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Neutron powder diffraction study on the magnetic ordering and structure of $Li_xMn_{3-x-y}Fe_yO_4$ spinels

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Abstract. Crystal and magnetic structures of a $Li_xMn_{3-x-y}Fe_yO_4$ single phase solid solutions series, formed between the normal spinel $LiMn_2O_4$ and the inverse spinel $Li_{0.5}Fe_{2.5}O_4$, have been studied using neutron powder diffraction. We present new results on the changes in cation distribution over the tetrahedral and octahedral spinel sublattices, and the crystal structure refinements resulting from Rietveld analysis of neutron powder diffraction data. Single phase spinel solid solutions, with the molar fraction $n_{Fe}=Fe:(Fe+Mn)$ = 0.1-0.5, have been investigated. The samples reveal different magnetic properties, from antiferromagnetic ordering at low temperature for n_{Fe}=0.1, to the distinct ferrimagnetic (uncompensated antiferromagnetic) exchange occurring between A and B sites in AB_2O_4 for n_{Fe}=0.472.

Introduction

The oxide intercalation compounds containing lithium ions are of great technological importance. Lithium-manganese oxides have been intensively studied in search of new cathodic materials for the lithium rechargeable batteries, whereas lithium ferrites are promising materials for the memory core and microwaves applications [1]. The cubic spinel phase system $LiMn_2O_4$-$Li_{0.5}Fe_{2.5}O_4$ forms a continuous series of solid solutions. Our previous investigations of lithium-iron-manganese oxides evidenced changes in the distribution of Li^+ ions over the spinel cationic sublattices, caused by Fe^{3+} substitution in the system. The preference of lithium to occupy the octahedral sites increases with the increasing iron content, resulting in the inverse spinel $Li_{0.5}Fe_{2.5}O_4$ phase [2]. X-ray powder diffraction results show clearly that a structural phase transformation, from cubic (*Fd3m*) to orthorhombic (*Fddd*), occurs at about 285K in the stoichiometric $LiMn_2O_4$ [3,4]. Substitution with Fe^{3+} ions reduces this effect and stabilizes the *Fd3m* structure [5]. The scattering amplitude of atoms for X-rays increases regularly with atomic number. On the basis of X-ray diffraction data alone, therefore, it is not possible to distinguish between neighbouring elements when these occur together in a compound. Due to the low scattering power of Li, and similar form factors of Fe and Mn, the precise determination of the Li^+, Fe^{3+} and Mn^{3+}/Mn^{4+} cation positions by X-ray diffraction was very difficult. With neutrons, however, the scattering amplitudes of such elements may be quite different and in these cases a distinction can be made between them from the diffraction intensity data [6]. It has been proved recently that application of the high-resolution X-ray powder diffraction (synchrotron radiation) enables to fix Li^+ ions in the A and B spinel positions [7]. The atomic distribution of the Fe and Mn ions, however, could be determined only using the neutron powder diffraction. By supplementing the structural knowledge already available from X-ray studies interesting information has been obtained in this way for a number of materials.

Determination of the magnetic structure of $Li_xMn_{3-x-y}Fe_yO_4$ spinel solid solutions appears to be essential, because the samples reveal different magnetic properties, from spin-glass behaviour of $LiMn_2O_4$ at low temperature [8], through the antiferromagnetic ordering [4], to the distinct ferrimagnetic exchange occurring between the A and B sublattices in AB_2O_4, with increasing Fe^{3+} ions content [9,10]. The relation between the cation distribution, structural phase transitions and magnetic ordering, would be the main question to undertake in this study.

Experimental details

Series of compounds with the $Li_xMn_{3-x-y}Fe_yO_4$ stoichiometry have been obtained 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 s (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. Lithium content was adjusted after the highest $Li:M_2O_3$ ratio to provide the formation of single phase spinel. After heating the preparations were quenched rapidly in the solid CO_2. Neutron diffraction data were collected in the multicounter high-resolution neutron powder diffractometer E9 (FIREPOD) installed at the BER II reactor in Hahn-Meitner Institute (Berlin), using Ge_{511} monochromator, λ=1.79740(2)Å. About 3g of sample were encapsulated into vanadium container. Standard orange cryostat/furnace have been used for measurements in the temperature range from 2K to 500K. Structure refinement was performed using *FullProf* program [Rodriguez-Carvajal, J., version June 2005, ILL.].

