

# The Influence of Mechanical Milling and Subsequent Calcination on the Formation of Lithium Ferrites

Hisham M. Widatallah\*<sup>†</sup> and Frank J. Berry\*<sup>1</sup>

\*Department of Chemistry, The Open University, Walton Hall, Milton Keynes, MK7 6AA, United Kingdom; and <sup>†</sup>Department of Physics, University of Khartoum, P.O. Box 321, Khartoum 11115, Sudan

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**The influence of ball milling and subsequent calcination of a 2.5:1 molar mixture of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Li<sub>2</sub>CO<sub>3</sub> on the formation of lithium ferrites has been investigated. Premilling was found to considerably lower the temperature at which the lithium ferrites LiFeO<sub>2</sub> and LiFe<sub>5</sub>O<sub>8</sub> are formed. A  $\beta$ -to- $\alpha$ -phase transition in LiFe<sub>5</sub>O<sub>8</sub> was found to take place on cooling from ca. 1000°C depending on the milling history and cooling regime.** © 2002

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## INTRODUCTION

The lithium ferrites of composition LiFeO<sub>2</sub> and LiFe<sub>5</sub>O<sub>8</sub> have attracted interest because of their technological applications as, for example, cathode materials in rechargeable lithium batteries and low-cost substitutes to garnets in microwave frequency applications (1–3). LiFeO<sub>2</sub> crystallizes in three modifications:  $\alpha$ -LiFeO<sub>2</sub>, which is a cation-disordered cubic phase;  $\beta$ -LiFeO<sub>2</sub>, which is a cation-disordered tetragonal phase; and  $\gamma$ -LiFeO<sub>2</sub>, which is a cation-ordered tetragonal phase (3). LiFe<sub>5</sub>O<sub>8</sub>, on the other hand, is known to occur in two crystalline forms (4). The  $\alpha$ -phase has a face-centered-cubic inverse spinel structure in which the Li<sup>+</sup> and Fe<sup>3+</sup> ions are distributed among the octahedral interstices in an ordered ratio of 1:3 and the remaining Fe<sup>3+</sup> ions are distributed on tetrahedral sites. A  $\beta$ -phase has the same structure but with the Li<sup>+</sup> and Fe<sup>3+</sup> ions randomly distributed in the octahedral interstices. The transition from the ordered  $\alpha$ -phase to the disordered  $\beta$ -phase occurs at ca 755°C (5, 6).

The preparation of polycrystalline lithium ferrites has been achieved by a variety of methods including flash firing (1), sintering of carbonates and oxides (6, 7), and spray drying of lithium and iron formates followed by

sintering (8). Lithium ferrites have also been prepared from mixtures of Li<sub>2</sub>CO<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and the structural properties found to depend on the sintering conditions (6, 9, 10). Although a substantial literature has accumulated on the synthesis of ferrites by ball milling (11–25), there is only limited information on the use of mechanical milling for the formation of lithium ferrites using the Li<sub>2</sub>CO<sub>3</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> system (1, 9) despite the developing significance of the technique for the preparation of inorganic solids (26, 27). Of particular interest is the earlier investigation which reported (1) that premilling lowers the decomposition temperature of Li<sub>2</sub>CO<sub>3</sub> and that a premilled mixture of Li<sub>2</sub>CO<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> forms Li<sub>0.5</sub>Fe<sub>2.5</sub>O<sub>4</sub> at a lower temperature than that required by the conventional solid state reaction. However, interestingly, the presence and role of LiFeO<sub>2</sub> in the process were not identified although the stoichiometry of the reactants presupposes its presence throughout the formation process (9).

In this paper we report on the formation of lithium ferrites from Li<sub>2</sub>CO<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> under the influence of mechanical milling and subsequent heating. In particular we discuss the changes brought about by premilling on the evolution of the different lithium ferrite phases.

## EXPERIMENTAL

A mixture of Li<sub>2</sub>CO<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with a lithium-to-iron molar ratio of 1:2.5 as used in a previous attempt to prepare lithium ferrites by mechanical milling (9) was prepared. One half of the mixture (30 g) was calcined for 20-h periods in air at temperatures between 300°C and 1000°C. The other half of the mixture was dry milled in air in a Retsch PM400 planetary ball mill using stainless steel vials (250 ml) and balls (20 mm) at 200 rpm for 130 h. The powder-to-ball weight ratio was 1:20. The milled powder was then calcined according to an identical regime. Materials heated at temperatures below 800°C were quenched in air whereas those produced at 850°C and 1000°C were examined after both quenching and slow cooling in the furnace.

