel lattice (space group *Fd3m*). The lithium-manganese oxides with spinel structure are of interest as cathode materials for the high energy density lithium batteries [1-2]. Most studies of $LiMn_2O_4$ have concentrated on the electrochemical character of the system, several disadvantages of stoichiometric $LiMn^{3+}Mn^{4+}O_4$ have been reported, including irreversible capacity loss due to the structural degradation during lithiation and delithiation cycle. Much research, including ours, is going on to find new materials for advanced lithium-ion batteries, as well as to obtain a deeper in understanding of the insertion mechanism [3].

The aim of this study was to determine the ion distribution in the single phase Li-Mn-Fe spinels, on the basis of high-resolution synchrotron X-ray powder diffraction measurements.

# Experimental details

Lithium-manganese-iron oxide samples of composition $Li_xMn_{3-x-y}Fe_yO_4$ with range of $0.5 \leq x \leq 1.0$ and $0.2 \leq y \leq 1.0$, were prepared by solid state reaction of $Li_2CO_3$ with the manganese oxide or iron-manganese oxide precursors. The precursors were prepared by coprecipitation of amorphous Mn-Fe-hydroxides from the mixed $Mn^{2+}/Fe^{3+}$-nitrate solutions of the mole ratio of $Fe/(Fe+Mn) = 0.1$, 0.2, 0.365 and 0.472, with sodium hydroxide. Washed and dried at room temperature, they were dehydrated for 2h at 250°C, and then successively at 400°C, 500°C and 600°C for 4h. Mixed with $Li_2CO_3$ in the $Li:M_2O_3$ ratios (M=Fe+Mn) corresponding to $0.5 \leq x \leq 1.0$ in $Li_xMn_{3-x-y}Fe_yO_4$, the samples underwent a successive thermal treatment in air, at 700°C and 800°C for 4h. After heating the preparations were quenched rapidly in the solid $CO_2$, because the products formed as a result of slow cooling samples are the multiphase system [4].

The x-ray diffraction experiments were carried out at the Desy/Hasylab high-resolution powder diffractometer at the beamline B2, equipped with Image Plate OBI detector [5-6]. The wavelength applied during experiments, determined by calibration using NIST silicon standard, was $\lambda=0.496008$Å and $\lambda=0.685356$Å. The structure refinements were performed using the FullProf program [7].

# Results and discussion

Figure 1 shows the X-ray diffraction patterns of $Li_xMn_{3-x-y}Fe_yO_4$ series, with the molar fraction $n_{Fe}=Fe/(Mn+Fe)$ from 0.1 to 0.472. The diffraction peaks of all the samples: ($n_{Fe}=0.1$) $Li_{0.95}Mn_{1.845}Fe_{0.205}O_4$, ($n_{Fe}=0.2$) $Li_{0.9}Mn_{1.68}Fe_{0.42}O_4$, ($n_{Fe}=0.365$) $Li_{0.72}Mn_{1.448}Fe_{0.832}O_4$, ($n_{Fe}=0.472$) $Li_{0.63}Mn_{1.251}Fe_{1.119}O_4$, correspond to a single-phase spinel.

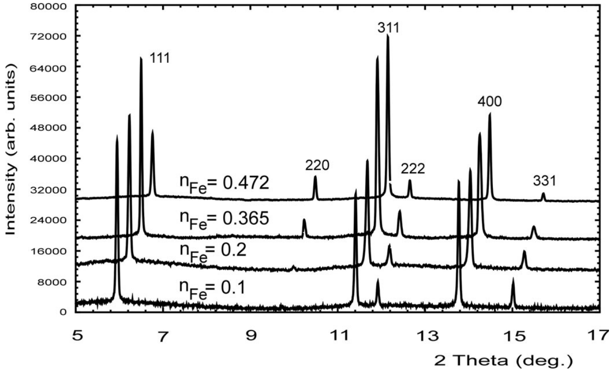

*Figure 1. X-ray powder diffraction patterns at the room temperature for samples:* $Li_{0.95}Mn_{1.845}Fe_{0.205}O_4$ ($n_{Fe}=0.1$), $Li_{0.9}Mn_{1.68}Fe_{0.42}O_4$; ($n_{Fe}=0.2$), $Li_{0.72}Mn_{1.448}Fe_{0.832}O_4$; ($n_{Fe}=0.365$), $Li_{0.63}Mn_{1.251}Fe_{1.119}O_4$ ($n_{Fe}=0.472$).

