Characterization of Structural Properties of $LiM_xFe_{5-x}O_8$ (M=Al, Cr, Mn) Spinel Solid Solutions

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The structural properties of series spinel oxides with the general formula, $LiM_{0.5}Fe_{4.5}O_8$ (M = Mn, Cr, Al), are investigated. The effect of limited substitution of manganese, chromium and aluminum ions in the lithium ferrite samples on the order–disorder phase transition in the spinel crystal lattice at room temperature is presented. In these materials it is found that the ordered structures have not been isolated as single phases under the present experimental conditions and this fact will certainly influence the magnetic behavior of the compounds. The Rietveld refinements of the synchrotron X-ray diffraction data revealed that transition metal ions hinders the ordering process and Al^{3+} ion was shown to be least effective in removing of order.

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1. Introduction

Spinel ferrites have potential applications in electrical components, memory devices over a wide range of frequencies and microwave devices because of their high resistivity [1]. Low cost, ease of fabrication, high Curie temperature and better temperature stability of saturation magnetization of lithium ferrites have made them attractive from commercial point of view and are good substitutes of garnets ($Y_3Fe_5O_{12}$) for microwave devices, such as isolators, circulators and gyrators. The magnetic properties of lithium ferrite may be improved by the addition of small amounts of other cations, e.g., manganese, chromium or aluminum ions [2–5].

Based on the inverse spinel structure, the lithium ferrite occurs in two crystalline forms [6]. The lattice of $LiFe_5O_8$ is disordered, though not completely random, at the temperature above 1000 K, and may be quenched in air down to

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the room temperature, displaying a spinel $Fd\bar{3}m$ structure, with Fe^{3+} at tetrahedral (8a) Wyckoff's positions, and a 1:3 mixture of Li^+ and Fe^{3+} ions at octahedral (16d) positions. Below 1000 K the structure becomes "ordered", and can be described by the cubic space group $P4_332$ or its enantiomorph $P4_132$, with Fe^{3+} in tetrahedral (8c) and octahedral (12d) sites, whereas Li^+ ions occupy the (4b) octahedral positions [6, 7].

When transitions metal ions with large octahedral site stabilization energy are substituted on the octahedral sites, the structure gradually reverts to the statistically face-centered form (space group $Fd\bar{3}m$), normally associated with spinel compounds. This is indicated by the disappearance of the superlattice lines in the X-ray diffraction pattern [2–5]. The 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" ($Fd\bar{3}m$) spinel forms with the increasing M^{3+} content, while aluminum ions do not influence the "ordered" ($P4_132$) structure in the whole range of solid solutions [2–5].

In the present work the loss of order in lithium spinel systems: $LiM_{0.5}Fe_{4.5}O_8$ (M = Mn, Cr, Al) is examined for limited substitution of Mn^{3+}, Cr^{3+} and Al^{3+} ions on the octahedral sites in the spinel crystal lattice. X-ray powder diffraction measurements, recorded using synchrotron radiation were performed on the materials to characterize the structural properties at room temperature. The Rietveld refinement was used to solve the problem of the cation ordering in these samples.

2. Experimental details

Series of $LiM_{0.5}Fe_{4.5}O_8$ solid solutions (M = Mn, Cr, Al) were obtained by the solid state reaction of Li_2CO_3 (Merck) with the oxides precursors.

The precursors were prepared by precipitation of amorphous Mn–Fe hydroxides, Cr–Fe hydroxides and Al–Fe hydroxides from mixed Mn^{2+}/Fe^{3+}-nitrate, Cr^{3+}/Fe^{3+}-nitrate and Al^{3+}/Fe^{3+}-nitrate solutions, of the mole ratio of M:(Fe+M) = 0.1, with sodium hydroxide. Washed and dried at room temperature, they were dehydrated at 400°C. Crystalline single-phase products: α-$Fe_{1.8}Mn_{0.2}O_3$, α-$Fe_{1.8}Cr_{0.2}O_3$, α-$Fe_{1.8}Al_{0.2}O_3$, displaying the hematite structure, ($R\bar{3}c$), were mixed with Li_2CO_3 in the $Li:M_2O_3$ ratio corresponding to $LiMn_{0.5}Fe_{4.5}O_8$, $LiCr_{0.5}Fe_{4.5}O_8$, $LiAl_{0.5}Fe_{4.5}O_8$, composition. The mixtures underwent the thermal treatment in air, successively at 700°C and 750°C for 6 h.