<sup>1</sup>To whom correspondence should be addressed. Fax: +44(0) 1908 858327. E-mail: [f.j.berry@open.ac.uk](mailto:f.j.berry@open.ac.uk).



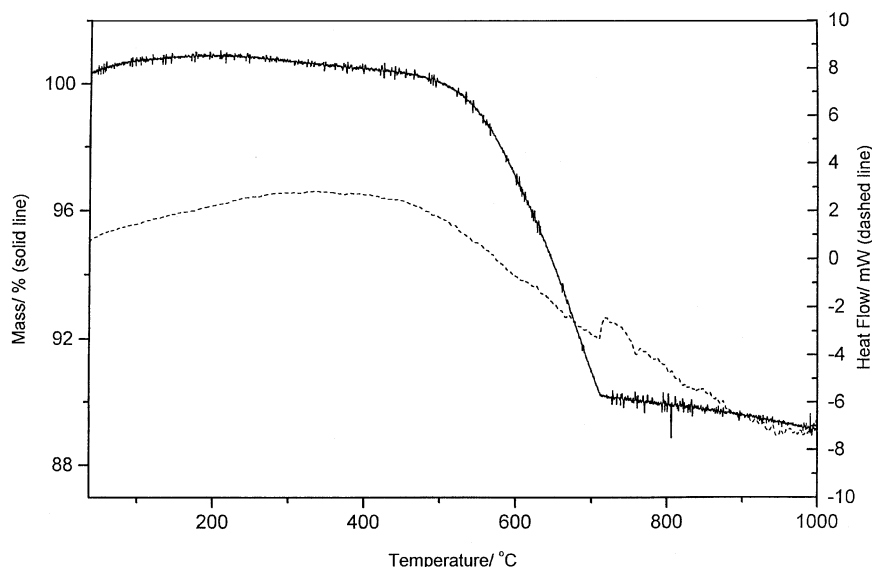


FIG. 2. TGA (solid line) and DSC (dashed line) recorded from the nonmilled mixture of  $\text{Li}_2\text{CO}_3$  and  $\alpha\text{-Fe}_2\text{O}_3$ .

the spinel-related  $\alpha\text{-LiFe}_5\text{O}_8$  phase (5, 7, 29, 30). We adopted a simple fitting model (29) to fit the  $^{57}\text{Fe}$  Mössbauer spectrum of  $\alpha\text{-LiFe}_5\text{O}_8$  with two overlapping sextets, A and B, for the octahedral and tetrahedral sites with areas proportional to the 3:2 occupancy of the  $\text{Fe}^{3+}$  ions. Assuming the same recoilless fraction for  $\alpha\text{-LiFe}_5\text{O}_8$  and  $\alpha\text{-LiFeO}_2$  the relative amount of iron in each phase determined from the Mössbauer spectrum is 3:1. The reaction stoichiometry may, therefore, be described as



which reflects both the 2.5:1 molar ratio of the reactants and the abundance of each phase in the products.

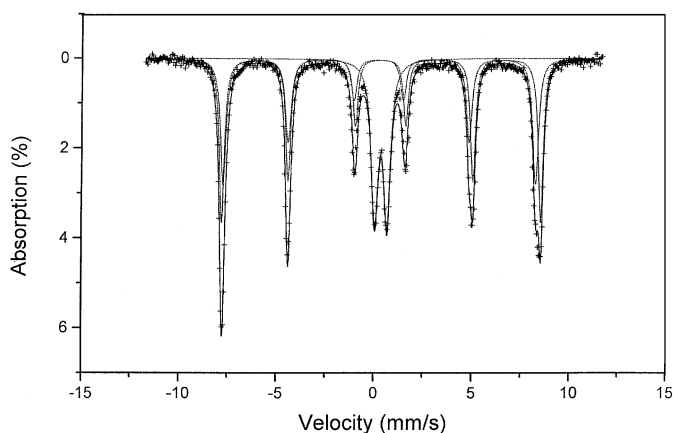


FIG. 3.  $^{57}\text{Fe}$  Mössbauer spectrum recorded from the nonmilled mixture of  $\text{Li}_2\text{CO}_3$  and  $\alpha\text{-Fe}_2\text{O}_3$  following calcination at  $700^\circ\text{C}$  (20 h) and quenching.

