Comparison of the Structure and Phase Transition Investigations with Different Detector Systems

E. Wolska,, W.Nowicki, P. Piszora, J. Darul and M. Knapp[1]

Laboratory of Magnetochemistry, Adam Mickiewicz University, Grunwaldzka 6, PL-60780 Poznan, Poland
[1]Institute of Materials Science, Darmstadt University of Technology, Petersenstr.32, D-64287 Darmstadt, Germany

Studies on the lithium-manganese oxide as a cathode material have concentrated on the stabilization of the cubic spinel structure, mainly by doping other transition metal ions into $LiMn_2O_4$ lattice. Partial substitution of Fe^{3+} ions for Mn^{3+} restrains the Jahn-Teller effect, owing to the reduction of Mn^{3+}/Mn^{4+} ratio. With increasing iron content the phase transitions from cubic to orthorhombic and/or tetragonal structure, appearing for $LiMn_2O_4$ below the room temperature, may be totally suppressed [1]. Series of compounds with the $LiFe_xMn_{2-x}O_4$ stoichiometry have been obtained by solid state reaction of Li_2CO_3 with the manganese oxide or iron-manganese oxide precursors, with the mole ratio of Fe:(Mn+Fe) = 0.0, 0.025, 0.05, 0.075 and 0.1 [2]. Investigations on the temperature phase transitions were carried out at HASYLAB (DESY, Hamburg), using the high-resolution X-ray diffractometer, equipped with He-cryostat, at the B2 beamline. Samples in form of powder discs and/or mounted in capillars, underwent the cooling and heating procedures, from 10K to 300K. Synchrotron X-ray powder diffraction data were collected in the range of 2θ = 25°-60°. In two series of measurements the wavelength, determined by calibration using NIST silicon standard, was 0.70032Å and 0.49920Å, respectively. Refinement of diffraction data, collected as a function of 2θ, and determination of unit cell parameters, was performed using a non-linear least square cell refinement program *UnitCell* [3], and *PowderCell* [4]. Hereafter we present new results of the crystalline phase identification, in the $LiFe_xMn_{2-x}O_4$ system, showing the effect of the different detectors application.

Two types of detector available on the B2 beamline were applied in the phase identification and the low-temperature phase transition experiments: an on-site readable position-sensitive image-plate detector (OBI), and a scintillation single counter(NaI) [5].

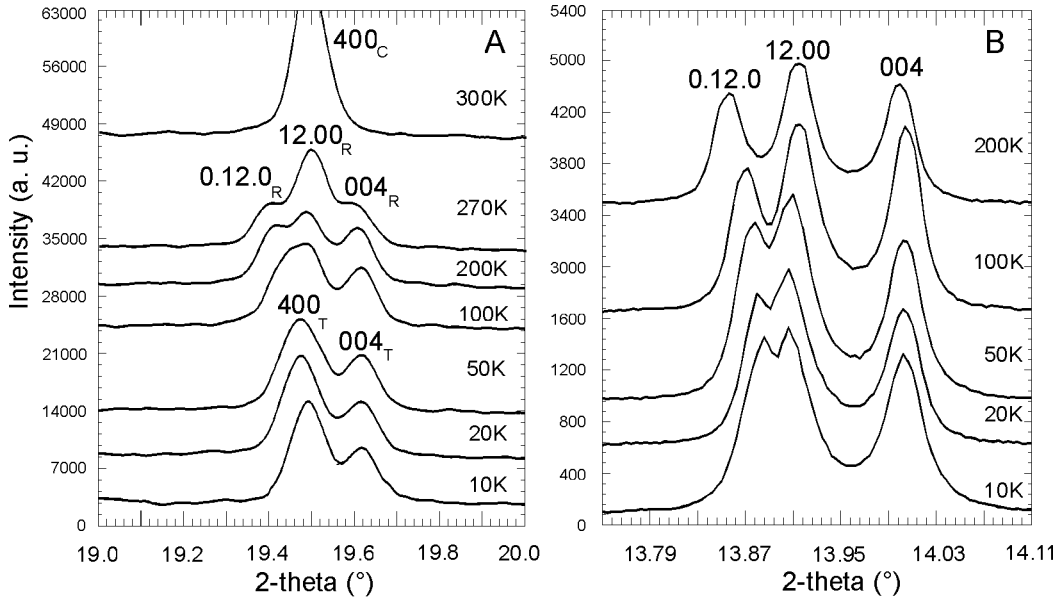

Figure 1: Thermal evolution of the spinel (400) X-ray diffraction peak, in the temperature region of phase transition *Fd3m* →*Fddd* →*F4₁/ddm*, of the $LiFe_{0.05}Mn_{1.95}O_4$ sample, recorded with the OBI detector (A), and with the NaI scintillator (B).