A strong decrease of the intensity ratio of $I_{111}/I_{311}$ lines (figure 2) corresponds with the decrease of lithium content in the A-sites of the spinel lattice. On the other hand, increase of (220) reflection, dependent exclusively on the cations occupying the tetrahedral spinel sites, confirms the presence of iron and/or manganese ions at A-positions. These results were consistent with those reported by Wende and Langbein [8].

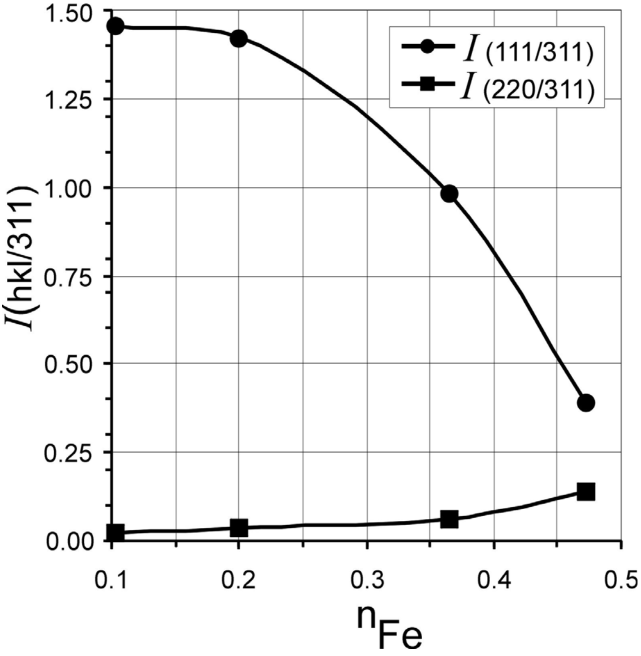

*Figure 2. Integrated intensities of the X-ray reflections for the samples of* $Li_xMn_{3-x-y}Fe_yO_4$ *series, as a function of the* $n_{Fe}$ *= Fe/(Fe+Mn).*

The structure refinement by Rietveld method was carried out to determine the cation distribution over tetrahedral *8a* and octahedral *16d* sites. It is well known that $Mn^{3+}$ and $Mn^{4+}$ ions prefer octahedral coordination because of their large crystal field stabilization energy in octahedral sites. On the contrary, $Mn^{2+}$ and $Fe^{3+}$ ions do not prefer any position in the spinel structure, and they are moved to the tetrahedral sites, if they occur near $Mn^{3+}$ and $Mn^{4+}$ ions with the strong preference for octahedral positions. Figures 3 and 4 shows the observed, calculated and difference profiles for two end-members of the series ($n_{Fe}$= 0.1 and $n_{Fe}$= 0.472). These models gave improvement in agreement between observed and calculated intensity data for (111), (220) and (331) peaks, which are very sensitive to the nature of atoms on the tetrahedral site.

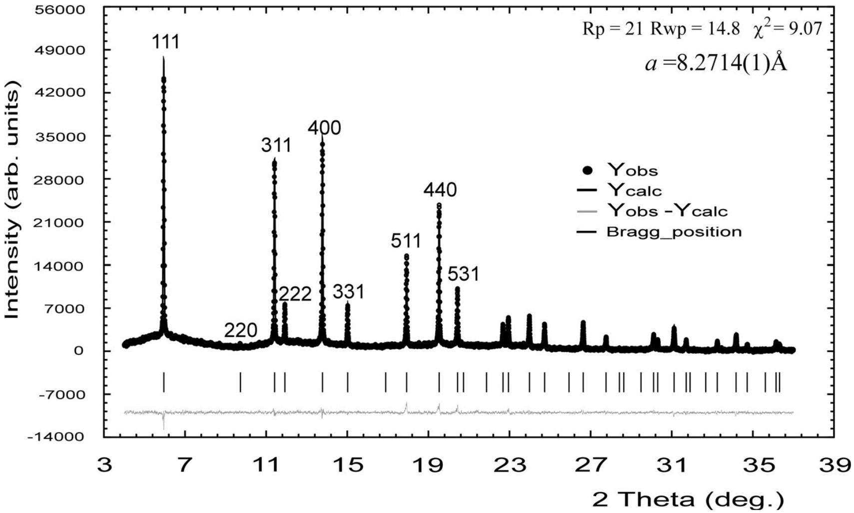

*Figure 3. Results of Rietveld analysis of synchrotron X-ray powder diffraction data for* $Li_{0.95}Mn_{1.845}Fe_{0.205}O_4$ *(*$n_{Fe}$*=0.1).*

