JOURNAL OF MATERIALS SCIENCE **37** (2002) 4621–4625

The influence of ball milling and subsequent calcination on the formation of $LiFeO_2$

H. M. WIDATALLAH
Department of Chemistry, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK; Department of Physics, University of Khartoum, Khartoum, PO Box 321, 11115, Sudan

C. JOHNSON, F. J. BERRY*
Department of Chemistry, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK
E-mail: f.j.berry@open.ac.uk

The influence of ball milling and subsequent calcination of a 1:1 molar mixture of α-Fe_2O_3 and Li_2CO_3 on the formation of $LiFeO_2$ has been investigated. Pre-milling was found to lower the temperature of ferrite formation by ca. 200°C and a thermally stable γ-$LiFeO_2$ phase was found to form in the temperature range 500–600°C. Slow cooling of the pre-milled mixture calcined at higher temperatures resulted in the formation of some $LiFe_5O_8$. © *2002 Kluwer Academic Publishers*

1. Introduction

The lithium ferrite of composition $LiFeO_2$ has attracted attention as a potential cathode material in lithium ion batteries [1–3]. $LiFeO_2$ crystallises in three polymorphs: α-$LiFeO_2$ which adopts a cation disordered cubic structure, β-$LiFeO_2$ which is a cation disordered tetragonal structure and γ-$LiFeO_2$ which is a cation ordered tetragonal phase [4]. Traditional solid state synthetic routes for the preparation of $LiFeO_2$ involve the calcination in air of a 1:1 molar mixture of α- or γ-Fe_2O_3 with either Li_2O or Li_2CO_3 [4–6] for prolonged periods of time. The use of mechanical milling for the preparation of inorganic solids is attracting increasing attention [7, 8] and we report here on the synthesis of $LiFeO_2$ by milling an equimolar mixture of α-Fe_2O_3 and Li_2CO_3 prior to calcination in air. We have also investigated the sensitivity of the ferrite to the cooling procedure following calcination.

2. Experimental

A mixture (ca. 60 g) of α-Fe_2O_3 (Fluka, +99%) and Li_2CO_3 (Aldrich, +99%) with an iron to lithium ratio of 1:1 was prepared. Half of the mixture was divided into three equal amounts. One portion was calcined in air at temperatures between 400 and 900°C for periods of 20 hours with the products being quenched in air. Another portion was calcined at 800°C (20 h) and the third at 900°C (20 h) and both were slowly cooled in the furnace. The other half of the mixture was dry milled in air using a Retsch PM400 planetary ball mill with stainless steel balls and vials (250 ml) at a milling speed of 200 rpm. The powder to ball mass ratio was 1:20. The milled powder was calcined according to identical regimes as those used for the unmilled mixture. X-ray powder diffraction data were recorded with a Siemens D5000 diffractometer using Cu K_α radiation. Thermogravimetric analysis (TGA) was performed with a Rheometric Scientific STA 1500 system using ca. 10 mg of sample and heating in air at a rate of 10°C min^{-1}.

3. Results and discussion

3.1. Calcination of the non-milled mixture of α-Fe_2O_3 and Li_2CO_3

The X-ray powder diffraction patterns recorded from the non-milled mixture following calcination in air at different temperatures for 20 h intervals are shown in Fig. 1.

The X-ray powder diffraction pattern recorded from the mixture following calcination at 400°C was similar to that of the initial mixture (Fig. 1a). Similar treatment at 500°C showed the peaks corresponding to α-Fe_2O_3 and Li_2CO_3 to remain dominant (Fig. 1b), however the appearance of weak reflections which were indexed to the tetragonal unit cell of γ-$LiFeO_2$ [9] was indicative of the onset of reaction between both components at this temperature. Further heating of the mixture at 600°C followed by rapid cooling in air (Fig. 1c) led to the disappearance of peaks corresponding to α-Fe_2O_3 and Li_2CO_3 and the concomitant development of reflections corresponding to both γ-$LiFeO_2$ and cubic α-$LiFeO_2$ phases [10].