The X-ray powder diffraction pattern recorded from the mixture after heating at  $800^\circ\text{C}$  (20 h) and quenching in air (Fig. 1e) showed the absence of the 210 and 211 peaks at  $24$  and  $26.2^\circ 2\theta$  and the transformation of most of the ordered  $\alpha\text{-LiFe}_5\text{O}_8$  phase to disordered  $\beta\text{-LiFe}_5\text{O}_8$ . The  $\alpha\text{-LiFeO}_2$  phase remained unchanged at  $800^\circ\text{C}$ . X-ray powder diffraction and  $^{57}\text{Fe}$  Mössbauer spectroscopy showed that no further changes in either the  $\beta\text{-LiFe}_5\text{O}_8$  or  $\alpha\text{-LiFeO}_2$  phases were induced by heating at  $850^\circ\text{C}$  (20 h) and quenching in air or slowly cooling in the furnace (Fig. 1f, Table 1).

The X-ray powder diffraction pattern recorded from the mixture following heating at  $1000^\circ\text{C}$  (20 h) and slow cooling in the furnace showed a transformation of the disordered  $\beta$ -polymorph of  $\text{LiFe}_5\text{O}_8$  to the ordered  $\alpha\text{-LiFe}_5\text{O}_8$  form. We would comment that no such phase transition was observed when the mixture was quenched in air following calcination at  $1000^\circ\text{C}$  (20 h) (Fig. 1h) and the result demonstrates, as might be expected, that the cooling regime is an important factor in establishing the occurrence of a specific phase. The  $\text{LiFe}_5\text{O}_8$ -to- $\text{LiFeO}_2$  abundance ratio remained unchanged (Table 1) following cooling from  $1000^\circ\text{C}$ .

#### Mechanical Milling of the Mixture of $\alpha\text{-Fe}_2\text{O}_3$ and $\text{Li}_2\text{CO}_3$

The X-ray powder diffraction patterns recorded from the mixture of  $\text{Li}_2\text{CO}_3$  and  $\alpha\text{-Fe}_2\text{O}_3$  following ball milling at room temperature for different time intervals are collected in Fig. 4.

The results show that after 40 h of milling (Fig. 4b) the peaks characteristic of  $\text{Li}_2\text{CO}_3$  decrease in intensity and those attributable to  $\alpha\text{-Fe}_2\text{O}_3$  begin to broaden. The crystallite size of the  $\alpha\text{-Fe}_2\text{O}_3$  phase determined from the X-ray

TABLE 1

<sup>57</sup>Fe Mössbauer Parameters Recorded at 298 K from the Nonmilled Mixture of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Li<sub>2</sub>CO<sub>3</sub> Following Calcination in Air

Calcination Conditions	Phase	Subspectrum	$\delta \pm 0.02$ (mm s <sup>-1</sup> )	$\Delta \pm 0.04$ (mm s <sup>-1</sup> )	$H \pm 0.3$ (T)	$\Gamma \pm 0.02$ (mm s <sup>-1</sup> )	Area $\pm 3$ (%)
700°C (20 h) (quenched)	$\alpha$ -LiFe <sub>5</sub> O <sub>8</sub>	Sextet A	0.23	0.00	50.1	0.30	29
	$\alpha$ -LiFe <sub>5</sub> O <sub>8</sub>	Sextet B	0.39	0.01	50.7	0.30	46
	$\alpha$ -LiFeO <sub>2</sub>	Doublet	0.37	0.64		0.40	25
850°C (20 h) (quenched)	$\beta$ -LiFe <sub>5</sub> O <sub>8</sub>	Sextet A	0.23	0.00	50.1	0.33	34
	$\beta$ -LiFe <sub>5</sub> O <sub>8</sub>	Sextet B	0.40	0.02	50.6	0.31	41
	$\alpha$ -LiFeO <sub>2</sub>	Doublet	0.37	0.63		0.41	25
1000°C (20 h) (slow cooled)	$\alpha$ -LiFe <sub>5</sub> O <sub>8</sub>	Sextet A	0.24	0.00	50.0	0.33	35
	$\alpha$ -LiFe <sub>5</sub> O <sub>8</sub>	Sextet B	0.40	0.02	50.5	0.30	40
	$\alpha$ -LiFeO <sub>2</sub>	Doublet	0.37	0.63		0.40	25

