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Influence of Simultaneous Doping of Li^+ and Fe^{3+} Ions in the $LiMn_2O_4$ Spinel Structure

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A series of compounds $Li_xMn_{3-x-y}Fe_yO_4$ ($x = 1.0125$; $0 \le y \le 0.05$) were synthesized by solid state reaction of Li_2CO_3 with the manganese oxide or iron–manganese oxide precursors. Investigations of the structure transformation effect of double substitution with Li^+ and Fe^{3+} ions in $LiMn_2O_4$, in the temperature range of 10–300 K, were undertaken using high-resolution X-ray powder diffraction at the HASYLAB (DESY) synchrotron. The $Li_{1.0125}Mn_{1.9625}Fe_{0.025}O_4$ transforms from cubic ($Fd\bar{3}m$) to orthorhombic ($Fddd$) below 250 K, and is stable to 10 K. Whereas in the $Li_{1.0125}Mn_{1.9375}Fe_{0.05}O_4$ oxide no phase transition was observed, this spinel remains in cubic structure down to the temperature of 10 K.

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1. Introduction

Lithium transition metal oxides have been widely studied as promising candidates for cathode materials in the lithium-ion batteries, because of their high voltage and rechargeable capacities [1, 2]. $LiMn_2O_4$ has a normal spinel structure and belongs to the space group $Fd\bar{3}m$. The distribution of cations in $LiMn_2O_4$ is represented by the following ionic formula: $(Li^+)_{8a}[Mn^{3+}Mn^{4+}]_{16d}O_4$, where 8a and 16d refer to the tetrahedral and octahedral sites of the cubic spinel structure. The stoichiometric $LiMn_2O_4$ transforms from cubic to orthorhombic at about 280 K [3]. For $Li_{1.0125}Mn_{1.9875}O_4$ the temperature of phase transition from cubic to orthorhombic decreases to about 260 K, whereas for $Li_{1.025}Mn_{1.975}O_4$ the transformation goes from cubic to tetragonal phase, at the temperature 220 K. No phase transition has been observed for the $Li_{1.0375}Mn_{1.9875}O_4$ cubic sample [4]. The partial substitution of Li^+ for Mn^{3+} restrains the Jahn–Teller effect, owing to reduction of the Mn^{3+}/Mn^{4+} ratio.

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Liu and Shen [5] reported that the phase transition ($Fd\bar{3}m \rightarrow Fddd$) was observed around 220 K for the Co-substituted $LiCo_{0.1}Mn_{1.9}O_4$ compound. Similar result may be obtained with the Fe^{3+} for Mn^{3+} substitution. Doping of Fe^{3+} ions ($y = 0.025$ in $LiMn_{2-y}Fe_yO_4$) decreases the temperature of cubic ($Fd\bar{3}m$) to orthorhombic ($Fddd$) transition to 240 K [6]. These effects may be largely intensified when the heterovalent (Li^+ for Mn^{3+}) and homovalent (Fe^{3+} for Mn^{3+}) substitution occur simultaneously.

The present study is intended to answer the following questions:

1. Does the simultaneous doping of lithium and iron ions influence the effect on the low temperature phase transitions in the $Li_xMn_{3-x-y}Fe_yO_4$ spinels system?
2. Is the distribution of Fe^{3+} ions changed in samples, with the lithium excess?

2. 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 (Mn_2O_3), or iron–manganese oxides ($Mn_{0.025}Fe_{1.975}O_3$, $Mn_{0.05}Fe_{1.95}O_3$) 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:(Mn+Fe) = 0.0, 0.0125 and 0.025 with sodium hydroxide. Washed and dried at the room temperature, they were dehydrated for 2 h at 250°C, and then successively at 400°C, 500°C and 600°C for 4 h. Crystalline single-phase precursors display the bixbyite, α-$(Mn,Fe)_2O_3$ ($Ia3$), structure [7, 8]. Mixed with Li_2CO_3 in the $Li:M_2O_3$ (M = Fe+Mn) ratios corresponding to $x = 1.0125$ 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 4 h. After heating, the preparations were either cooled slowly to the room temperature during 24 h.

Laboratory X-ray powder diffraction experiments were performed with a computerized TUR-61 (HZG-3) diffractometer, employing the Mn-filtered Fe K_α radiation ($\lambda = 1.93604$ Å). For precise determination of the lattice parameters, and for measurements of the integrated intensities, the powder diffraction patterns were recorded in the range of $15° \leq 2\theta \leq 150°$ by step scanning, using 2θ increments of 0.04° and fixed counting time of 7.5 s/step. The phase identification and structure refinement were performed using the programs Fullprof [9] and Unitcell [10]. Data from 20° to 140° (2θ) were included into calculations.

