THE INFLUENCE OF TiO₂ POLYMORPH, MECHANICAL MILLING AND SUBSEQUENT SINTERING ON THE FORMATION OF Ti-SUBSTITUTED SPINEL-RELATED Li₀.₅Fe₂.₅O₄

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Abstract

Single-phased spinel-related titanium-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$ has been synthesized by sintering in air a mechanically pre-milled mixture of lithium carbonate, corundum-related iron (III) oxide and the rutile polymorph of titanium (IV) oxide at 700°C (12h). This temperature is ca. 450-500°C less than the temperatures at which the material is normally prepared by conventional ceramic techniques. On replacing the rutile polymorph of titanium (IV) oxide in the pre-milled mixture by the anatase form the formation of single-phased titanium substituted Li$_{0.5}$Fe$_{2.5}$O$_4$ was not achieved even after sintering the mixture at 1000°C (12h).
1. Introduction

The ferrimagnetic lithium ferrite Li$_{0.5}$Fe$_{2.5}$O$_4$ adopts an inverse spinel structure in which all the Li$^+$ ions and 3/5 of all Fe$^{3+}$ ions occupy the octahedral B-sites whilst the remaining Fe$^{3+}$ ions occupy tetrahedral A-sites [1]. The material is extensively studied due to its desirable electric and magnetic properties that render it attractive in microwave and memory-core applications[1-4]. The magnetic moments on the A- and B-sub-lattices are antiparallel, indicating that the dominant contribution to magnetization comes from the octahedral B-sub-lattice. The magnetic properties of Li$_{0.5}$Fe$_{2.5}$O$_4$ can, thus, be modified by substituting magnetic and/or diamagnetic cations for Fe$^{3+}$ ions on either sub-lattice, thus allowing the material to be tailored for a specific application [1]. Ti$^{4+}$, for instance, is known to have a strong octahedral site preference and therefore works very well for magnetization reduction [1]. The incorporation of Ti$^{4+}$ in the spinel-related structure of Li$_{0.5}$Fe$_{2.5}$O$_4$ is stabilized by excess Li$^+$ ions above the number in Li$_{0.5}$Fe$_{2.5}$O$_4$, that substitute Fe$^{3+}$ on tetrahedral sites, leading to a formula of the type Li$_{0.5+0.5X}$Fe$_{2.5-1.5X}$Ti$_X$O$_4$ [1,5,6]. Normally, the material is prepared by the conventional ceramic double sintering method in which solid state reactions between oxides and/or carbonates of Li, Fe(III) and Ti(IV) require prolonged heat exposure at elevated temperatures (typically $\sim$1200$^{\circ}$C) [1,7,8]. One of the disadvantages of high temperature sintering is the volatility of Li$_2$O and the irreversible reduction of Fe$^{3+}$ to Fe$^{2+}$ with the consequent precipitation of $\alpha$-Fe$_2$O$_3$ and Fe$_3$O$_4$ depending on the cooling regime adopted [1,4]. As a result, the saturation magnetization of the material is lowered and its conductivity increased limiting its use in, for example, microwave applications where high saturation magnetization and high resistivity are required [1,9]. As a remedy, it has been pointed out that to avoid the drawbacks associated with high temperature-sintering, substituted lithium ferrites should be synthesized at or below 850$^{\circ}$C [10].

We note that although a substantial literature has accumulated on the use of mechanical milling for lowering the temperatures of formation for many ferrites [11], there is only limited information on the use of the technique to synthesize pure or substituted lithium ferrites [4,5,12]. Of particular interest is an earlier investigation [5] which reported the formation of Ti-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$ at 870 $^{\circ}$C by milling a mixture of the anatase polymorph of TiO$_2$, $\alpha$-Fe$_2$O$_3$ and Li$_2$O followed by double sintering under oxygen flow for 36h. However, the influence of other polymorphs of TiO$_2$ on the formation of the material was not investigated and the role of the milling process in lowering the material temperature of formation was not identified. It can also be noted that prolonged sintering adopted (36h in total) under oxygen flow makes that preparation route both technically demanding and costly. We report here on a simple method for synthesizing single-phased Ti-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$ by sintering in air a pre-milled mixture of $\alpha$-Fe$_2$O$_3$, Li$_2$CO$_3$ and the rutile polymorph of TiO$_2$ at the relatively low temperature of 700$^{\circ}$C for a period 12h. In contrast, we show that sintering a similarly pre-milled mixture, in which the anatase polymorph replaces the rutile form of TiO$_2$, does not lead to the formation of a single-phased Ti-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$ even at 1000$^{\circ}$C (12h). The role of milling in lowering the formation temperature is stressed.