powder diffraction data using the Scherrer method (Table 2) decreased from ca. 1.155  $\mu\text{m}$  to ca. 20 nm after 40 h of milling and underwent no further change in crystallite size on subsequent milling treatment. The X-ray powder diffraction pattern showed the intensity of the Li<sub>2</sub>CO<sub>3</sub> peaks to decrease after milling for 100 h and 130 h (Figs. 4c and 4d). The intensities of the 104 and 110 reflections of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (at ca. 33° and 36° 2 $\theta$ ) changed in a way similar to that observed when tin is incorporated within the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (31). Furthermore, the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> unit cell parameters for the material milled for 130 h were found to decrease (Table 3) in a way similar to that observed when lithium is incorporated within the corundum-related matrix by chemical methods (32). Taken together these results indicate that milling induces the progressive incorporation of lithium within the nanocrystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> structure. Since both Li<sub>2</sub>CO<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> are different in their mechanical properties (33), the

small crystallite size (ca. 20 nm) inferred from the X-ray powder diffraction data and the nearly complete disappearance of peaks characteristic of Li<sub>2</sub>CO<sub>3</sub> suggests the formation of nanoaggregates consisting of lithium-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> together with particles where both reactants enjoy a large interface and are tightly pressed together.

#### Calcination of the Premilled Mixture of $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Li<sub>2</sub>CO<sub>3</sub>

The X-ray powder diffraction patterns recorded from the mixture of Li<sub>2</sub>CO<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> milled for 130 h and following calcination treatment similar to that used for the nonmilled mixture are shown in Fig. 5.

Heating the premilled mixture at 400°C for 20 h followed by quenching in air (Fig. 5a) resulted in the disappearance of all the peaks corresponding to Li<sub>2</sub>CO<sub>3</sub>. New peaks corresponding to  $\gamma$ -LiFeO<sub>2</sub> appeared. The intensities of the peaks

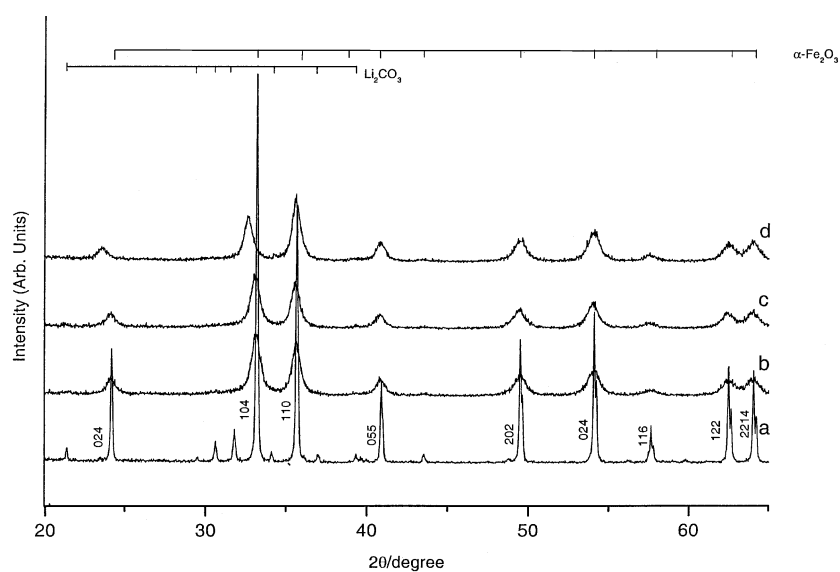


FIG. 4. X-ray powder diffraction patterns recorded from the mixture of Li<sub>2</sub>CO<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> milled for (a) 0 h; (b) 40 h; (c) 100 h; and (d) 130 h.