The X-ray powder diffraction pattern recorded from the mixture heated at 700°C and quenched in air (Fig. 1d) showed only peaks corresponding to α-$LiFeO_2$ and thereby demonstrated complete conversion of γ-$LiFeO_2$ to α-$LiFeO_2$. The TGA curve recorded from the reaction mixture (Fig. 2a) showed a mass loss of ca. 20% to take place at ca. 750°C consistent with the reaction between α-Fe_2O_3 and Li_2CO_3 according

---

*Author to whom all correspondence should be addressed.

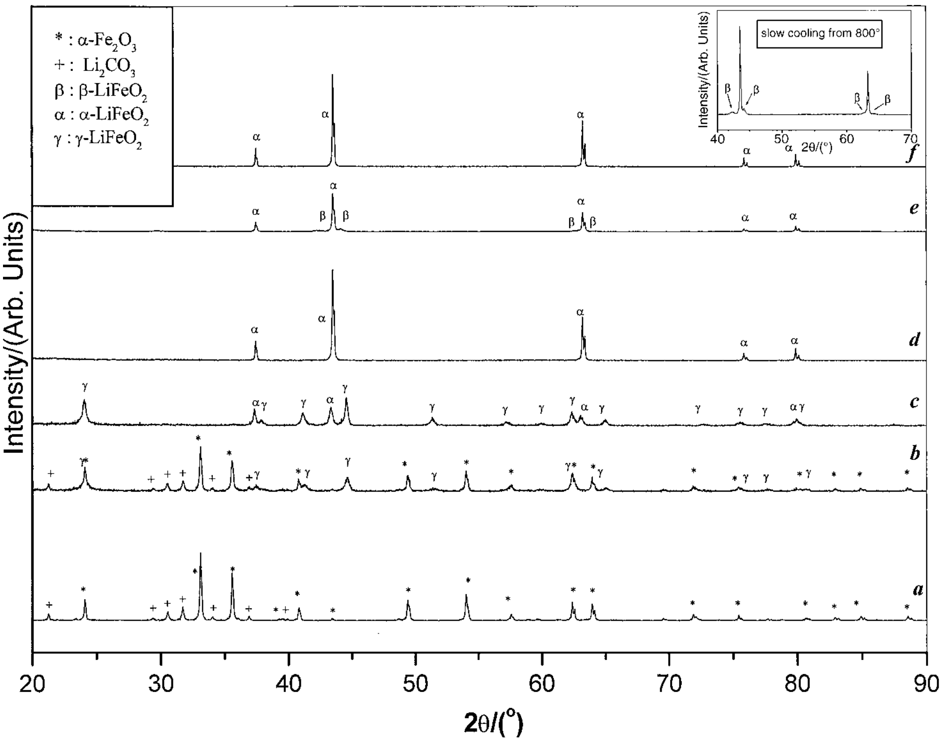

Figure 1 (a) X-ray powder diffraction patterns recorded from a non-milled 1:1 molar mixture of Li_2CO_3 and α-Fe_2O_3 and following calcination at (b) 500°C (quenched); (c) 600°C (quenched); (d) 700°C (quenched); (e) 800°C (slow cooled); (f) 900°C (quenched). The inset shows the X-ray powder diffraction pattern recorded from the non-milled 1:1 molar mixture of Li_2CO_3 and α-Fe_2O_3 after heat treatment at 800°C (20 h) showing the formation of a small amount of β-$LiFeO_2$ via slow cooling.