2. Experimental

To prepare Ti-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$ of the composition Li$_{0.65}$Fe$_{2.05}$Ti$_{0.3}$O$_4$ (i.e. x= 3 in the general formula Li$_{0.5+0.5X}$Fe$_{2.5-1.5X}$Ti$_X$O$_4$), the corresponding molar amounts of TiO$_2$ (in either the anatase or rutile form), $\alpha$-Fe$_2$O$_3$ and Li$_2$CO$_3$ were well mixed and dry-milled in a Retsch PM400 planetary ball mill with a stainless steel vial (250 ml) and balls (20mm) operating at a milling speed of
200 rpm for 190 hours. The powder to ball weight ratio was 1:20. Small amounts of milled powders were removed at intervals during the milling. The milled powder was then sintered for 12-h periods in air at temperatures between 300°C and 1000°C. Following each heat-treatment the material is quenched in air. X-ray powder diffraction patterns were recorded with a Siemens D5000 diffractometer using CuKα radiation. The program powdercell was used to analyze the X-ray powder diffraction [13]. 57Fe Mössbauer measurement was recorded at room temperature using a microprocessor-controlled Mössbauer spectrometer with a 25 mCi 57Co/Ph source. Chemical isomer shift data are quoted relative to that of metallic iron at room temperature.

3. Results and Discussion

3.1.a Milling the rutile-containing mixture

The X-ray powder diffraction patterns recorded from the mixture of α-Fe₂O₃, Li₂CO₃ and the rutile polymorph of TiO₂ following mechanical milling in air for various periods of time are collected in Fig. 1.

![Fig.1: X-ray powder diffraction patterns recorded from the mixture of α-Fe₂O₃ (ξ), rutile modification of TiO₂ (ζ) and Li₂CO₃ (B) following ball milling at the times indicated. 110 and 104 are the Miller indices of the α-Fe₂O₃ reflection peaks shown indicated.](image)

The X-ray powder diffraction pattern of the non-milled (0h) mixture shows the peaks characteristic of the initial reactants. The very low peak-intensities of the rutile and Li₂CO₃ components relative to those of α-Fe₂O₃ reflects both their small quantities as well as the low scattering factors of both Ti⁴⁺ and Li⁺ relative to that of Fe³⁺[5]. After milling for 3h, the peaks corresponding to Li₂CO₃ and rutileTiO₂ almost disappear, while those attributable to α-Fe₂O₃ start to broaden and decrease in intensity indicating a significant decrease in the crystallite size for all components. Milling the mixture for periods between 10h and 190h shows a gradual broadening and intensity decrease of the reflection peaks of the α-Fe₂O₃ related phase. The variation of the crystallite
size of this phase, determined from the X-ray diffraction data using the Scherrer formula, versus milling time is shown in Fig. 2. While a fast decrease in the crystallite size is observed in the first 10h of milling from ca. 1.1 µm to ca. 17nm , for the next 180h only a slight decrease is observed.

![Graph](image)

**Fig. 2**: Variation of the crystallite size with milling time for the α-Fe₂O₃ related phase for the mixture of α-Fe₂O₃, rutile modification of TiO₂ and Li₂CO₃.

It is interesting to note that with increasing milling time, the intensity of the 104 reflection peak of the α-Fe₂O₃-related phase (at ca. 33° 2θ) (Fig. 1) decreases relative to that of the 110 peak (at ca. 36° 2θ) until both peaks become approximately equal in intensity. A similar behavior was reported when Li⁺ [4] or Ti⁴⁺ [14] were incorporated in the α-Fe₂O₃ structure. This is suggestive that milling induces a reaction between the reactants to form Li⁺- and Ti⁴⁺- substituted α-Fe₂O₃ nanoparticles. This is confirmed by comparing the lattice parameters obtained from the α-Fe₂O₃-related phase after milling for 190h with those of pure α-Fe₂O₃. While the variation in the c parameter was not significant, the a and b parameters were found to be 5.027Å relative to 5.035 Å for pure α-Fe₂O₃. We have reported a similar decrease when Li⁺ was incorporated in both pure and Ti-substituted α-Fe₂O₃-related matrix [4,15].

Taken together these results indicate that milling the rutile-containing mixture for 190h induces a reaction that leads to the progressive incorporation of Li⁺, Ti⁴⁺ or both in the nanocrystalline α-Fe₂O₃ structure. Additionally, the absence of reflection peaks attributable Li₂CO₃ and rutile TiO₂ in the X-ray diffraction patterns recorded from samples milled for 10h and above can originate from nanoaggregates in which unreacted particles enjoy a large interface and are tightly pressed together.

