

Influence of Mn^{3+} , Cr^{3+} and Al^{3+} Substitution on the Phase Transition Temperature in Spinel Lithium Ferrite

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Spinel ferrites, such as $LiFe_5O_8$, are soft magnetics, with the high Curie temperature, a square hysteresis loop and high magnetization, that are of interest as low cost materials for the memory core and microwave applications. The magnetic properties of lithium ferrite may be improved by addition of small amounts of other cations, e.g. manganese and chromium ions [1]. Spinel lithium ferrite occurs in two crystalline forms. In the ‘ordered’ form (space group $P4_132/P4_332$) the Fe^{3+} ions are at octahedral $12d$ and tetrahedral $8c$ sites, and Li^+ occupy the octahedral $4b$ positions in the cubic primitive cell. The ‘disordered’ $LiFe_5O_8$ has an inverse spinel structure (space group $Fd3m$), with Fe^{3+} at tetrahedral $8a$ positions and $Li^+ + Fe^{3+}$ randomly distributed over the $16d$ octahedral sites [2].

Substitution with manganese and chromium ions reduces the 1:3 cation ordering in the solid solution series of $LiM_xFe_{5-x}O_8$, and the ‘disordered’ spinel forms with the increasing M^{3+} content, while aluminium ions do not influence the ‘ordered’ structure in the whole range of solid solutions [3-5]. However, a limited substitution with Mn^{3+} , Cr^{3+} and Al^{3+} affects the temperature of an ‘order-disorder’ transition in $LiMn_{0.5}Fe_{4.5}O_8$, $LiCr_{0.5}Fe_{4.5}O_8$ and $LiAl_{0.5}Fe_{4.5}O_8$. We present new results, obtained from synchrotron X-ray powder diffraction studies, in the temperature range of 300K - 1173K, on the role of manganese, chromium and aluminium ions in the ‘order-disorder’ phase transition in the spinel lithium ferrite.

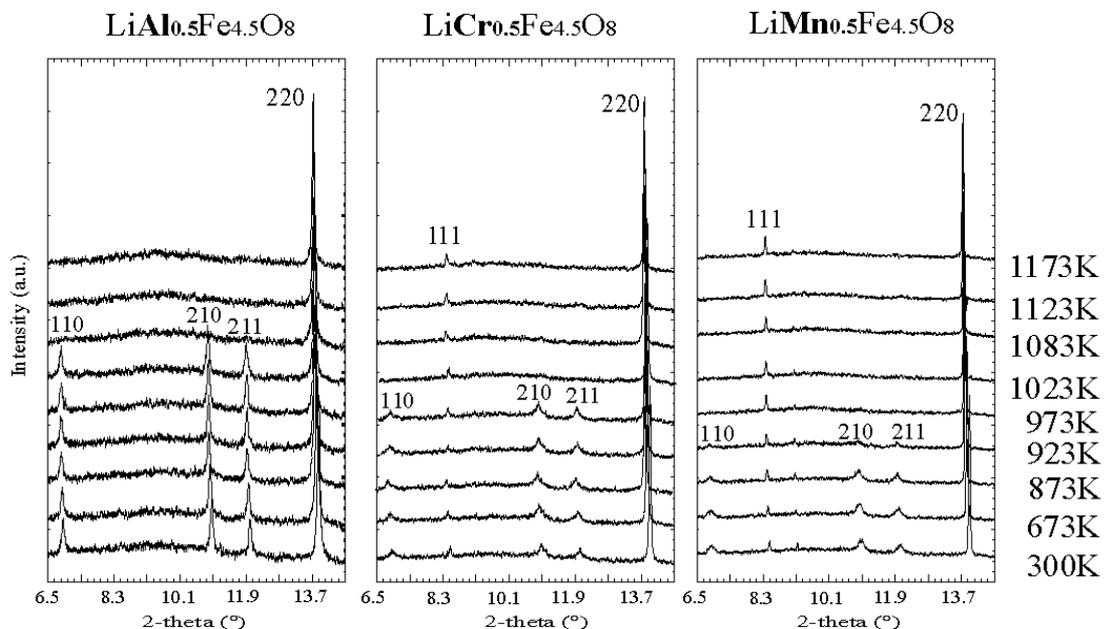


Figure 1: Synchrotron X-ray powder diffraction patterns, in the region of the ordered spinel ‘superstructure’ reflections, in the temperature range of 300K-1173K, for the $LiM_xFe_{4-x}O_8$ series ($M = Al, Cr, Mn; x=0.5$), showing the effect of M^{3+} substitution on the temperature of $F4_132 \rightarrow Fd3m$ phase transition.