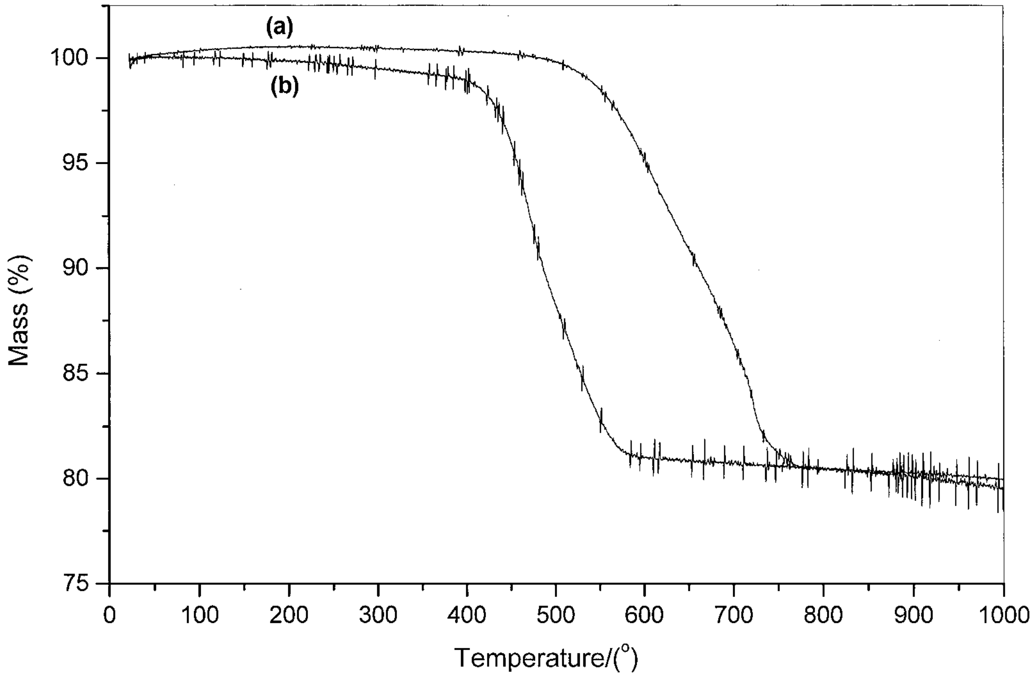

Figure 2 TGA recorded from (a) the non-milled 1:1 molar mixture of Li_2CO_3 and α-Fe_2O_3 and (b) the pre-milled 1:1 molar mixture of Li_2CO_3 and α-Fe_2O_3.

to the equation α-$Fe_2O_3 + Li_2CO_3 \rightarrow 2LiFeO_2 + CO_2$ which implies a mass loss of 19%. The result suggests that γ-$LiFeO_2$ is an intermediate phase at temperatures between 400 and 700°C and that it undergoes constant conversion to α-$LiFeO_2$ within this temperature range.

The X-ray powder diffraction pattern recorded from the mixture calcined at 800°C and quenched in air showed only the presence of the α-$LiFeO_2$ phase in the quenched product. However, slow cooling of the product formed at 800°C gave a material from which the X-ray powder diffraction pattern (Fig. 1e) showed a splitting of the 200 and 311 peaks at ca. 44° and 63.5° 2θ as is observed in the pattern for β-$LiFeO_2$ [3] and indicates that a small amount of α-$LiFeO_2$ undergoes a tetragonal distortion to β-$LiFeO_2$ during slow cooling. This is more clearly seen in the inset in Fig. 1. The result indicates the importance of the cooling procedure in the formation of different polymorphs of $LiFeO_2$.