The investigations with synchrotron radiation were executed on the HASYLAB (beamline B2) high-resolution X-ray diffractometer equipped with He cryostat. Sample in form of a powder disk underwent the cooling and heating procedures, in the temperature range of 10–300 K. X-ray powder diffraction data were recorded in the region corresponding to 311, 222, 400, 331 and 440 cubic spinel reflections (in the range of $20° \leq 2\theta \leq 60°$). The wavelength, determined by calibration using a NIST silicon standard (SRM640b, $a = 5.43094$ Å), was 1.12422 Å.

3. Results and discussion

All the prepared samples, $\mathrm{Li}_x\mathrm{Mn}_{3-x-y}\mathrm{Fe}_y\mathrm{O}_4$, with a composition range $0 \leq y \leq 0.05$ and $x = 1.0125$, were identified at the room temperature, as single phase cubic spinels ($Fd\bar{3}m$). In the previous work ut has been shown that the structural transition from cubic ($Fd\bar{3}m$) to orthorhombic ($Fddd$) undergoes for $\mathrm{Li}_{1.0125}\mathrm{Mn}_{1.9875}\mathrm{O}_4$ composition at about 260 K [4]. The X-ray patterns in Fig. 1 for $\mathrm{Li}_{1.0125}\mathrm{Mn}_{1.9625}\mathrm{Fe}_{0.025}\mathrm{O}_4$, i.e., for sample doped with small quantities of iron ions reveal the decrease in transition temperature below 250 K. The low-temperature orthorhombic phase for the $\mathrm{Li}_{1.0125}\mathrm{Mn}_{1.9875}\mathrm{O}_4$ displaces a su-

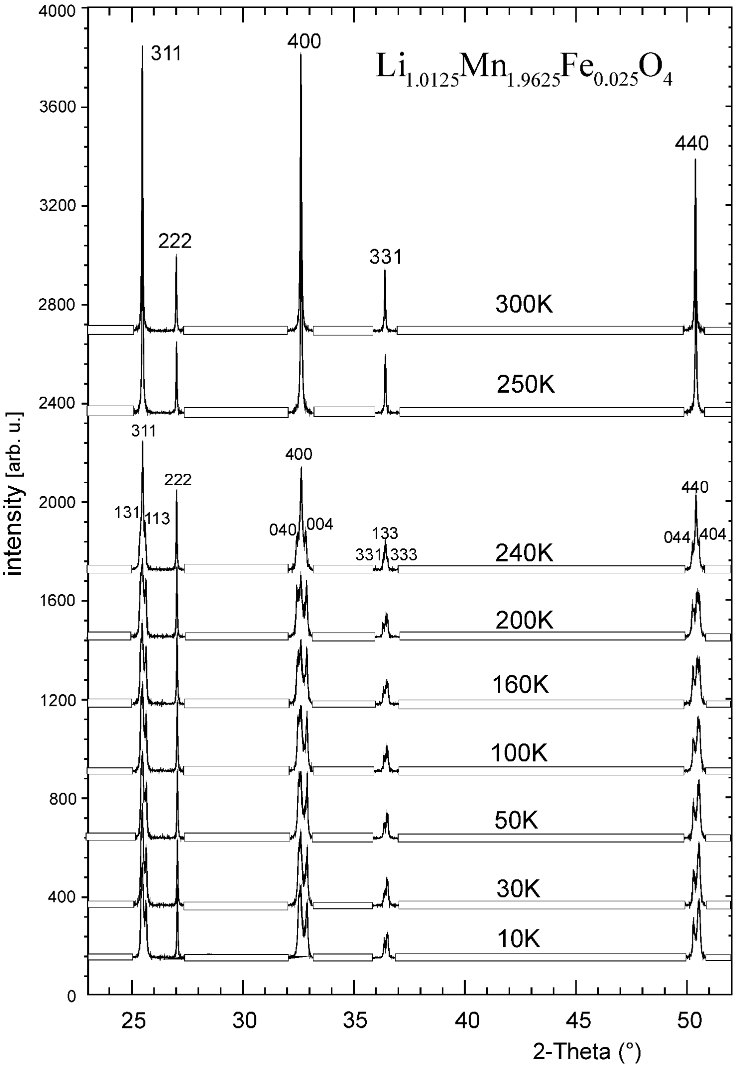

Fig. 1. Thermal evolution of the synchrotron X-ray powder diffraction peaks of $\mathrm{Li}_{1.0125}\mathrm{Mn}_{1.9625}\mathrm{Fe}_{0.025}\mathrm{O}_4$ sample in the temperature range 10–300 K.