**TABLE 2**  
Variation of Crystallite Size with Milling Time

Milling time (h)	Particle size (nm)
0	1155
40	20
100	19
130	20

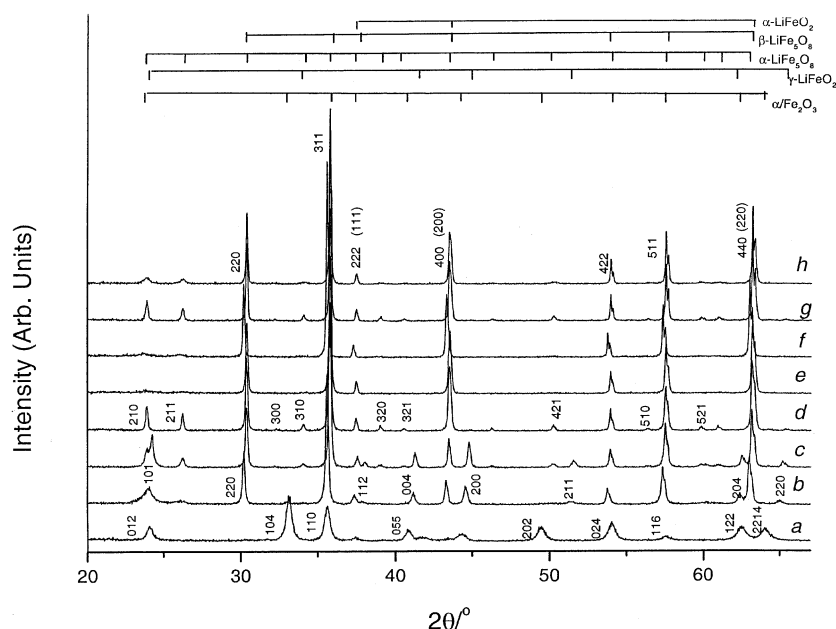
corresponding to the 104 and 110 reflections of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> at ca 33° and 36° 2 $\theta$  reverted to those expected for pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with lattice parameters also characteristic of the pure material (Table 3). The results suggest that mild thermal treatment converts lithiated  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> to  $\gamma$ -LiFeO<sub>2</sub> as well as initiating a reaction between unreacted Li<sub>2</sub>CO<sub>3</sub> and some  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> to form  $\gamma$ -LiFeO<sub>2</sub>. This is endorsed by the TGA curve (Fig. 6) recorded from the premilled mixture which shows an initial gradual mass loss due to the decomposition of Li<sub>2</sub>CO<sub>3</sub> with increasing temperature and which dramatically increases at ca. 360°C. A comparison of these results with those obtained from the nonmilled mixture shows that premilling lowers the decomposition temperature of Li<sub>2</sub>CO<sub>3</sub> in the mixture thereby leading to the formation of  $\gamma$ -LiFeO<sub>2</sub> at 400°C as opposed to ca. 500°C when the mixture is not premilled.

The influence of milling on the subsequent reaction of the premilled powder at higher temperatures is also illustrated by the X-ray powder diffraction data recorded following

**TABLE 3**  
Variation of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> Lattice Parameters with Milling Time and Calcination Temperature

Milling time (h)	Calcination temperature (°C)			
	$a \pm 0.005$ (Å)	$b \pm 0.005$ (Å)	$c \pm 0.005$ (Å)	
0	5.034	5.034	13.763	
40	5.038	5.038	13.771	
100	5.037	5.037	13.775	
130	5.012	5.012	13.704	
130	5.032	5.032	13.755	

treatment at 500°C and quenching in air (Figs. 5b). The pattern corresponded to the formation of spinel-related LiFe<sub>5</sub>O<sub>8</sub> together with a small amount of  $\gamma$ -LiFeO<sub>2</sub>. No peaks corresponding to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Li<sub>2</sub>CO<sub>3</sub> could be identified, indicating that the reaction is complete at this temperature. However, the identification of the nature of the LiFe<sub>5</sub>O<sub>8</sub> phase is difficult since the X-ray powder diffraction peaks (Fig. 5b) are broad, thus precluding identification of any of the weak superstructure peaks. The decomposition of Li<sub>2</sub>CO<sub>3</sub> and formation of the lithium ferrites was also demonstrated by the TGA curve which showed the sharp mass loss due to the decomposition of Li<sub>2</sub>CO<sub>3</sub> to be completed at ca. 500°C and to be accompanied by a sharp and deep endothermic peak ( $T_{\max} \approx 460^\circ\text{C}$ ) in the corresponding DSC curve (Fig. 6). Comparing these results with those



**FIG. 5.** X-ray powder diffraction patterns recorded from the mixture of Li<sub>2</sub>CO<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> premilled for 130 h following calcination at (a) 400°C (quenched); (b) 500°C (quenched); (c) 600°C (quenched); (d) 700°C (quenched); (e) 800°C (quenched); (f) 850°C (quenched); (g) 1000°C (slow cooled); and (h) 1000°C (quenched).