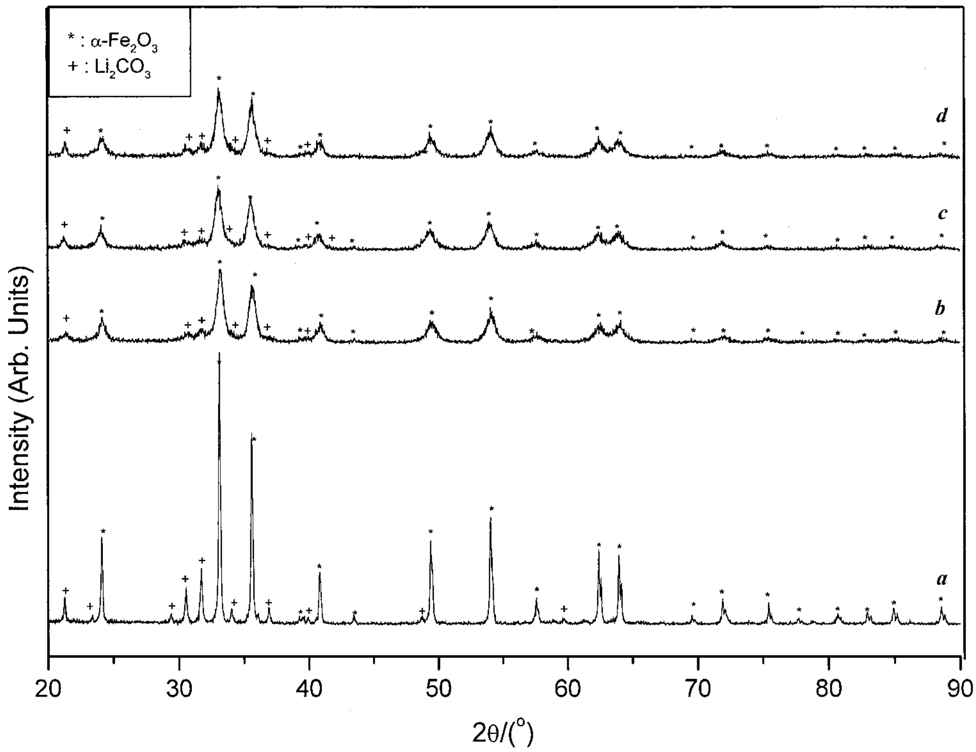

Figure 3 X-ray powder diffraction patterns recorded from the 1:1 molar mixture of Li_2CO_3 and α-Fe_2O_3 milled for (a) 0 h; (b) 50 h; (c) 75 h; and (d) 135 h.

The X-ray powder diffraction patterns recorded from the product heated at 900°C for 20 hours and cooled rapidly (Fig. 1f) and slowly showed only the presence of α-$LiFeO_2$. This result contrasts with that described by other workers [5] who reported that calcination at 900°C for only 6 hours of an equimolar mixture of α-Fe_2O_3 and Li_2CO_3 followed by quenching resulted in the partial transformation of α-$LiFeO_2$ to $LiFe_5O_8$.

3.2. Mechanical milling of α-Fe_2O_3 and Li_2CO_3

The X-ray powder diffraction patterns recorded from the equimolar mixture of α-Fe_2O_3 and Li_2CO_3 followed by mechanical milling for different periods of time are shown in Fig. 3.

The results show that after 50 hours of milling (Fig. 3b), the peaks characteristic of α-Fe_2O_3 and Li_2CO_3 decrease in intensity and begin to broaden. The crystallite size of the α-Fe_2O_3 phase determined by the Scherrer method from the X-ray powder diffraction data decreased from ca. 440 nm to ca. 20 nm after milling for 50 hours. No significant change in the crystallite size was achieved by subsequent milling for 75 hours (Fig. 3c) and 135 hours (Fig. 3d). Given the nature of mechanical milling, the results suggest that high surface area particles of Li_2CO_3 and α-Fe_2O_3 are formed by milling for periods of time exceeding 50 hours and it would be reasonable to expect these particles to be tightly pressed together with a large interface between the reactant particles.

3.3. Calcination of the pre-milled mixture of α-Fe_2O_3 and Li_2CO_3

The X-ray powder diffraction patterns recorded from the mixture of Li_2CO_3 and α-Fe_2O_3 milled for 135 hours and subsequently calcined according to a similar regime used for the non-milled mixture are shown in Fig. 4.

Heating the pre-milled mixture at 400°C followed by quenching in air (Fig. 4a) resulted in the appearance of a broad peak of low intensity at ca. 43–44° 2θ in the X-ray powder diffraction pattern. A comparison of this result with that obtained from the non-milled mixture calcined at the same temperature shows that pre-milling of the reactants lowers the temperature at which they begin to react by ca. 100°C.

The influence of milling on the reactivity of the pre-milled powder at higher temperatures is illustrated by the X-ray powder diffraction data recorded after treatment at 500°C followed by quenching in air (Fig. 4b). The pattern can be indexed to the tetragonal γ-$LiFeO_2$ phase, suggesting that the reaction between Li_2CO_3 and α-Fe_2O_3 is almost complete at ca. 500°C. These results contrast with that recorded from the non-milled mixture when heated at 500°C (Fig. 1c) in which only a small amount of γ-$LiFeO_2$ was formed. The result was confirmed by TGA (Fig. 2b) which showed the mass loss to be complete at ca. 550°C as compared to ca. 750°C in the case of the non-milled mixture (Fig. 2a) and leads to the general conclusion that pre-milling of the reactants not only lowers the temperature of the onset of $LiFeO_2$ formation by ca. 100°C, but also lowers the temperature at which the formation of $LiFeO_2$ is complete by ca. 200°C. The results also demonstrate that calcination at ca. 500°C in air of a pre-milled equimolar mixture of α-Fe_2O_3 and Li_2CO_3 gives monophasic γ-$LiFeO_2$ by a solid state reaction and with a crystallite size determined from the X-ray powder diffraction data of ca. 85 nm.