Results and discussion

In the present experiment single phase spinel solid solutions, with the molar fraction n_{Fe}=*Fe:(Fe+Mn)* increasing from 0.1 to 0.472, of the composition $Li_{0.95}Mn_{1.845}Fe_{0.205}O_4$, $Li_{0.90}Mn_{1.680}Fe_{0.420}O_4$, $Li_{0.72}Mn_{1.448}Fe_{0.832}O_4$, and $Li_{0.63}Mn_{1.251}Fe_{1.119}O_4$, have been investigated. Patterns in figure 1 have been recorded for samples with the *Fe:(Fe+Mn)* molar ratio of 0.1, 0.2, 0.365 and 0.472, at the temperature of 250K. Variations of the intensity of *111*, *311* and *440* reflections evidence the occupancy of tetrahedral sites with Fe^{3+} and/or Mn^{2+}. On the diffraction pattern of the n_{Fe}=0.1 sample, at the temperature of 2K, a new reflection at about 32° (*2θ)* can be visible, pointing to a low-temperature antiferromagnetic ordering [5,7].

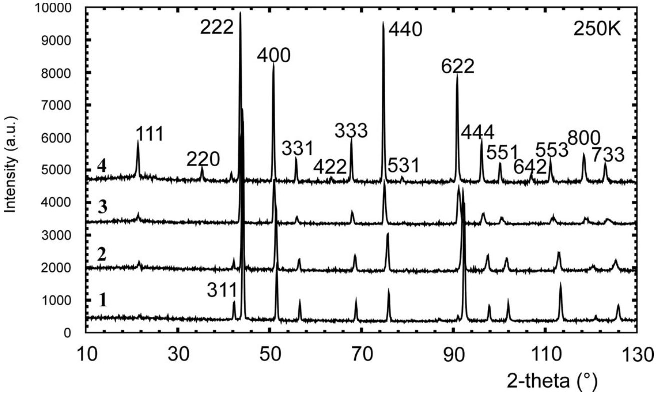

Figure 1. Neutron powder diffraction patterns recorded at the temperature of 250K, for samples: ***1.*** *$Li_{0.95}Mn_{1.845}Fe_{0.205}O_4$ (n_{Fe}=0.1);* ***2.*** *$Li_{0.9}Mn_{1.68}Fe_{0.42}O_4$ (n_{Fe}=0.2);* ***3.*** *$Li_{0.72}Mn_{1.448}Fe_{0.832}O_4$ (n_{Fe}=0.365) and* ***4.*** *$Li_{0.63}Mn_{1.251}Fe_{1.119}O_4$ (n_{Fe}=0.472).*

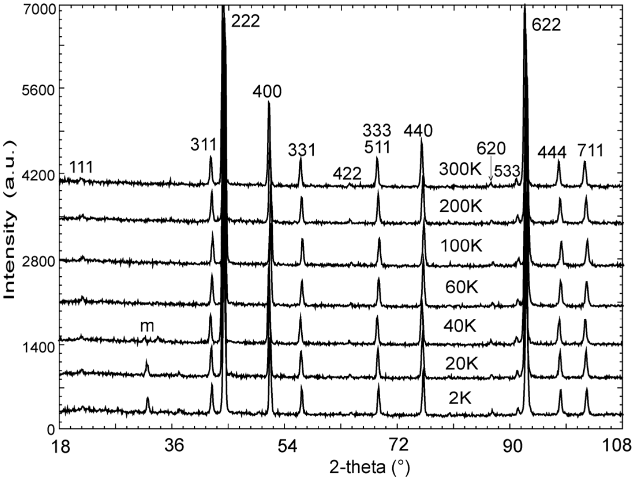

Figure 2. Neutron powder diffraction patterns of spinel phase $Li_{0.95}Mn_{1.845}Fe_{0.205}O_4$ in the temperature range 2K-300K. (m - presumable low temperature magnetic reflection).

The set of patterns in figure 2 reveals the temperature dependence of this peak: it disappears at 60K. No such effect has been observed on the neutron diffraction patterns of n_{Fe}=0.2 and n_{Fe}=0.365 samples, recorded down to 2K. Explanation of that apparent disappearance of magnetic ordering requires further neutron powder diffraction experiments. Structure refinement by the Rietveld method has been focused on the assignment of cation distribution over the tetrahedral and octahedral sites, based on the difference of neutron scattering factors of Mn (-0.36) and Fe (+0.96). The precise determination of lattice constants of the cubic unit cell of the $LiMn_2O_4/Li_{0.5}Fe_{2.5}O_4$ solid solution series reveals that the replacement of Mn^{3+} with Fe^{3+}, having equal ionic radii, causes the increase of the spinel unit-cell volume, and indirectly indicates the presence of Mn^{2+} ions in the lattice. The distribution of cations in $Li_{0.95}Mn_{1.845}Fe_{0.205}O_4$ resulting from Rietveld analysis, presented in figure 3, clearly confirmed the presence of Fe^{3+} and Mn^{2+} in the tetrahedral spinel sublattice.