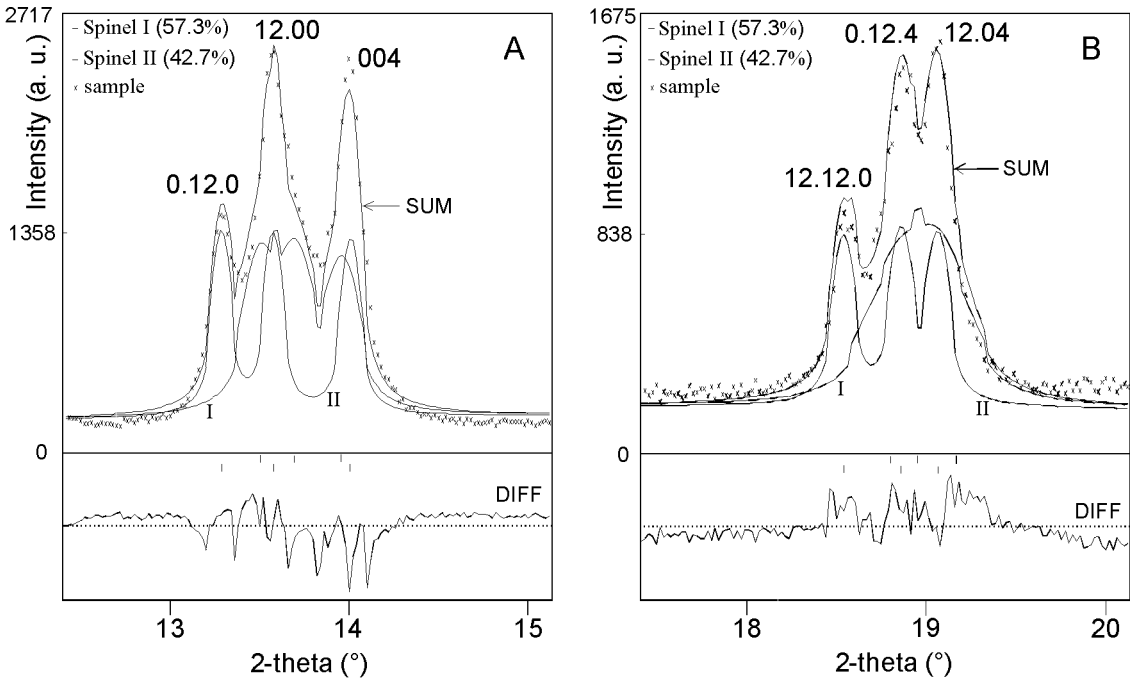

Figure 2: X-ray diffraction patterns of the orthorhombic (160K) $LiFe_{0.025}Mn_{1.975}O_4$ sample, in the region of *400* (A) and *440* (B) spinel reflections, recorded with the NaI scintillator.

Fig.1(A) illustrates the cubic (*Fd3m*)→orthorhombic (*Fddd*) transition, which was found to occur in the $LiFe_{0.05}Mn_{1.95}O_4$ spinel at about 200K, and a possible second transformation into tetragonal phase below 100K. The splitting of reflections and their intensity reveal clearly the tetragonal structure (space group $F4_1/ddm$) [6]. The X-ray pattern on Fig.1(B) of the same sample, recorded with the NaI detector, evidences, however, the orthorhombic (*Fddd*) phase present down to 10K. Our studies of structural phase transformations in the Fe^{3+} substituted lithium manganite spinels yield another example of excellence of a scintillation single counter (NaI) in the precise identification of crystal structure. In Fig.2 we present two sections of X-ray diffraction pattern of a sample with assumed composition $LiFe_{0.025}Mn_{1.975}O_4$, recorded with NaI detector. The two-phase system, observable in the Fig.2, evidenced with the NaI detector, whereas with OBI it appeared as a single phase [2,6], enhances the importance of the high-resolution possibilities in some experiments on structure identification and refinement.

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