United Nations Educational Scientific and Cultural Organization
and
International Atomic Energy Agency

THE ABDUS SALAM INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

SYNTHESIS, STRUCTURAL AND MAGNETIC CHARACTERIZATION OF
ALUMINIUM-SUBSTITUTED Li$_{0.5}$Fe$_{2.5}$O$_4$ SPINEL LITHIUM FERRITE

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MIRAMARE – TRIESTE
November 2002

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Abstract

Spinel-related aluminum-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$ has been synthesized by heating a mixture of aluminum-substituted corundum-related α-Fe$_2$O$_3$ with Li$_2$CO$_3$ at 700°C which is ca. 450-500°C lower than temperatures at which the material is normally prepared with conventional ceramic methods. Rietveld structural refinement of the X-ray diffraction data is in favour of a model in which Al$^{3+}$ ions exclusively occupy octahedral sites replacing Fe$^{3+}$ and Li$^+$ with some replaced Li$^+$ ions substituting for Fe$^{3+}$ at tetrahedral sites. $^{57}$Fe Mössabuer spectroscopy and magnetic measurements are consistent with this structural model.

1. Introduction

The lithium ferrite Li$_{0.5}$Fe$_{2.5}$O$_4$, on both disordered and ordered forms, adopts an inverse spinel structure with Fe$^{3+}$ at tetrahedral A sites (Wyckoff 8c positions) and a 1 : 3 mixture of Li$^+$ and Fe$^{3+}$ at octahedral B sites. The latter are the 16d Wyckoff positions for the Fd-3m disordered polymorph and 4b + 12d for Li$^+$ and Fe$^{3+}$ respectively in the ordered P4$_1$32/P4$_3$32 polymorph [1,2]. The magnetic properties of Li$_{0.5}$Fe$_{2.5}$O$_4$, which are explicable in terms of Neel’s molecular field model for ferromagnetism [3], can be modified by the introduction of diamagnetic cationic substitutes for Fe$^{3+}$ into either the tetrahedral A or octahedral B sublattice [3] allowing the material to be tailored for a specific application as done, for instance, in microwave and memory-core industries[1,4,5].

Common routes for synthesizing cation-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$ generally involve the use of high temperatures and include methods such as high temperature sintering of oxides or precursors for prolonged times [1,6,7], self-propagating high-temperature synthesis [8] and synthesis from melts [9]. The high temperatures (>1000°C) used in these methods lead to the development of adverse electric and magnetic properties such as high dielectric loss and lower magnetisation which limit the use of the material from an applied viewpoint as shown elsewhere [1,10].

As a part of our ongoing research on non-conventional synthesis and physical charaterisation of metal-substituted lithium ferrites, we have recently reported on synthesising Mg-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$ at
a temperature which is substantially lower than those at which it is normally produced conventionally [10]. In this paper, we report on adopting a similar route to lower the formation temperature of Al-substituted $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$. The effect of calcination on the formation process of the aluminum–substituted lithium ferrite is discussed. The cationic distribution in the material is investigated by means of Rietveld refinement of X-ray powder diffraction data, Mössbauer spectroscopy and magnetic measurements.

2. Experimental

Aluminum-substituted $\alpha$-$\text{Fe}_2\text{O}_3$ of the composition $\text{Fe}_{1.76}\text{Al}_{0.24}\text{O}_3$ was prepared hydrothermally using an aqueous mixture of iron (III) chloride hexahydrate and aluminum chloride with aqueous amonia. The preparation procedure was described previously [11]. A 7 : 1 molar mixture of the Al-substituted $\alpha$-$\text{Fe}_2\text{O}_3$ and $\text{Li}_2\text{CO}_3$ was ground in agate mortar for 30 min and calcined in air at temperatures between 300 and 700ºC for 12h with the product being quenched in air after each run.

X-ray powder diffraction data were recorded with a Siemens D5000 diffractometer in reflection mode using CuKα radiation. The program MAUD (version 1.91) was used for Rietveld structural refinement and simulation of patterns for a specific structural model [12]. $^{57}\text{Fe}$ Mössbauer spectra were recorded at room temperature in the standard transmission geometry using a 5mCi $^{57}\text{Co}$/Rh source. Chemical isomer shifts are given relative to $\alpha$-$\text{Fe}$. Elemental analysis was done using the inductively-coupled plasma (ICP) method. The thermal dependence of the magnetisation was measured at a heating rate of 4K/min using a Faraday balance in a magnetic field of 1.5T with a relative accuracy better than 1%. The temperature was stabilised within 0.5K.