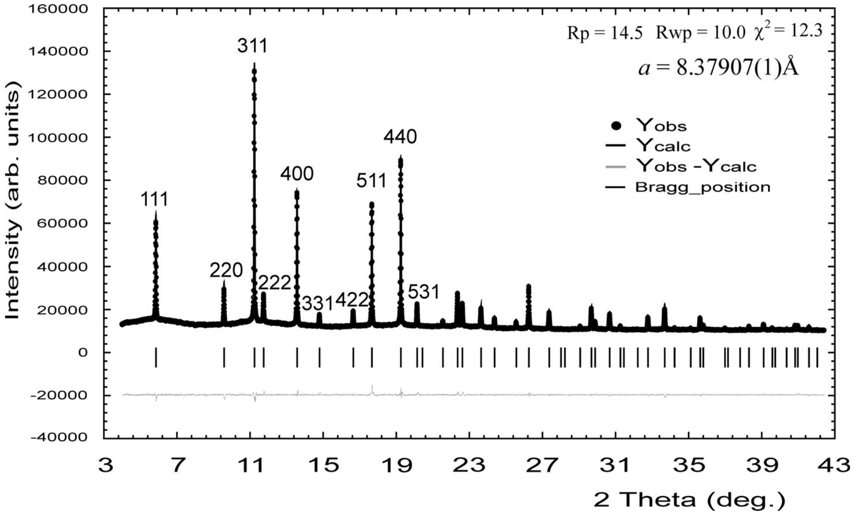

*Figure 4. Observed, calculated and difference plots resulting from Rietveld analysis of synchrotron X-ray powder diffraction data of* $Li_{0.63}Mn_{1.251}Fe_{1.119}O_4$ *(*$n_{Fe}$*=0.472).*

Composition and structural details obtained from the Rietveld refinement are given in table 1. We can explain the increase of the lattice constant with the decrease of lithium content by the partial disproportionation of $Mn^{3+}$, and the filling up of tetrahedral positions with $Mn^{2+}$ and $Fe^{3+}$. Manganese and iron have similar numbers of electrons, their X-ray scattering powers are almost identical, it is therefore difficult to distinguish them by X-ray methods. Occupancy factors of iron and manganese were refined from Rietveld analysis of neutron powder diffraction data [9].

*Table 1. Structural parameters for the* $Li_xMn_{3-x-y}Fe_yO_4$ *series obtained from the Rietveld refinement in the Fd3m space group.*

*a)* $Li_{0.95}Mn_{1.845}Fe_{0.205}O_4$

| atom | site | Coordinates | | | Occupancy | B [Å$^2$] |
|---|---|---|---|---|---|---|
| | | x | y | z | | |
| Li(1) | 8a | 1/8 | 1/8 | 1/8 | 0.950(4) | 1.27(2) |
| Mn2(1) | 8a | 1/8 | 1/8 | 1/8 | 0.011 | 1.27(2) |
| Fe(1) | 8a | 1/8 | 1/8 | 1/8 | 0.038 | 1.27(2) |
| Fe(2) | 16d | 1/2 | 1/2 | 1/2 | 0.083 | 0.57(3) |
| Mn3(2) | 16d | 1/2 | 1/2 | 1/2 | 0.461 | 0.57(3) |
| Mn4(3) | 16d | 1/2 | 1/2 | 1/2 | 0.456 | 0.57(3) |
| O(1) | 32e | 0.26031(14) | 0.26031(14) | 0.26031(14) | 1.0000 | 1.28(3) |
| *a*= 8.2714(1), unit cell: $(Li^{+}_{7.6}Mn^{2+}_{0.09}Fe^{3+}_{0.31})[Fe^{3+}_{1.33}Mn^{3+}_{7.38}Mn^{4+}_{7.29}]O_{32}$ | | | | | | |

*b)* $Li_{0.9}Mn_{1.68}Fe_{0.42}O_4$

| atom | site | Coordinates | | | Occupancy | B [Å$^2$] |
|---|---|---|---|---|---|---|
| | | x | y | z | | |
| Li(1) | 8*a* | 1/8 | 1/8 | 1/8 | 0. 901(5) | 0.96(1) |
| Mn2(1) | 8*a* | 1/8 | 1/8 | 1/8 | 0.029 | 0.96(1) |
| Fe(1) | 8*a* | 1/8 | 1/8 | 1/8 | 0.069 | 0.96(1) |
| Fe(2) | 16*d* | 1/2 | 1/2 | 1/2 | 0.193 | 0.46(1) |
| Mn3(2) | 16*d* | 1/2 | 1/2 | 1/2 | 0.392 | 0.46(1) |
| Mn4(3) | 16*d* | 1/2 | 1/2 | 1/2 | 0.415 | 0.46(1) |
| O(1) | 32*e* | 0.26029(18) | 0.26029(18) | 0.26029(18) | 1.0000 | 0.96(1) |
| *a*= 8.2867(2), unit cell: $(Li^{+}_{7.2}Mn^{2+}_{0.24}Fe^{3+}_{0.56})[Fe^{3+}_{3.08}Mn^{3+}_{6.28}Mn^{4+}_{6.64}]O_{32}$ | | | | | | |

