High-resolution X-ray powder diffraction studies on the phase transitions in LiMn$_2$O$_4$

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Stoichiometric spinel oxide, LiMn$_2$O$_4$, has the Li$^+$ ions occupying the tetrahedral *8a* sites, and a 1:1 mixture of Mn^{3+} and Mn^{4+} ions randomly distributed over the octahedral *16d* Wyckoff's positions. It displays a cubic, normal-spinel structure (space group *Fd3m*) at room temperature. The occurrence of different structural phase transformations in the stoichiometric LiMn$_2$O$_4$ spinel has been reported. The cubic$\rightarrow$tetragonal phase transition has been observed at 280 K, based on combined experimental results from thermal analysis and X-ray powder diffraction [1]. Subsequent investigations have shown, however, that the low-temperature phase has rather an orthorhombic structure [2,3]. The present study was intended as a step towards systematization of low-temperature phase transitions of LiMn$_2$O$_4$ spinel.

The LiMn$_2$O$_4$ sample has been obtained by solid state reaction of Li$_2$CO$_3$ with the manganese oxide precursor, α-Mn$_2$O$_3$ (*Ia3*, bixbyite structure). After successive thermal treatment in air at 700°C and 800°C for 4h, the preparation was quenched rapidly in the solid CO$_2$. The conventional laboratory X-ray powder diffraction data (FeKα radiation) at room temperature confirm the cubic spinel structure, with the lattice constant a =8.2466(9) Å [4].

Structure refinement by the Rietveld profile analysis, based on the laboratory X-ray patterns, has been performed on the stoichiometric, cubic-spinel samples, stable at room temperature [5], but the resolution of the instrument used was not sufficient for unambiguous determination of the symmetry of low-temperature phases. The investigations on the temperature phase transitions in stoichiometric LiMn$_2$O$_4$, using the high-resolution X-ray powder diffractometer (B2 beamline) equipped with He-cryostat. The geometry included a long parallel-foil collimator at the detector arm, ascertaining resolution suitable for analysis of overlapping peaks of LiMn$_2$O$_4$ phases. The wavelength was determined by calibration using a NIST silicon standard to be 1.12422 Å. A polycrystalline sample was studied during a heating run in the temperature range of 20 K-300 K. X-ray powder diffraction patterns were recorded in selected angular ranges between 2Θ = 25° and 60°. A splitting of the spinel X-ray lines *311, 400, 440, 531, 533* and *662*, recorded during the test, evidenced the reversible formation of cubic, orthorhombic and tetragonal structures. X-ray patterns in Fig.1 reveal clearly the first order structural transitions, attributed to the Jahn-Teller distortion, caused by Mn^{3+} ions. Diffraction spectra collected with increasing temperature from 20 K show that below 100 K the first structural transition, tetragonal $\rightarrow$ orthorhombic, occurs, with the coexistence of both phases for patterns registered at 40 K, 60 K and 100 K. The second transformation starts at about 260 K with increasing symmetry (orthorhombic $\rightarrow$ cubic). Both phases coexist up to the vicinity of room temperature (~290 K). At 300 K, the pure cubic phase remains.