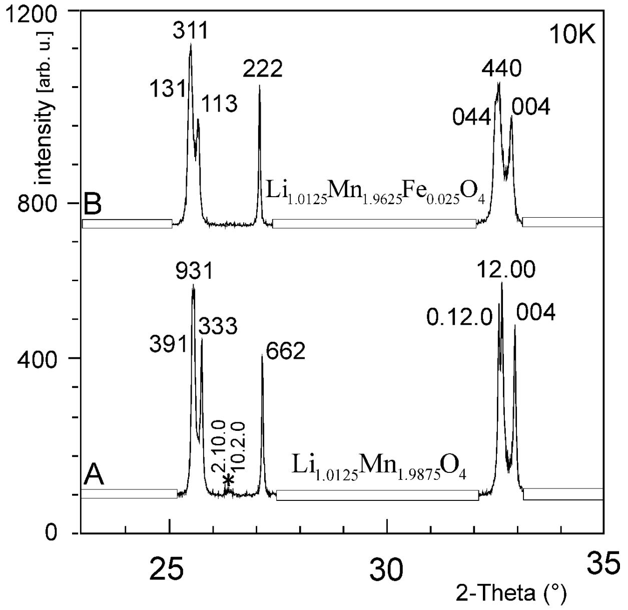

Fig. 2. X-ray powder diffraction patterns in the region of 311, 222 and 400 spinel reflections recorded at 10 K, for $Li_{1.0125}Mn_{1.9875}O_4$ (A) and $Li_{1.0125}Mn_{1.9625}Fe_{0.025}O_4$ (B) (* — superlattice reflections).

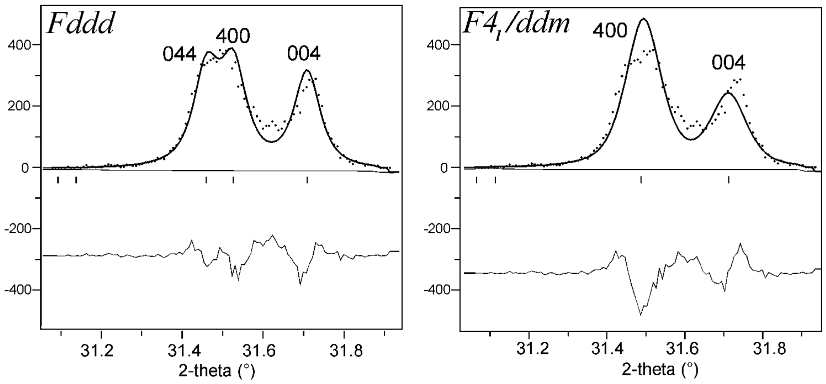

Fig. 3. Profile matching of the X-ray diffraction patterns $Li_{1.0125}Mn_{1.9625}Fe_{0.025}O_4$ at 10 K, using the orthorhombic cell with the space group $Fddd$ compared to the tetragonal cell $F4_1/ddm$.

perstructure of the cubic unit-cell, consisting of nine spinel units ($3a \times 3a \times a$). The small amount of Fe for Mn ions substitution, restrains the partial ordering of Mn^{3+} and Mn^{4+} ions in this sample, as demonstrated in Fig. 2. Furthermore, with decreasing temperature the formation of the orthorhombic poly-