3.1.1 Sintering the pre-milled rutile-containing-mixture
The X-ray powder diffraction patterns recorded from the 190h-milled mixture of \( \alpha \text{-Fe}_2\text{O}_3 \), rutile TiO2 and Li2CO3 following heating at different temperature for 12-h intervals in air are shown in Fig. 3.

Sintering the mixture at 400°C (12h) followed by quenching in air resulted in the appearance of very broad peaks of low intensity in the X-ray diffraction indicated by \( \alpha \) in Fig. 3. These new peaks are indexed to an \( \alpha \)-LiFeO2-related phase (most intense peak is at ca. 43.5°)[16]. A similar phase evolution has been observed when a pre-milled mixture of \( \alpha \)-Fe2O3 and Li2CO3 was submitted to a similar thermal treatment [4]. The enhancement of intensity of the 104 peak relative to that of 110 signifies the removal of Li\(^{2+}\) ions from the \( \alpha \)-Fe2O3 structure to form the \( \alpha \)-LiFeO2-related phase.

When the mixture was sintered at 500°C (12h) and then quenched in air, the peaks corresponding to the \( \alpha \)-Fe2O3-related phase remain dominant. However a spinel-related Li\(_{0.5}\)Fe\(_{2.5}\)O\(_4\) phase is also formed at this temperature as indicated by the appearance, in Fig. 3, of reflection peaks that could be indexed to it. This is indicative that the \( \alpha \)-LiFeO2-related phase is an intermediate one in the formation process of the spinel-related lithium ferrite phase. Sintering of the mixture at 600°C (12h) and then quenching in air shows the X-ray reflection peaks of the \( \alpha \)-Fe2O3-related phase to nearly disappear while those of the inverse spinel-related Li\(_{0.5}\)Fe\(_{2.5}\)O\(_4\) phase dominate implying that the reaction between the initial components is almost complete.

Further sintering at 700°C (12h) and subsequent quenching in air resulted in the development of a single inverse spinel-related Li\(_{0.5}\)Fe\(_{2.5}\)O\(_4\) phase. To see whether Ti\(^{4+}\) ions are
incorporated in the Li$_{0.5}$Fe$_{2.5}$O$_4$ structure, we note that only the main spinel reflection peaks originating from the crystalline planes (220), (311), (400), (422), (511) and (440) appear in the pattern. The super-lattice structure peaks that appear in the X-ray diffraction pattern of pure Li$_{0.5}$Fe$_{2.5}$O$_4$ at 700°C due to the ordered distribution of Fe$^{3+}$ and Li$^+$ over octahedral B-sites are missing. This in turn indicates that the Ti$^{4+}$ ions are incorporated in Li$_{0.5}$Fe$_{2.5}$O$_4$ resulting in a random cation distribution over the octahedral B-sites. The value of the lattice parameter $a$ obtained is 0.833 nm which is nearly the same as that of pure Li$_{0.5}$Fe$_{2.5}$O$_4$ (0.832 nm) is consistent to values reported by other workers for Ti-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$ and reflects nearly equal ionic radii of Ti$^{4+}$ (0.064 nm), Li$^+$ (0.068 nm) and Fe$^{3+}$ (0.068 nm) [3,7].

As a further confirmation that monophasic Ti-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$ was prepared by sintering the rutile-containing mixture at 700°C, Fig. 4 shows the Mössbauer spectrum recorded at room temperature from the material. The spectrum was best-fitted with two overlapping sextets corresponding to Fe$^{3+}$ ions on both tetrahedral A- and octahedral B-sites of the lithium spinel ferrite. The hyperfine parameters obtained are summarized in Table 1. The isomer shift, quadrupole and magnetic hyperfine field values for both sextets agree well with those reported for Ti-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$ [7,8].

The observed decrease in values of $H_{hf}$ on both sites (Table 1) relative those of pure Li$_{0.5}$Fe$_{2.5}$O$_4$ (50.5T and 51.0T for the A- and B- site respectively [7]) is explicable in terms of Neel’s molecular field model theory. The substitution of the non-magnetic ions Ti$^{4+}$ and Li$^+$ for Fe$^{3+}$ on the B- and A- sites respectively, leads to decreasing the number of Fe$^{3+}$-O$_{2-}$-Fe$^{3+}$ magnetic bonds on both sites and consequently their hyperfine field values decrease.

![Mössbauer Spectrum](image)

**Fig. 4:** The room temperature $^{57}$Fe Mössbauer spectrum recorded from the 190h-pre-milled mixture of α-Fe$_2$O$_3$, the rutile modification of TiO$_2$ sintered in air at 700°C (12h).