*c)* $Li_{0.72}Mn_{1.448}Fe_{0.832}O_4$

| atom | site | Coordinates | | | Occupancy | B [Å$^2$] |
|---|---|---|---|---|---|---|
| | | x | y | z | | |
| Li(1) | 8*a* | 1/8 | 1/8 | 1/8 | 0.720(2) | 0.65(3) |
| Mn2(1) | 8*a* | 1/8 | 1/8 | 1/8 | 0.101 | 0.65(3) |
| Fe(1) | 8*a* | 1/8 | 1/8 | 1/8 | 0.179 | 0.65(3) |
| Fe(2) | 16*d* | 1/2 | 1/2 | 1/2 | 0.288 | 0.65(1) |
| Mn3(2) | 16*d* | 1/2 | 1/2 | 1/2 | 0.479 | 0.65(1) |
| Mn4(3) | 16*d* | 1/2 | 1/2 | 1/2 | 0.232 | 0.65(1) |
| O(1) | 32*e* | 0.25917(10) | 0.25917(10) | 0.25917(10) | 1.0000 | 1.10(1) |
| *a*= 8.3493(1), unit cell: $(Li^{+}_{5.76}Mn^{2+}_{0.2}Fe^{3+}_{2.04})[Fe^{3+}_{4.61}Mn^{3+}_{7.67}Mn^{4+}_{3.72}]O_{32}$ | | | | | | |

*d)* $Li_{0.63}Mn_{1.251}Fe_{1.119}O_4$.

| atom | site | Coordinates x | y | z | Occupancy | B [Å$^2$] |
|---|---|---|---|---|---|---|
| Li(1) | 8*a* | 1/8 | 1/8 | 1/8 | 0.493(3) | 0.623(3) |
| Mn2(1) | 8*a* | 1/8 | 1/8 | 1/8 | 0.090 | 0.623(3) |
| Fe(1) | 8*a* | 1/8 | 1/8 | 1/8 | 0.417 | 0.623(3) |
| Li(2) | 16*d* | 1/2 | 1/2 | 1/2 | 0.0687(2) | 0.67(3) |
| Fe(2) | 16*d* | 1/2 | 1/2 | 1/2 | 0.350 | 0.67(3) |
| Mn3(2) | 16*d* | 1/2 | 1/2 | 1/2 | 0.4067 | 0.67(3) |
| Mn4(3) | 16*d* | 1/2 | 1/2 | 1/2 | 0.175 | 0.67(3) |
| O(1) | 32*e* | 0.26043(8) | 0.26043(8) | 0.26043(8) | 1.0000 | 1.12(3) |
| *a*= 8.37907(1), unit cell: $(Li^{+}_{3.94}Mn^{2+}_{0.72}Fe^{3+}_{3.34})[Li^{+}_{1.1}Fe^{3+}_{5.6}Mn^{3+}_{6.5}Mn^{4+}_{2.8}]O_{32}$ | | | | | | |

# Concluding remarks

Single phase compounds with spinel structure have been obtained for all the samples: $Li_{0.95}Mn_{1.845}Fe_{0.205}O_4$, $Li_{0.9}Mn_{1.68}Fe_{0.42}O_4$, $Li_{0.72}Mn_{1.448}Fe_{0.832}O_4$, $Li_{0.63}Mn_{1.251}Fe_{1.119}O_4$.
The results of Rietveld analysis performed the high-resolution X-ray diffraction measurements show that the lithium ions occupy the tetrahedral sites exclusively, for the molar ratio $0 \leq Fe/(Mn+Fe) \leq 0.365$, whereas the formation of inverse spinel ($Li^+$ in octahedral sites) starts from Fe/(Fe+Mn) = 0.472.

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**Acknowledgements.** The synchrotron measurements at HASYLAB were supported by the IA-SFS-Contract No. RII3-CT-2004-06008 of European Commission, and by the Committee for Scientific Research (Poland) by the grant 128/E-336/SPB//DESY/KN/DWM/108/2005-2006.