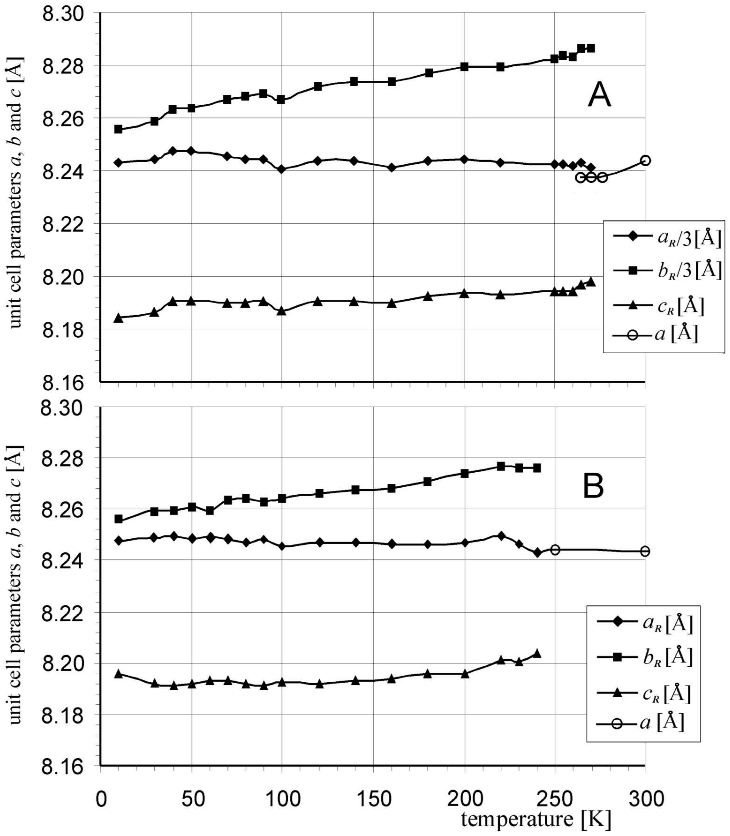

Fig. 4. Lattice parameters a, b, c of the $Li_{1.0125}Mn_{1.9875}O_4$ (A) and $Li_{1.0125}Mn_{1.9625}Fe_{0.025}O_4$ (B) samples, with the cubic and/or orthorhombic spinel structure, plotted as a function of temperature.

morphs of compounds $Li_{1.0125}Mn_{1.9875}O_4$ and $Li_{1.0125}Mn_{1.9625}Fe_{0.025}O_4$, shifts the crystal symmetry close to the pseudo-tetragonal. The investigated samples have been classified into two different space groups: orthorhombic $Fddd$ and tetragonal $F4_1/ddm$. The structure refinement using a model with $Fddd$ space group gave better agreement between observed and calculated intensity of X-ray lines, corresponding to (400) spinel reflection (Fig. 3). The changes of lattice parameters of the cubic and orthorhombic polymorphs of these samples are presented in Fig. 4. Figure 5 illustrates the relation between the b and a unit-cell parameters, of the $Li_{1.0125}Mn_{1.9875}O_4$ (A) and $Li_{1.0125}Mn_{1.9625}Fe_{0.025}O_4$ (B), plotted as a function of temperature. It may be seen that the difference between a and b is lower for the latter compound (B) for each temperature.

It has been reported that in the $Li_{1.0125}Mn_{1.9375}Fe_{0.05}O_4$ oxide no phase transition have been observed, and this spinel remains cubic down to the temperature of 10 K [11]. It has been decided to resolve the problem of iron dis-

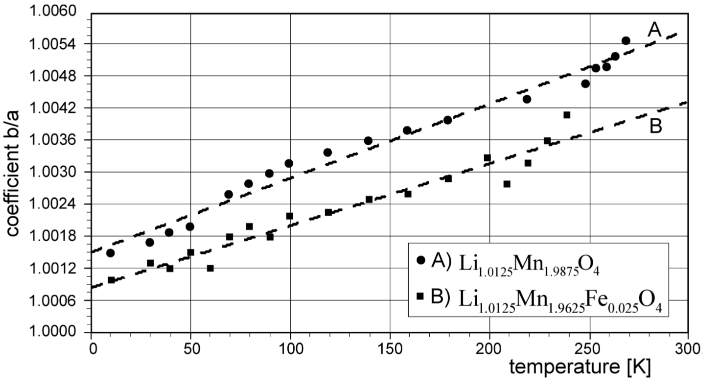

Fig. 5. Changes of the coefficient b/a (axial ratio) of the $Li_{1.0125}Mn_{1.9875}O_4$ (A) and $Li_{1.0125}Mn_{1.9625}Fe_{0.025}O_4$ (B) with the temperature.