**Table 1.** Room temperature $^{57}$Fe Mössbauer parameters of Ti-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$ prepared by sintering the pre-milled rutile-containing mixture at 700°C (see text).
Taking all Ti$^{4+}$ and excess Li$^+$ ions to substitute for Fe$^{3+}$ at the B- and A-sites respectively [6] and assuming a similar recoilless fraction in both sites, the intensities of both sextets (Table 1) suggest for the material obtained at 700°C a compositional formula of Li$_{0.75}$Ti$_{0.50}$Fe$_{1.75}$O$_4$ compared to the initially sought Li$_{0.65}$Ti$_{0.30}$Fe$_{2.05}$O$_4$. While this is not a rigorous way to obtain the composition formula, it nevertheless gives a hint that the amount of Ti$^{4+}$ relative to that of Fe$^{3+}$ in the final product can slightly be larger than initially intended. This may be attributed to α-Fe$_2$O$_3$ fine particles that adhere to the walls and the lid of the milling vial during the initial milling stages and hence do not take part in the milling-induced reaction. Consequently this leads to decreasing the Fe$^{3+}$ content in the final product. The discrepancy between the desired composition and the final composition can be minimized by frequently opening the vial and mildly filing the accumulated layer of the reactants on the inner surface of the vial. Of course, the final composition has to be determined using a reliable analytical technique.

We intended the preceding discussion to show that both X-ray diffraction and Mössbauer spectroscopy have shown the material obtained at 700°C by sintering the pre-milled rutile-containing mixture to be single-phased Ti-substituted Li$_0.5$Fe$_2.5$O$_4$. This temperature is ca. 450-500°C lower than the temperatures normally used to prepare the material by conventional ‘ceramic’ double sintering techniques. The efficient sintering in terms of both in the short duration and the low temperature of formation of the final product, achieved here relative to conventional double sintering is obviously a consequent of the prolonged milling process. While short-time milling has been used routinely to produce fine particles with large surface area to facilitate sintering [1,5] in the present work prolonged milling was used to induce a solid state reaction between the initial components as well. Both the fine particles where the initial reactants are tightly pressed and the Li$^+$ and/or Ti$^{4+}$-substituted α-Fe$_2$O$_3$ nanoparticles derived from the milling process lead to a large number of ionic diffusion paths that accelerate completion of the reaction using a lower thermal activation energy and hence lower temperature than required conventionally.

### 3.2.a Milling the anatase-containing mixture

The X-ray powder diffraction patterns recorded from the mixture of α-Fe$_2$O$_3$, Li$_2$CO$_3$ and the anatase polymorph of TiO$_2$ following identical milling conditions in air to that used in the case of the rutile-containing mixture are shown in Fig. 5.

<table>
<thead>
<tr>
<th>sub-spectrum</th>
<th>IS (mm/s)</th>
<th>QS (mm/s)</th>
<th>H$_{hf}$ (T)</th>
<th>I (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.23</td>
<td>0.00</td>
<td>49.2</td>
<td>43</td>
</tr>
<tr>
<td>B</td>
<td>0.29</td>
<td>0.00</td>
<td>50.9</td>
<td>57</td>
</tr>
</tbody>
</table>

IS= isomer shift; QS= quadrupole splitting; H$_{hf}$ = hyperfine magnetic field; I = intensity relative to total spectrum.
Fig. 5: X-ray powder diffraction patterns recorded from a mixture of α-Fe₂O₃ (ξ), anatase modification of TiO₂ (η) and Li₂CO₃ (Β) following ball milling at the times indicated. 110 and 104 are the Miller indices of the α-Fe₂O₃ reflection peaks shown.