Series of $LiM_{0.5}Fe_{4.5}O_8$ single phase solid solutions ($M = Mn, Cr, Al$) were prepared in our laboratory, as described in [3,5]. Research in the framework of HASYLAB (DESY, Hamburg)

project made possible the investigations on the phase transition temperature, using the high-resolution X-ray diffractometer (beamline B2).

For the high temperature experiments STOE-high-temperature-chamber and the on-site readable Image Plate OBI detector were used (at the temperature range from 300K to 1173K) [6]. The wavelength was 0.709901Å. 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* [7].

Investigation of thermal transformations of the lattice of ordered LiFe_5O_8 in the range of 300K- 1173K, enabled us to determine, relatively precisely, the order-disorder phase transition temperature. Three sets of X-ray powder diffraction patterns, presented in Fig.1, recorded in the temperature range from 300K to 1173K, show the ordered spinel structure ($P4_132$) and disordered ($Fd3m$) structure, respectively. The additional “superstructure” reflections, e.g., 110 , 210 , 211 , characteristic for the cubic primitive $P4_132$ symmetry of ordered LiFe_5O_8 vanish, which proves that the phase transition arises clearly in this temperature region. Temperatures of the ‘order-disorder’ phase transition, recorded in this experiment are: 923K-933K for $\text{LiMn}_{0.5}\text{Fe}_{4.5}\text{O}_8$, 1003K-1013K for $\text{LiCr}_{0.5}\text{Fe}_{4.5}\text{O}_8$ and 1073K-1083K for $\text{LiAl}_{0.5}\text{Fe}_{4.5}\text{O}_8$, compared to 1033-1043K for LiFe_5O_8 [3].

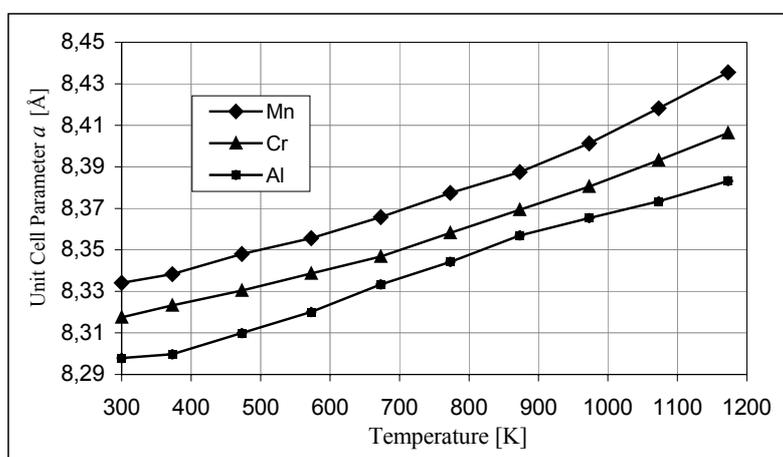


Figure 2: Changes of the spinel unit-cell parameter, a , of solid solutions $\text{LiAl}_{0.5}\text{Fe}_{4.5}\text{O}_8$ (Al), $\text{LiCr}_{0.5}\text{Fe}_{4.5}\text{O}_8$ (Cr) and $\text{LiMn}_{0.5}\text{Fe}_{4.5}\text{O}_8$ (Mn), as a function of temperature, in the range of 300K-1173K.

Variation of the lattice parameter, a , of the cubic unit cell, with the temperature has been measured for all three solid solutions. Fig.2 illustrates the evolution of a , calculated from X-ray data collected during the heating and cooling procedure, plotted as a function of temperature.

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