3. Results and Discussion

3.1 Calcination of the mixture of aluminum-substituted $\alpha$-$\text{Fe}_2\text{O}_3$ and $\text{Li}_2\text{CO}_3$

The X-ray powder diffraction patterns recorded from the mixture following calcinations at different temperatures and subsequently quenching in air are shown in Figure 1.
Heating the mixture at 400°C for 12h (Fig. 1b) resulted in the removal of Al$^{3+}$ ions from the α-Fe$_2$O$_3$ corundum-related structure which reacted with Li$_2$CO$_3$ and from small amounts of lithium aluminates, namely γ-LiAlO$_2$ and Li$_{0.5}$Al$_{2.5}$O$_4$ as evident from the low intensity peaks corresponding to both phases [13]. No reaction with Li$_2$CO$_3$, however, in which Fe$^{3+}$ ions were involved, took place at this stage as peaks corresponding to any resultant lithium ferrite do not exist. The formation of the lithium aluminates following this thermal treatment can be represented as follows:

$$Fe_{2-x}Al_xO_3 + \frac{x}{2}Li_2CO_3 \xrightarrow{400^\circ C(12h)} xLiAlO_2 + (1-\frac{x}{2})Fe_2O_3 + \frac{x}{2}CO_2 \uparrow$$  \hspace{1cm} (1)$$

$$4Fe_{2-x}Al_xO_3 + xLiAlO_2 \xrightarrow{400^\circ C(12h)} (4-2x)Fe_2O_3 + xLiAl_5O_{8}$$  \hspace{1cm} (2)$$
Heating of the mixture at 500°C for 12h (Fig. 1c) only resulted in a slight enhancement of the Li$_{0.5}$Al$_{2.5}$O$_4$ phase with a concomitant decrease in the γ-LiAlO$_2$ one in favour of reaction (2) above. Further heating of the mixture at 600°C for 12h (Fig. 1d) resulted in lowering the intensity of the reflection peaks corresponding to Li$_{0.5}$Al$_{2.5}$O$_4$ and the growth of low-intensity peaks associated with the inverse spinel-related Li$_{0.5}$Fe$_{2.5}$O$_4$ phase. This suggests the formation of a single-phase solid solution of both lithium spinel-related aluminate Li$_{0.5}$Al$_{2.5}$O$_4$ and ferrite Li$_{0.5}$Fe$_{2.5}$O$_4$ in which both can be indexed to the P4$_3$33 space group [14]. The formation of the lithium ferrite following this thermal treatment can be represented by the following equation:

$$5Fe_2O_3 + Li_2CO_3 \xrightarrow{600^\circ C(12h)} LiFe_5O_8 + CO_2 \uparrow$$

(3)

It is clear from the high intensity of the reflection peaks of the original corundum-related of α-Fe$_2$O$_3$ that the reaction between the components is still weak following calcination at this temperature. However, further heating the mixture at 700°C for 12h (Fig. 1e) resulted in the development of a single Al-substituted ordered Li$_{0.5}$Al$_{2.5}$O$_4$ spinel-related phase. This temperature is ~ 450-500°C lower than those at which the material has been formed by traditional sintering techniques [14,15]. ICP analysis of the metallic components showed the lithium content of the product to be 2.02%, that of aluminum to be 3.66% and that of iron to be 60.43% of the total ferrite weight. This gives an Al : Fe atomic ratio of ~ 1: 8.

In contrast to the formation of pure Li$_{0.5}$Al$_{2.5}$O$_4$ (or Ti$^{4+}$- or Cu$^{2+}$-substituted variants of which) via the α-Fe$_2$O$_3$/Li$_2$CO$_3$ system and under similar heating conditions [16], no intermediate polymorph of LiFeO$_2$ develops during the formation process of the Al-substituted Li$_{0.5}$Al$_{2.5}$O$_4$ outlined here.