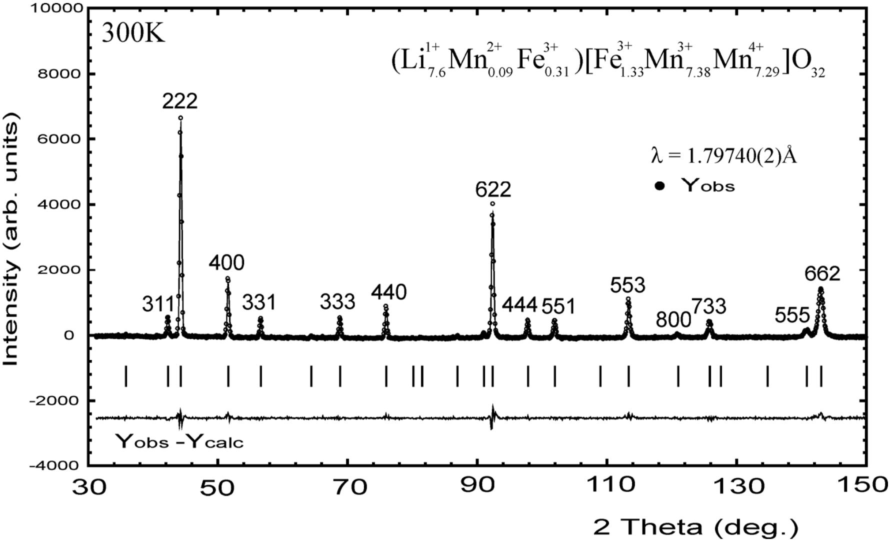

Figure 3. Observed, calculated and difference plots resulting from Rietveld analysis of neutron powder diffraction data of $Li_{0.95}Mn_{1.845}Fe_{0.205}O_4$ ($n_{Fe}=0.1$), recorded at 300K, ($R_p=15.6$; $R_{wp}=14.5$; $\chi^2=2.33$).

The increase of Fe^{3+} ions in the $Li_xMn_{3-x-y}Fe_yO_4$ lattice has been accompanied with the decrease of lithium ions content, the end-members of solid solution series being $LiMn_2O_4$ and $Li_{0.5}Fe_{2.5}O_4$. Thus the single phase samples investigated in our experiment have been more and more "lithium deficient" compared to $LiMn_2O_4$, with tetrahedral sites occupied exclusively by Li^+ ions. Results of Rietveld refinement confirm the increasing quantity of Fe^{3+} ions in these positions, in samples with $n_{Fe}=0.2$ and $n_{Fe}=0.365$. Data are gathered in table 1.

Table 1. Molar fraction, $n_{Fe}=Fe:(Fe+Mn)$, the chemical composition of $Li_xMn_{3-x-y}Fe_yO_4$ samples, temperature of the recording of neutron diffraction pattern (T_r), unit-cell parameter (a) at T_r, and the cation distribution obtained from Rietveld refinement.

n_{Fe}	Composition $Li_xMn_{3-x-y}Fe_yO_4$	T_r (K)	*a* (Å) at T_r	Cation distribution /unit cell $(A_8)[B_{16}]O_{32}$
0.103	$Li_{0.95}Mn_{1.845}Fe_{0.205}O_4$	300	8.2717(2)	$(Li^{+}_{7.6}Mn^{2+}_{0.09}Fe^{3+}_{0.31})[Fe^{3+}_{1.33}Mn^{3+}_{7.38}Mn^{4+}_{7.29}]O_{32.}$
0.200	$Li_{0.90}Mn_{1.680}Fe_{0.420}O_4$	300	8.2917(2)	$(Li^{+}_{7.2}Mn^{2+}_{0.24}Fe^{3+}_{0.56})[Fe^{3+}_{3.08}Mn^{3+}_{6.28}Mn^{4+}_{6.64}]O_{32}$
0.365	$Li_{0.72}Mn_{1.448}Fe_{0.832}O_4$	400	8.3585(4)	$(Li^{+}_{5.76}Mn^{2+}_{0.2}Fe^{3+}_{2.04})[Fe^{3+}_{4.61}Mn^{3+}_{7.67}Mn^{4+}_{3.72}]O_{32}$
0.472	$Li_{0.63}Mn_{1.251}Fe_{1,119}O_4$	500	8.3845(2)	$(Li^{+}_{3.94}Mn^{2+}_{0.72}Fe^{3+}_{3.34})[Li^{+}_{1.1}Fe^{3+}_{5.6}Mn^{3+}_{6.5}Mn^{4+}_{2.8}]O_{32}$