Although the final structure refinements for the orthorhombic and tetragonal polymorphs should be based on a larger 2Θ-range, the present results show that the applied X-ray diffraction records, the high resolution synchrotron X-ray instrument enables structure determination for LiMn$_2$O$_4$ phases, because ambiguities due to severe peak overlap are minimised. This investigation enabled preliminary indexing and determination of the space group. The X-ray patterns of both orthorhombic and tetragonal polymorphs of LiMn$_2$O$_4$ show the superstructure reflections (e.g., *2.10.0*), pointing to the partial ordering of manganese Mn^{3+} and Mn^{4+} ions [6]. Therefore a supercell corresponding to (*3a x3a x a*), where *a* - spinel unit-cell constant, has been considered for the low-temperature phases (see *hkl*-indices in Fig.1). The lattice constants determined for the three polymorphs of LiMn$_2$O$_4$ are as follows: for cubic-spinel phase (300 K, space group *Fd3m*) a = 8.2441(9) Å; for orthorhombic phase (250 K, space group *Fddd*) a = 24.730(3) Å, b = 24.836(3) Å , c = 8.1925(9) Å ; and for the low-temperature tetragonal phase (20 K, space group *F4$_1$/ddm*) a = 24.763(3) Å , c = 8.1918(9) Å.
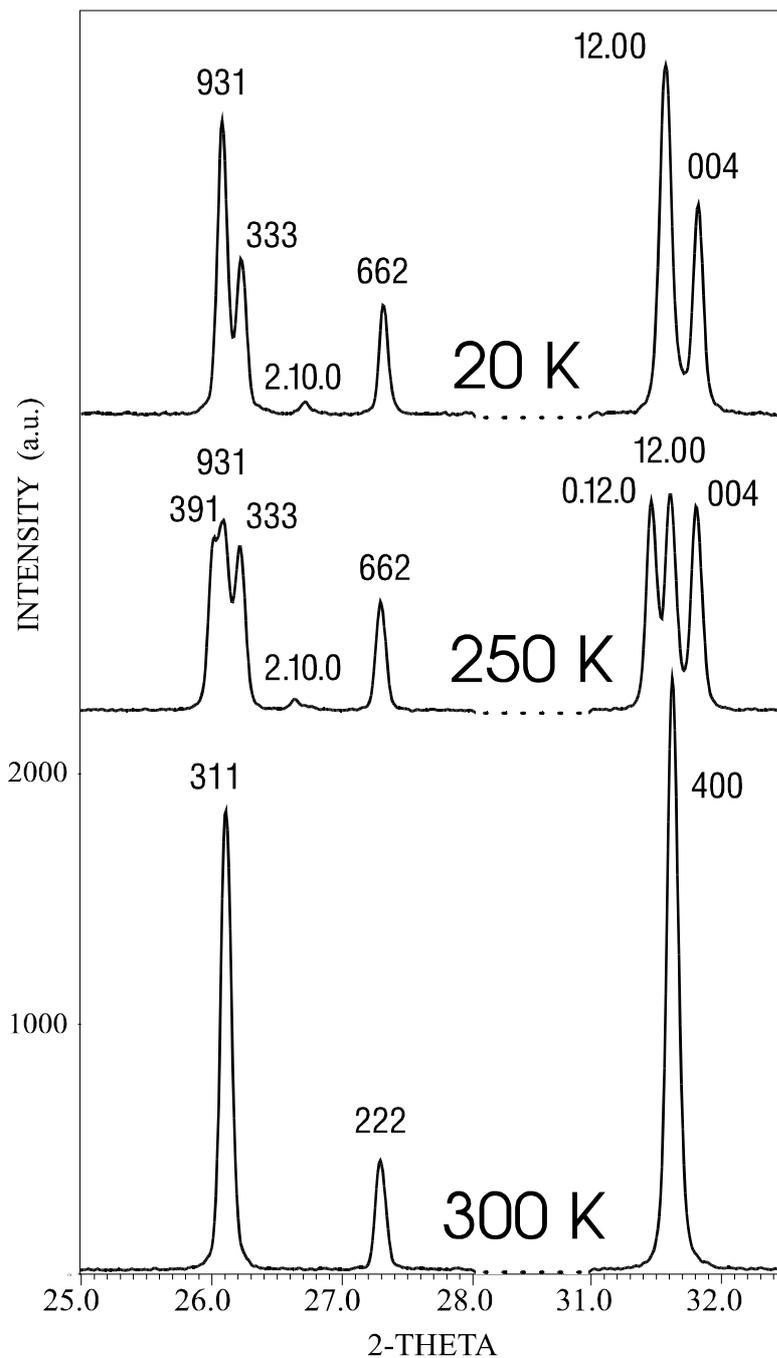
Figure 1: X-ray powder diffraction patterns of LiMn$_2$O$_4$, recorded in the region of *311*, *222* and *400* spinel reflections, at the temperature of 300K (cubic phase), 250K (orthorhombic phase) and 20K (tetragonal phase)

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