The compounds formation and crystallinity of the materials were identified by X-ray diffraction (XRD) patterns, which were recorded on a Bruker D8 Advance diffractometer, with Cu K radiation (= 1.5421 Å).

X-ray powder diffraction data for structural refinements were collected at the synchrotron beamline B2 at HASYLAB (DESY, Hamburg). The diffractometer was equipped with the on-site readable image-plate detector OBI [8]. The polycrystalline samples were placed in a glass capillary of 0.3 mm diameter. The wavelength, determined by calibration using a NIST silicon standard, was 0.709901 Å.

Diffraction patterns were analyzed by the Rietveld method and the GSAS software [9].

3. Results and discussion

According to the previously published results, samples of $LiFe_5O_8$ prepared in solid state reaction between α-Fe_2O_3 and Li_2CO_3, followed by slow cooling of products to the room temperature, displayed the "ordered" ($P4_132$) spinel structure, whereas rapid cooling (quench) preserved "disordered" ($Fd\bar{3}m$) crystalline form of spinel lithium ferrite. On the other hand, substitution with manganese ions in $LiFe_{5-x}Mn_xO_8$ suppresses the ordering of Li^+ in the 4b octahedral positions, and for $x = 1$ the disordered spinel was formed [10, 11].

Structural characterization of the $LiM_{0.5}Fe_{4.5}O_8$ solid solutions (M = Mn, Cr, Al) at room temperature was carried out by the Rietveld method. The XRD patterns confirmed the formation of highly crystalline cubic phases for all compositions. The reflections were characteristic of a spinel structure ($Fd\bar{3}m$) in which some additional superstructure lines appear. Therefore, the investigated samples exhibited cation ordering on the octahedral sites, resulting in superstructure that could be refinement in the ($P4_132$) space group.

However, it was found that a slight improvement in the fit was achieved by using a multiphase refinement using both the ordered ($P4_132$) and disordered $Fd\bar{3}m$ structures. The Rietveld analysis indicated that at room temperature the sample with $LiMn_{0.5}Fe_{4.5}O_8$ stoichiometry contained 33% of superstructure (or ordered form) and 67% of disordered structure, whilst chromium doped sample contained 44% of superstructural component and 56% of disordered component.

However, the presence of a low-angle superstructure reflections in the XRD patterns as observed for all compositions (Fig. 1) is conclusive evidence of cation order, the ordered structures have not been isolated as single phases under the present experimental conditions.

When spherically symmetric ions such as Ga^{3+} or Al^{3+} are substituted in lithium ferrite, long-range order is retained [12], which suggests that the disorder in the Cr substituted compounds probably arises because of the large octahedral site stabilization energy of Cr^{3+}. On the basis of site stabilization alone Mn^{3+} ion should be least effective in removing of order, however being a Jahn–Teller ion it also creates localized distortions in the structure (the formation of Mn^{3+} ion clusters) [12].