### 3.2 Rietveld Refinement of the X-ray powder diffraction pattern of aluminum-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$:

The X-ray powder diffraction pattern recorded from the Al-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$ sample following calcination at 700°C for 12h is similar to that of ordered Li$_{0.5}$Fe$_{2.5}$O$_4$ which is characterized by superstructure reflection peaks [17] and indexed to the P4$_3$32 space group implying an atomic order of the
1:3 type among the heterovalent cations in the octahedral sublattice. The best Rietveld structural refinement of the X-ray powder diffraction data (Fig. 2 and Table 1) obtained was based on a model in which Al$^{3+}$ substitutes both Fe$^{3+}$ and Li$^{+}$ at 12$d$ and 4$b$ octahedral sites respectively with some substituted lithium replacing Fe$^{3+}$ at tetrahedral sites rather than a model in which Al$^{3+}$ only substitutes Fe$^{3+}$ on octahedral sites.

Figure 2: Observed (solid circles), calculated (solid line) and difference X-ray powder diffraction patterns of aluminum-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$.

Table 1: Refined atomic parameters form powder X-ray diffraction for aluminum-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$. % Li (analysis): 2.13, %Li (XRD): 1.75, % Al (analysis): 3.64, %Al (XRD): 5.02, % Fe (analysis): 60.14, % Fe (XRD): 60.71; unit cell P4$_3$ 32; $a=8.3002(1)$. Constraints: $B_{iso}$ all equal. Occupancy Al1 = 4 - Li1, Al2 = 12 - Fe2, Li2 = 8 - Fe1.R-factors: $R_{exp} = 7.8\%$, $R_{wp} = 11.4\%$ $R_{exp}$ and $R_{wp}$ have their normal significance and relate to regions of the profile at which Bragg peaks contribute.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyck. position</th>
<th>$x/a$</th>
<th>$y/b$</th>
<th>$z/c$</th>
<th>Occ.</th>
<th>$B_{iso}$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li1</td>
<td>4$b$</td>
<td>0.6250(0)</td>
<td>0.6250(0)</td>
<td>0.6250(0)</td>
<td>3.16 (6)</td>
<td>0.16(4)</td>
</tr>
<tr>
<td>Al1</td>
<td>4$b$</td>
<td>0.6250(0)</td>
<td>0.6250(0)</td>
<td>0.6250(0)</td>
<td>0.84(6)</td>
<td>0.16(4)</td>
</tr>
<tr>
<td>Fe1</td>
<td>8$c$</td>
<td>0.0000(0)</td>
<td>0.0000(0)</td>
<td>0.0000(0)</td>
<td>7.26 (6)</td>
<td>0.16(4)</td>
</tr>
<tr>
<td>Li2</td>
<td>8$c$</td>
<td>0.0000(0)</td>
<td>0.0000(0)</td>
<td>0.0000(0)</td>
<td>0.74(6)</td>
<td>0.16(4)</td>
</tr>
<tr>
<td>Fe2</td>
<td>12$d$</td>
<td>0.1250(0)</td>
<td>0.3670(4)</td>
<td>0.8826(4)</td>
<td>10.13(23)</td>
<td>0.16(4)</td>
</tr>
<tr>
<td>Al2</td>
<td>12$d$</td>
<td>0.1250(0)</td>
<td>0.3670(4)</td>
<td>0.8826(4)</td>
<td>1.87(23)</td>
<td>0.16(4)</td>
</tr>
<tr>
<td>O</td>
<td>8$c$</td>
<td>0.3849(9)</td>
<td>0.3849(9)</td>
<td>0.3849(9)</td>
<td>8.00(0)</td>
<td>0.16(4)</td>
</tr>
<tr>
<td>O</td>
<td>24$e$</td>
<td>0.1172(9)</td>
<td>0.1251(7)</td>
<td>0.3836(8)</td>
<td>24.00(0)</td>
<td>0.16(4)</td>
</tr>
</tbody>
</table>
Using the structural data in Table 1, it can be shown that the unequal numbers of \( \text{Al}^{3+} \) impurities substituting \( \text{Li}^{+} \) ions and \( \text{Li}^{+} \) impurities substituting tetrahedral \( \text{Fe}^{3+} \) ions (or \( \text{Al}^{3+}_{\text{Li}} \) and \( \text{Li}^{+}_{\text{Fe}} \) in the Kröger–Vink notation) lead to a net charge of \( \sim +0.05 \) per formula unit. This suggests that the overall charge balancing may be due to the reduction of \( \sim 0.3\% \text{Fe}^{3+} \) to \( \text{Fe}^{2+} \) which is too small to be detected by any of the techniques used in the present investigation. This structural model suggests a compositional formula for the material of the type \( \text{Li}_{0.4875}\text{Al}_{0.2625}\text{Fe}_{2.1778}\text{O}_4 \) in which the ratio \( \text{Al}:\text{Fe} \) is \( \sim 1:8 \) which is similar to that detected by chemical analysis. One notes that even though the 1 : 3 atomic order of among the heterovalent cations in the octahedral sublattice is not strictly obeyed, the superstructure reflection peaks are still present. This implies a long range ordering within the crystal lattice which is not disturbed by isolated local defects. It remains to be noted that while this structural model is consistent with published reports that in aluminum-substituted lithium ferrites, \( \text{Al}^{3+} \) ions are located at octahedral sites, it is different in showing that \( \text{Li}^{+} \) ions are not exclusively located on B sites as suggested by Zhilyakov and Naiden [15] but are partially transferred to A sites. The lattice constant of the Al-substituted \( \text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4 \) obtained is 8.3002(1)Å which is slightly smaller than corresponding value of 8.3311Å for pure \( \text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4 \) [17] and reflects the smaller ionic radius of \( \text{Al}^{3+} \) (0.53Å) relative to that of \( \text{Fe}^{3+} \) (0.65Å)[18].