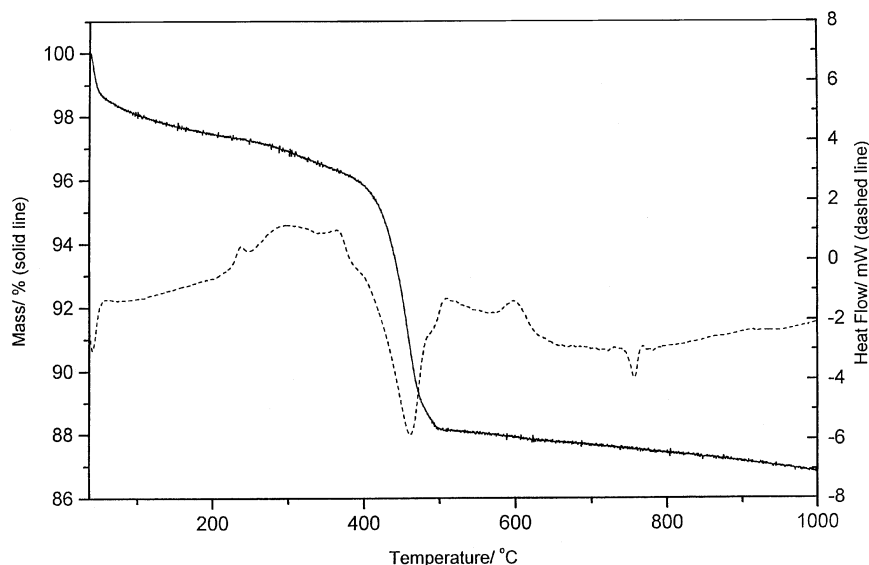


FIG. 6. TGA (solid line) and DSC (dashed line) recorded from the premilled mixture of  $\text{Li}_2\text{CO}_3$  and  $\alpha\text{-Fe}_2\text{O}_3$ .

obtained from the nonmilled mixture, where the disappearance of X-ray powder diffraction peaks corresponding to the reactants was achieved only after calcination at ca.  $700^\circ\text{C}$ , shows that premilling lowers by ca.  $200^\circ\text{C}$  the temperature at which the reaction is complete and lithium ferrites are formed.

X-ray powder diffraction (Fig. 5c) showed that following further treatment at  $600^\circ\text{C}$  and rapid quenching, the premilled mixture was converted into a mixture of ordered  $\alpha\text{-LiFe}_5\text{O}_8$  and  $\gamma\text{-LiFeO}_2$ . Further heating to  $700^\circ\text{C}$  (20 h) and quenching in air resulted in the disappearance of the peaks corresponding to the  $\gamma\text{-LiFeO}_2$  phase (Fig. 5d). The  $^{57}\text{Fe}$  Mössbauer spectrum (Table 4) showed the  $\gamma\text{-LiFeO}_2$  to transform to the  $\alpha\text{-LiFeO}_2$  polymorph with the relative amount of iron in the  $\alpha\text{-LiFe}_5\text{O}_8$  and  $\alpha\text{-LiFeO}_2$  phases being present in the expected 3:1 ratio. This result is at

variance with results previously reported (9) where only  $\text{LiFe}_5\text{O}_8$  was reported to form under identical conditions.

Further heating of the premilled mixture at  $800^\circ\text{C}$  and  $850^\circ\text{C}$  (20 h) followed by quenching gave X-ray powder diffraction patterns (Figs. 5e and 5f) that corresponded to disordered  $\beta\text{-LiFe}_5\text{O}_8$  and a small amount of  $\alpha\text{-LiFe}_5\text{O}_8$ . The DSC curve (Fig. 6) showed a sharp endothermic peak at ca.  $755^\circ\text{C}$  marking the order-disorder  $\alpha\text{-}\beta$  phase transition in  $\text{LiFe}_5\text{O}_8$  as found for the nonmilled mixture. No significant difference was observed in the X-ray powder diffraction patterns when the product was formed by slow cooling in the furnace.