A sudden change was observed for the solid solution with nominal n_{Fe}=0.472. The intensity of almost entirely magnetic *111* reflection suggests an alteration of magnetic ordering.
Figure 4a shows the sections of diffraction patterns indicating the presence of Fe^{3+} ions in the tetrahedral *8a* spinel sites (increasing intensity of *220* reflection) [1], and the A-B ferrimagnetic ordering below the room temperature (high intensity of the predominantly magnetic *111* reflection) [7]. Thermal evolution of this peak enabled us to fix the temperature of the magnetic order-disorder transition (Curie temperature) at about 400K, and separate the nuclear and magnetic scattering effect. The gradual decrease of intensity of the *111* reflection, presented as the (*111/222*) ratio, illustrates figure 4b, comprising additionally the temperature plot of the unit cell constants.

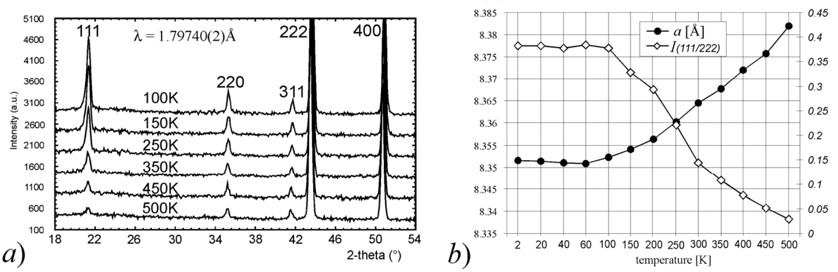

Figure 4. Neutron powder diffraction patterns of the $Li_{0.63}Mn_{1.251}Fe_{1.119}O_4$ spinel solid solution, recorded in the temperature range of 100K-500K. ***(a)****. Unit cell constant, a, and integrated intensity ratio, $I_{(111/222)}$, plotted as a function of temperature* ***(b)****.*

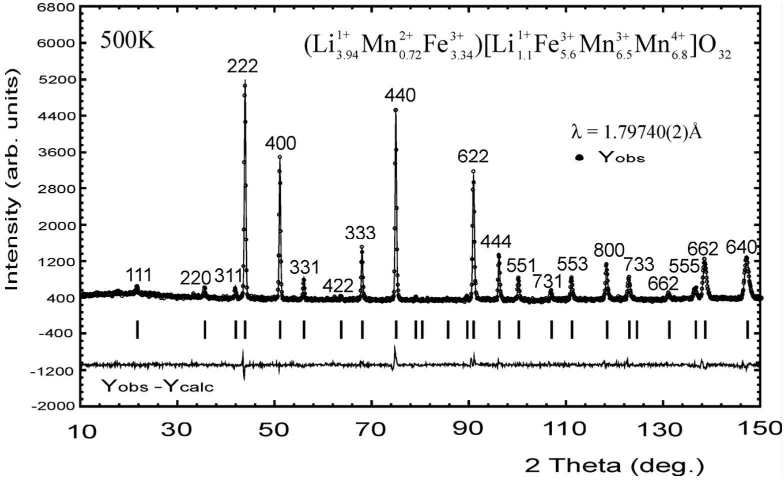

Figure 5. Observed, calculated and difference plots resulting from Rietveld analysis of neutron powder diffraction data of $Li_{0.63}Mn_{1.251}Fe_{1,119}O_4$ (n_{Fe}=0.472), recorded at 500K, (R_p=16.4; R_{wp}=14.3; χ^2=2.32).

The intensity measurements of magnetic reflection *111* enabled to separate the nuclear and magnetic scattering effect. It has to be stressed that the calculation of cation distribution over the tetrahedral and octahedral sublattices, and the spinel structure refinement, could be performed on the basis of neutron powder diffraction patterns recorded at the temperature above Curie point. For the sample with n_{Fe}=0.472 we have chosen the pattern from 500K. Figure 5 shows the results of Rietveld refinement for $Li_{0.63}Mn_{1.251}Fe_{1.119}O_4$.

Concluding remarks

Neutron powder diffraction experiments on the solid solution series $Li_xMn_{3-x-y}Fe_yO_4$ allowed to determine the changes in distribution of the, iron, manganese and lithium ions over the tetrahedral and octahedral spinel sublattices, with the increase of Fe^{3+} ions in the system. Rietveld method was applied for the refinement of structure and for quantifying the chemical composition of spinel samples and precursors. Recording of the magnetic order-disorder transition enabled separation of the nuclear and magnetic scattering effects.

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