Generally, as in the case of the rutile-containing mixture, the peaks corresponding to the corundum-related α-Fe₂O₃ progressively broaden and decrease in intensity with increasing milling time up to 190h. The peaks corresponding to Li₂CO₃ completely disappear after 10h of milling, and the relative intensities of the 104 and 110 of α-Fe₂O₃ change in a similar way to that encountered in the case of the rutile-containing mixture. This indicates that milling leads cationic substitution of the α-Fe₂O₃ structure. However, unlike the case of the rutile-containing mixture where the rutile reflection peaks disappear after 3h of milling, the most intense reflection peak of anatase (ca. 25.5° 2θ), can be observed even after 40h of milling. This is indicative that the milling-induced reaction rate between α-Fe₂O₃ with anatase TiO₂ is weaker relative to that with rutile TiO₂. The values of the lattice parameters obtained for the α-Fe₂O₃ related phase following milling the anatase-containing mixture for 190h do reflect that. While the c lattice parameters has remained similar to that of pure α-Fe₂O₃, the value of the a and b parameters were found to be 5.031 Å relative to 5.027Å for the corresponding phase obtained from the rutile-containing mixture. Thus we conclude that less Ti⁴⁺ and Li⁺ ions are incorporated in the α-Fe₂O₃ structure when anatase was used instead of rutile. To explain that we note that milling pure anatase TiO₂ under identical conditions to those used here converts it after 20h to the rutile form of TiO₂ [17]. However, the anatase-to-rutile conversion mechanism can be precluded in the presence of other phases[17,18]. Since this is applicable to our present case, we conclude that following 190h of milling, the anatase-containing mixture transforms into a mixture of Ti⁴⁺ and/or Li⁺ substituted α-Fe₂O₃ as well as unreacted α-Fe₂O₃ and anatase particles that did not undergo conversion to rutile.
3.2.2 Sintering the pre-milled anatase-containing-mixture

The X-ray powder diffraction patterns recorded from the mixture of $\alpha$-Fe$_2$O$_3$, the anatase polymorph of TiO$_2$ and Li$_2$CO$_3$ milled for 190h following sintering at different temperature for 12-h intervals in air are shown in Fig. 6.

![X-ray powder diffraction patterns](image)

**Fig. 6**: X-ray powder diffraction patterns recorded from the 190h-pre-milled mixture of $\alpha$-Fe$_2$O$_3$, anatase modification of TiO$_2$ and Li$_2$CO$_3$ following sintering in air for 12-h periods at the temperatures indicated; $\alpha$ refers to $\alpha$-LiFeO$_2$ related phase.

Sintering the pre-milled anatase-containing mixture at 500°C (12h) followed by quenching in air resulted in the appearance of a broad peak of low intensity centered around ca. 43.5° 20 in the X-ray diffraction (indicated by $\alpha$ in Fig. 6) which may be indexed, as before, to an $\alpha$-LiFeO$_2$-related phase. The presence of this weak peak (which is the most intense of $\alpha$-LiFeO$_2$) reflects its small amount as well as the weakness of the induced reaction between the components of the mixture. Comparing this finding with that obtained from the rutile-containing pre-milled mixture sintered at 500°C, viz. the onset of the formation of Li$_{0.5}$Fe$_{2.5}$O$_4$ related-phase, indicates that the presence of anatase TiO$_2$ nanoparticles in pre-milled mixture slows the reaction rate. A simple explanation to that can be the low concentration of both Li$^+$ and Ti$^{4+}$ in the $\alpha$-Fe$_2$O$_3$ particles relative to those achieved in the case of the rutile-containing mixture. This, in turn, weakens the ionic interdiffusion rates in the anatase-containing mixture.

Sintering the anatase-containing pre-milled mixture at 600°C (12h) followed by quenching in air resulted in the development of a Li$_{0.5}$Fe$_{2.5}$O$_4$- related-phase coexisting with unreacted $\alpha$-Fe$_2$O$_3$-related phase. Both phase co-existed as the sintering temperature is increased even up to 1000°C (12h) as seen in Fig. 6.
Thus while it was easy to obtain a monophasic Ti-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$ from a pre-milled rutile-containing mixture, the same was not possible when the rutile in the mixture was replaced by the anatase form of TiO$_2$ using identical milling and sintering regimes. A similar finding was reported by Berry and co-workers [17] who found the formation of monophasic pervoskite-related CaTiO$_3$ to be more easily achieved by milling CaO with the rutile modification of TiO$_2$ than with the anatase form. The arguments given in the present work can be equally valid in that case.

4. Conclusion

Sintering a 190h pre-milled mixture of Li$_2$CO$_3$, α-Fe$_2$O$_3$ and the rutile polymorph TiO$_2$ led to the formation of a single-phase spinel-related Ti-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$ at 700°C (12h). X-ray diffraction and Mössbauer techniques confirm the similarity of the structural and hyperfine parameters of the resulting material to those of Ti-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$ prepared using other routes. The lowering in the formation temperature is a consequence of both particle size and milling-induced reaction that led to the diffusion of Li$^+$ and Ti$^+$ as substitute cations in the α-Fe$_2$O$_3$ structure resulting in a large number of ionic diffusion paths that accelerate the reaction. Formation of monophasic Ti-substituted Li$_{0.5}$Fe$_{2.5}$O$_4$ was not possible using a similar pre-milled mixture containing anatase rather than rutile TiO$_2$ even after sintering at 1000°C (12h). This is related to the resistance of anatase to convert to rutile when milled in the presence of other phases.

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