The XRD pattern of the premilled mixture heated at  $1000^\circ\text{C}$  (20 h) and subsequently slowly cooled in the furnace (Fig. 5g) showed a phase transition to ordered  $\alpha\text{-LiFe}_5\text{O}_8$  similar to that observed unexpectedly for the nonmilled

TABLE 4

$^{57}\text{Fe}$  Mössbauer Parameters Recorded at 298 K from the Premilled Mixture of  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{Li}_2\text{CO}_3$  Following Calcination in Air

Calcination conditions	Phase	Subspectrum	$\delta \pm 0.02$ ( $\text{mm s}^{-1}$ )	$\Delta \pm 0.04$ ( $\text{mm s}^{-1}$ )	$H \pm 0.3$ (T)	$\Gamma \pm 0.02$ ( $\text{mm s}^{-1}$ )	Area $\pm 3$ (%)
700°C (20 h) (quenched)	$\alpha\text{-LiFe}_5\text{O}_8$	Sextet A	0.27	0.00	49.6	0.31	30
	$\alpha\text{-LiFe}_5\text{O}_8$	Sextet B	0.36	0.01	50.7	0.30	45
	$\alpha\text{-LiFeO}_2$	Doublet	0.37	0.63		0.42	25
850°C (20 h) (quenched)	$\beta\text{-LiFe}_5\text{O}_8$	Sextet A	0.27	0.01	49.6	0.33	33
	$\beta\text{-LiFe}_5\text{O}_8$	Sextet B	0.36	0.01	50.7	0.31	42
	$\alpha\text{-LiFeO}_2$	Doublet	0.37	0.63		0.43	25
1000°C (20 h) (slow cooled)	$\alpha\text{-LiFe}_5\text{O}_8$	Sextet A	0.27	0.01	49.6	0.33	32
	$\alpha\text{-LiFe}_5\text{O}_8$	Sextet B	0.36	0.01	50.6	0.31	43
	$\alpha\text{-LiFeO}_2$	Doublet	0.37	0.63		0.41	25

mixture. The room temperature Mössbauer parameters of samples prepared between 700°C and 1000°C were all similar (Table 4). When the premilled mixture was quenched from 1000°C (20 h) in air, the X-ray powder diffraction pattern (Fig. 5h) also showed a significant partial disorder-order  $\beta$ - $\alpha$  phase transition in  $\text{LiFe}_5\text{O}_8$  resulting in a significant amount of  $\alpha$ - $\text{LiFe}_5\text{O}_8$ . This is in contrast with the X-ray powder diffraction pattern of the nonmilled mixture (Fig. 1h) where only a small amount of  $\alpha$ - $\text{LiFe}_5\text{O}_8$  was observed after similar treatment. This suggests that the premilling of the reactants is important in inducing a disorder-order phase transition in  $\text{LiFe}_5\text{O}_8$  following heat treatment at 1000°C (20 h).

### CONCLUSION

Premilling a 2.5:1 molar mixture of  $\alpha$ - $\text{Fe}_2\text{O}_3$  and  $\text{Li}_2\text{CO}_3$  induces the incorporation of lithium within the nanocrystalline  $\alpha$ - $\text{Fe}_2\text{O}_3$  and increases the interface between the reactants, leading to the formation of lithium ferrites at lower temperatures.  $\gamma$ - $\text{LiFeO}_2$  was found to form at ca. 400°C compared with ca. 500°C when the mixture was not premilled. The reaction to form lithium ferrites  $\text{LiFe}_5\text{O}_8$  and  $\text{LiFeO}_2$  from a milled mixture of reactants was found to be complete at ca. 500°C as compared to ca. 700°C when the mixture was not premilled. A  $\beta$ - to- $\alpha$ -disorder-to-order phase transition in  $\text{LiFe}_5\text{O}_8$  was found to take place in both the nonmilled and premilled cases when the sample was slowly cooled from 1000°C. The premilled reactants were also found to undergo a partial but significant  $\beta$ - to- $\alpha$ -disorder-to-order phase transition in  $\text{LiFe}_5\text{O}_8$  at 1000°C when the sample was quenched from 1000°C.

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