In spite of the fact, reported by Arakawa et al. [4], that aluminum ions do not influence the "ordered" ($P4_132$) structure in the whole range of solid solutions, from XRD results we confirmed that $LiAl_{0.5}Fe_{4.5}O_8$ sample showed 76% ordered phase with a minority disordered component (24%). Structural data for all samples obtained by the Rietveld refinements are reported in Tables I–III and the R-factors indicate a reliable structural model. It may be seen that the unit cell dimension of sample $LiMn_{0.5}Fe_{4.5}O_8$ differ only slightly from $LiFe_5O_8$ [13], because of similarity
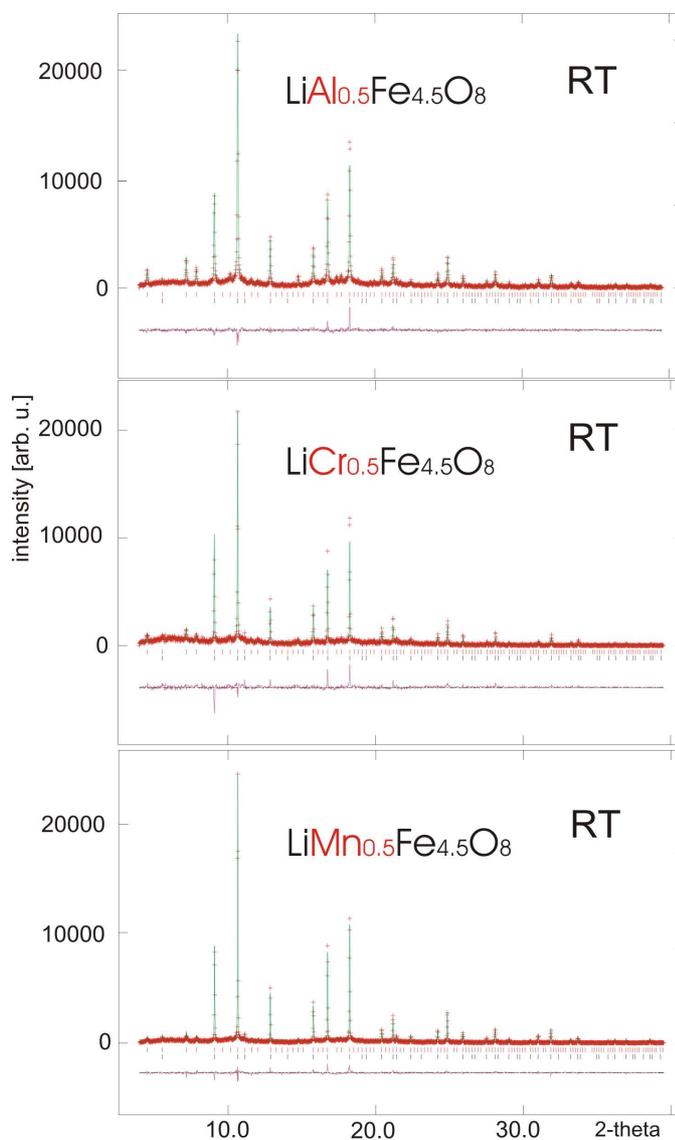
Fig. 1. Observed, calculated and difference profiles resulting from the Rietveld analysis of synchrotron X-ray powder diffraction data of $LiM_{0.5}Fe_{4.5}O_8$ solid solutions (M = Mn, Cr, Al) at room temperature [peak positions characteristic of $P4_132$ space group (upper vertical marks) and of $Fd\bar{3}m$ space group (lower vertical marks) are indicated just below the patterns].

of the ionic radii of Fe^{3+} and Mn^{3+}. Moreover, doping Al^{3+} and Cr^{3+} ions in the spinel type structure causes the lattice constant decrease for $LiAl_{0.5}Fe_{4.5}O_8$ and $LiCr_{0.5}Fe_{4.5}O_8$, compared to $LiFe_5O_8$ [13]. It indicates that the ionic radii of

Unit cell parameters, a, and R-factors for $LiM_{0.5}Fe_{4.5}O_8$ spinel solid solutions (M = Al, Cr, Mn) obtained by X-ray refinement at room temperature.

	$LiAl_{0.5}Fe_{4.5}O_8$		$LiCr_{0.5}Fe_{4.5}O_8$		$LiMn_{0.5}Fe_{4.5}O_8$	
Space group	$P4_132$	$Fd\bar{3}m$	$P4_132$	$Fd\bar{3}m$	$P4_132$	$Fd\bar{3}m$
%	76(4)	24(7)	44(3)	56(9)	33(6)	67(8)
a [Å]	8.2958(2)	8.2986(4)	8.3175(3)	8.3177(9)	8.3287(4)	8.3292(8)
R_{wp} [%]	6.56		6.78		6.34	
R_p [%]	5.16		5.41		5.02	

Structural parameters obtained from the Rietveld refinement of the powder diffraction patterns of $LiM_{0.5}Fe_{4.5}O_8$ spinel solid solutions (M = Al, Cr, Mn) at room temperature; space group $P4_132$ was used with positions: A (Fe and M) at (x, x, x), B (Li) at $(0.625, 0.625, 0.625)$, (Fe and M) at $(0.125, y, z)$, and O(1) at (x, x, x), O(2) at (x, y, z); (B) octahedral and (A) tetrahedral sites.