### 3.3 Mössbauer and magnetic measurements

The \( ^{57}\text{Fe} \) Mössbauer spectrum recorded at 298K from Al-substituted \( \text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4 \) prepared at 700°C (Fig. 3 and Table 2) showed a well defined Zeeman six-line pattern characteristic of spinel ferrite superimposed on a weak paramagnetic doublet. The isomer shift quadrupole splitting values of the doublet, 0.28 mms\(^{-1}\) and 0.26mms\(^{-1}\) respectively, are comparable to those reported for crystalline \( \text{Fe}^{2+}\text{Al}^{5+} \) [19] which are 0.24mms\(^{-1}\) and 0.26mms\(^{-1}\) respectively. Since no phase, other than the Al-substituted \( \text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4 \) inverse spinel-related phase was detected by X-ray powder diffraction we may attribute this paramagnetic doublet to \( \text{Fe}^{3+} \) sites which have Al atoms at the nearest neighbourhood in the substituted ferrite. A simple model was adopted to fit the six-line magnetic part of the Mössbauer spectrum, which accounts to \( \sim 92\% \) of the spectral area, with two overlapping sextets corresponding to \( \text{Fe}^{3+} \) ions on the
tetrahedral A and octahedral B coordination sites. The chemical isomer shift and quadrupole splitting values for both sites were found to be similar to those reported previously for pure Li$_{0.5}$Fe$_{2.5}$O$_4$, thus indicating a negligible influence on the s-electron charge distribution of the Fe$^{3+}$ ions [8,10,20].

Figure 3: $^{57}$Fe Mössbauer spectrum recorded from the aluminum-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$. The solid line is the best fit to experimental data (solid circles). The bars refer to theoretical subspectra.

Table 2: $^{57}$Fe Mössbauer parameters for aluminum–substituted Li$_{0.5}$Fe$_{2.5}$O$_4$ at 298K

<table>
<thead>
<tr>
<th>Subspectrum</th>
<th>$\delta$ ± 0.01 (mm s$^{-1}$)</th>
<th>$\Delta$ ± 0.01 (mm s$^{-1}$)</th>
<th>$H_{\text{eff}}$ ± 0.1(T)</th>
<th>A ±(1%) relative to total spectrum</th>
<th>A ±1(%) relative to magnetic component</th>
</tr>
</thead>
<tbody>
<tr>
<td>sextet A</td>
<td>0.15 ± 0.01</td>
<td>0.01</td>
<td>49.3 ± 0.1</td>
<td>35</td>
<td>38</td>
</tr>
<tr>
<td>sextet B</td>
<td>0.35 ± 0.00</td>
<td>0.00</td>
<td>50.2 ± 0.1</td>
<td>57</td>
<td>62</td>
</tr>
<tr>
<td>doublet C</td>
<td>0.28 ± 0.26</td>
<td>0.26</td>
<td>8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\delta$ = chemical isomer shift, $\Delta$ = quadrupole splitting, $H_{\text{eff}}$ = hyperfine magnetic field, A = spectral area.