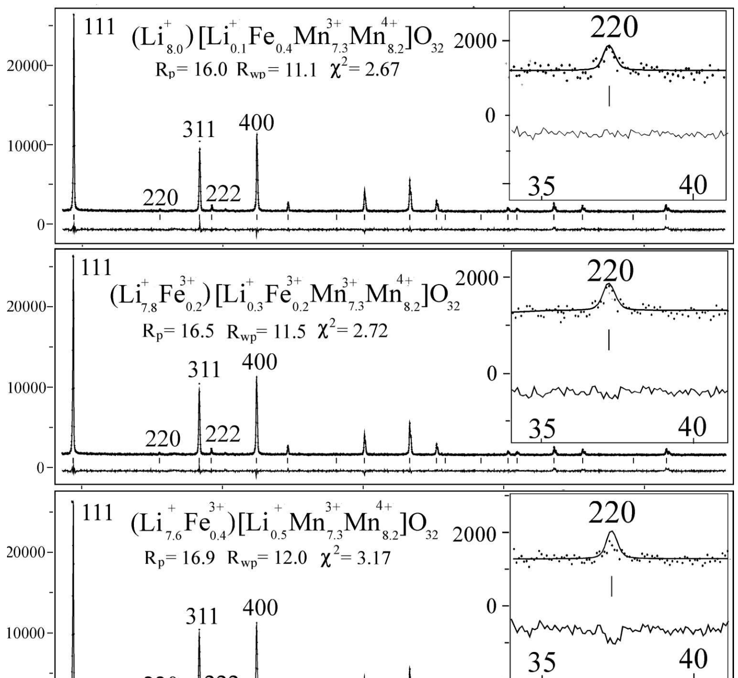

Fig. 6. Comparison of the refinement results, obtained from the three models for the $Li_{1.0125}Mn_{1.9375}Fe_{0.05}O_4$ spinel sample. XRD pattern recorded at the room temperature.

tribution in the $Li_{1.0125}Mn_{1.9375}Fe_{0.05}O_4$ of the lithium-excess sample. Structure refinement by the Rietveld method was carried out, to determine the cation distributions over the tetrahedral (8a) and octahedral (16d) sites. The refinement results obtained from the three models: $(\mathrm{Li}^+_{8.0})[\mathrm{Li}^+_{0.1}\mathrm{Fe}^{3+}_{0.4}\mathrm{Mn}^{3+}_{7.3}\mathrm{Mn}^{4+}_{8.2}]\mathrm{O}_{32}$, $(\mathrm{Li}^+_{7.8}\mathrm{Fe}^{3+}_{0.2})[\mathrm{Li}^+_{0.3}\mathrm{Fe}^{3+}_{0.2}\mathrm{Mn}^{3+}_{7.3}\mathrm{Mn}^{4+}_{8.2}]\mathrm{O}_{32}$ and $(\mathrm{Li}^+_{7.6}\mathrm{Fe}^{3+}_{0.4})[\mathrm{Li}^+_{0.5}\mathrm{Mn}^{3+}_{7.3}\mathrm{Mn}^{4+}_{8.2}]\mathrm{O}_{32}$, for the $\mathrm{Li}_{1.0125}\mathrm{Mn}_{1.9375}\mathrm{Fe}_{0.05}\mathrm{O}_4$ compound has been compared. Results of the Rietveld refinement of X-ray powder diffraction data of this sample are presented in Fig. 6. The intensity of 220 reflection depends exclusively on the cations occupying 8a positions [12]. The refinement was good for the first or second model structure with the similar conventional Rietveld R factors. The quantitative location of cations, using X-ray diffraction was difficult because of low electron density of Li$^+$ and of similarity of the Fe and Mn form factors. Neutron diffraction should be much more useful to determine the precise distribution of Li, Fe, and Mn ions in the $\mathrm{Li}_{1.0125}\mathrm{Mn}_{1.9375}\mathrm{Fe}_{0.05}\mathrm{O}_4$ spinel oxide. A more detailed report on the structure refinement, based on the neutron powder diffraction experiments will be published before long.

4. Conclusions

1. The cubic spinel sample of the composition $\mathrm{Li}_{1.0125}\mathrm{Mn}_{1.9625}\mathrm{Fe}_{0.025}\mathrm{O}_4$ undergoes a transition from cubic ($Fd\bar{3}m$) directly to orthorhombic ($Fddd$) structure below 250 K.
2. Substitution of Fe^{3+} ions restrains the partial ordering of Mn ions in the spinel lattice and reduces superstructure in the $\mathrm{Li}_{1.0125}\mathrm{Mn}_{1.9875}\mathrm{O}_4$ spinel oxide.
3. The Rietveld analysis on X-ray data applied to determine the distribution of Fe^{3+} cations in the $\mathrm{Li}_{1.0125}\mathrm{Mn}_{1.9375}\mathrm{Fe}_{0.05}\mathrm{O}_4$ compound suggests either the absence or presence of very small quantities of this transition metal in the tetrahedral (8a) sites. Further investigation on the structure properties of the $\mathrm{Li}_x\mathrm{Mn}_{3-x-y}\mathrm{Fe}_y\mathrm{O}_4$ system are indispensable.

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