	Site	$LiAl_{0.5}Fe_{4.5}O_8$	$LiCr_{0.5}Fe_{4.5}O_8$	$LiMn_{0.5}Fe_{4.5}O_8$
A	8c			
$(x = y = z)$		–0.0011(2)	–0.0015(5)	–0.0013(2)
$U_{iso} \times 10^2$ [Å^2]		1.194(5)	1.067(2)	1.13(9)
Li	4b	0.625	0.625	0.625
$U_{iso} \times 10^2$ [Å^2]		1.903(4)	1.591(9)	1.442(6)
Fe/M	12d			
y		0.3697(2)	0.3709(5)	0.3686(3)
z		–0.1197(7)	–0.1209(6)	–0.1183(7)
Fe/M $U_{iso} \times 10^2$ [Å^2]		1.903(4)	1.591(9)	1.442(6)
O(1)	8c			
$(x = y = z)$		0.3825(3)	0.3813(6)	0.3809(4)
O(1) $U_{iso} \times 10^2$ [Å^2]		1.376(8)	1.618(4)	1.811(5)
O(2)	24e			
x		0.1220(9)	0.1198(2)	0.1234(4)
y		0.1301(3)	0.1271(7)	0.1122(8)
z		0.3808(4)	0.3767(8)	0.3785(2)
O(2)$U_{iso} \times 10^2$ [Å^2]		1.376(8)	1.618(4)	1.811(5)

Al^{3+} (0.51 Å) and Cr^{3+} (0.63 Å) are smaller than that of Fe^{3+} (0.64 Å) [14]. Additionally, disordered form in which the $Li^+/Fe^{3+}/M^{3+}$ (M = Mn, Cr, Al) ions are distributed randomly over the octahedral sites, had a marginally higher lattice parameter in the investigated series of compounds.

TABLE III

Structural parameters obtained from the Rietveld refinement of the powder diffraction patterns of $LiM_{0.5}Fe_{4.5}O_8$ spinel solid solutions (M = Al, Cr, Mn) at room temperature; space group $Fd\bar{3}m$ was used with positions: A (Fe and M) at (0.125, 0.125, 0.125), B (Fe and M) at (0.5, 0.5, 0.5), and O at $(u,\ u,\ u)$.

	Site	$LiAl_{0.5}Fe_{4.5}O_8$	$LiCr_{0.5}Fe_{4.5}O_8$	$LiMn_{0.5}Fe_{4.5}O_8$
A	8a			
$U_{iso} \times 10^2$ [Å^2]		1.025(3)	1.522(7)	1.633(2)
Fe	16d			
M	16d			
Fe/M $U_{iso} \times 10^2$ [Å^2]		1.337(5)	1.628(3)	1.521(4)
O	32e			
(u, u, u)		0.2541(5)	0.2564(6)	0.2536(2)
O $U_{iso} \times 10^2$ [Å^2]		1.605(3)	1.744(3)	1.711(3)

A new report on the role of limited substitution with Mn^{3+}, Cr^{3+} and Al^{3+} ions on the temperature of an "order–disorder phase" transition in lithium ferrites and on the thermal expansion of their spinel lattices based on the synchrotron powder diffraction experiments will be published before long.

4. Conclusions

X-ray diffraction experiments were performed on the series spinel solid solutions $LiM_{0.5}Fe_{4.5}O_8$ (M = Mn, Cr, Al). The data show that ordered structures have not been isolated as single phases under the present experimental conditions. An evidence is given that limited substitution (0.5 Fe ions per formula unit) by manganese, chromium and aluminum ions in the crystal lattice of ordered $LiFe_5O_8$, affects the 1:3 ordering of Li^+ and Fe^{3+} ions in the octahedral spinel sublattice.

Acknowledgments

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