The values of the hyperfine magnetic field $H_{\text{eff}}$ for both sites are smaller than the corresponding values reported for Li$_{0.5}$Fe$_{2.5}$O$_4$ (50.5 T and 51.0 T for the A site and B site respectively) [21]. This is attributed to
the presence of the non-magnetic Al$^{3+}$ and Li$^+$ ions in the neighbourhood of Fe$^{3+}$ ions on both sites which leads to a decrease of the Fe$_A$-O-Fe$_B$ exchange interaction. If the diamagnetic Al$^{3+}$ ions exclusively substitute Fe$^{3+}$ ions on the B site only, the relative spectral area of the B sextet should decrease appreciably from the corresponding value for pure Li$_{0.5}$Fe$_{2.5}$O$_4$, (60%) as the number of octahedral Fe$^{3+}$ ions will decrease. Table 2, however, shows that the relative areas of the A sextet and B sextet in the magnetic spectrum of the Al-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$ (38% and 62% respectively) are, within experimental errors, similar to those of pure Li$_{0.5}$Fe$_{2.5}$O$_4$. This, therefore, excludes the possibility of Fe$^{3+}$ ions being expelled from the B site only following substitution by diamagnetic Al$^{3+}$ and suggests that Fe$^{3+}$ ions are expelled from both A and B sublattices. This is consistent with the structural model suggested by the Rietveld refinement of the X-ray diffraction pattern in which Al$^{3+}$ substitutes octahedral Fe$^{3+}$ and Li$^+$ partially substitutes tetrahedral Fe$^{3+}$.

![Figure 4](image)

**Figure 4:** Temperature dependence of magnetization of aluminum-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$ (open squares) and Li$_{0.5}$Fe$_{2.5}$O$_4$ (solid squares).

Fig. 4 shows the thermal variation of the magnetization for both pure and Al-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$. The magnetization, for both compounds, decreases monotonically with increasing
temperature. The steep decrease in the magnetization value at the Curie temperature was used to estimate the Curie temperature. It is seen, throughout the temperature range studied, that the magnetization of the Al-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$ sample is lower than that of the corresponding pristine. This can, also, be accounted for in terms of the structural model discussed above. From Table 1, it can be deduced that the number of Fe$^{3+}$ ions replaced by non-magnetic Al$^{3+}$ ones at the 12d octahedral sites (16% of the total sublattice occupancy) is higher than those replaced by non-magnetic Li$^+$ ions at the 8c tetrahedral sites (10% of the total occupancy). This will lead to a decrease of the net magnetization which is given by $M_B - M_A$ (where $M_A$ and $M_B$ are the magnetic moment of sublattices A and B respectively). The presence of the non-magnetic Al$^{3+}$ and Li$^+$ ions in both A and B sites does weaken the inter-sublattice exchange interaction which becomes comparable to the intra-sublattice exchange interaction. This, in turn, leads to spin canting in both sublattices which can result in the lower magnetization values observed. This reasoning can also be used to explain the apparent decrease in the Curie temperature from 887K for pure Li$_{0.5}$Fe$_{2.5}$O$_4$ [22] to ~ 840K for Al-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$.

4. Conclusion

Spinel-related aluminum-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$ has been synthesized from hydrothermally prepared aluminum-substituted corndum related $\alpha$-Fe$_2$O$_3$ and Li$_2$CO$_3$ at lower temperatures than those at which it synthesized by conventional ceramic techniques. Rietveld refinement of the X-ray powder diffraction data suggests a model in which Al$^{3+}$ substitutes both Fe$^{3+}$ and Li$^+$ at octahedral sites while the substituted lithium replaces Fe$^{3+}$ at tetrahedral sites. Chemical analysis, $^{57}$Fe Mössbauer and magnetic data are consistent with this structural model.

Acknowledgements

We thank the Abdus Salam International Centre for Theoretical Physics, Trieste, Italy (ICTP), UNESCO and the Swedish International Co-operation and Development Agency (SIDA) for financial and research support to HMW within the framework of the ICTP Associateship Scheme.
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