The X-ray powder diffraction data showed no further change in the phase composition following subsequent heat treatment at 600°C and rapid quenching.

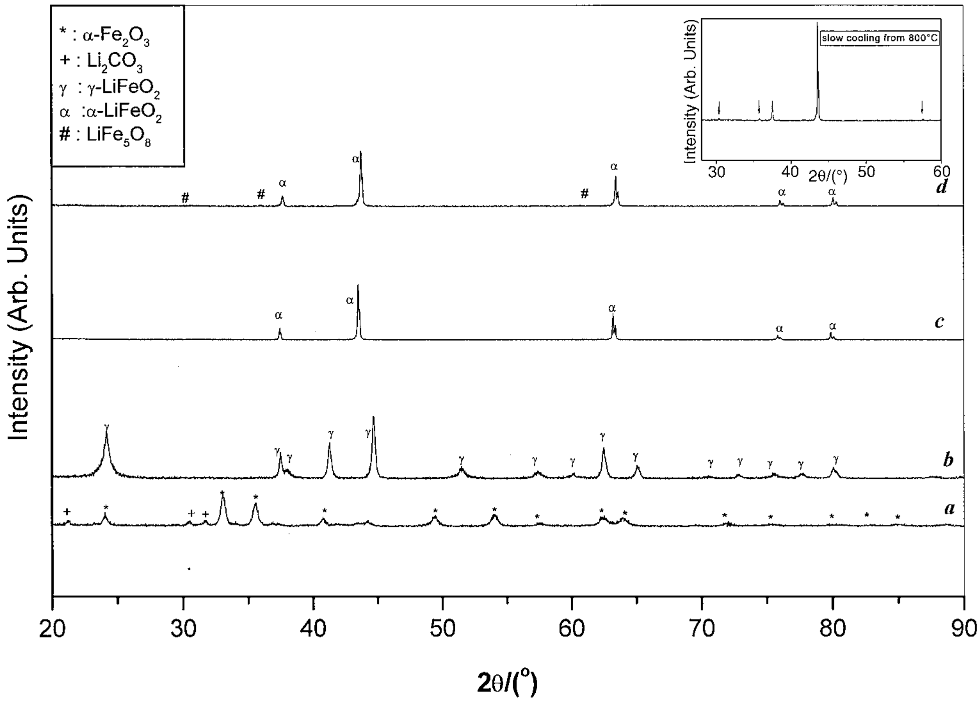

Figure 4 X-ray powder diffraction patterns recorded from a 1:1 molar mixture of Li_2CO_3 and α-Fe_2O_3 pre-milled for 135 h and following calcination at (a) 400°C (quenched); (b) 500°C (quenched); (c) 700°C (quenched); (d) 800°C (slow cooled). The inset shows the X-ray powder diffraction pattern recorded from the milled 1:1 molar mixture of Li_2CO_3 and α-Fe_2O_3 after heat treatment at 800°C (20 h) showing the formation of a small amount of $LiFe_5O_8$ via slow cooling. The arrows refer to reflection peaks characteristic of $LiFe_5O_8$.

Comparing these results with those obtained from the non-milled mixture following similar thermal treatment shows that pre-milling of the reactants leads to the formation of a single γ-$LiFeO_2$ phase which is stable in the temperature range 500–600°C. We note that other workers [4] have been unable to obtain a single γ-$LiFeO_2$ phase from a non-milled Li_2CO_3 and α-Fe_2O_3 mixture. The formation of a monophasic thermally stable γ-$LiFeO_2$ phase may therefore be associated with the pre-milling of the reactants. Although single phase we were unable to confirm the degree of order of the lithium and iron ions over the cationic sub-lattice. The pattern is more similar to that of ordered γ-$LiFeO_2$ [9] but attempts to refine the pattern to this structure were not completely successful and indicate that some fraction of the γ-$LiFeO_2$ is in the disordered state.

Further heating of the pre-milled mixture to 700°C followed by rapid cooling in air resulted in a phase transition from γ- to α-$LiFeO_2$ (Fig. 4c) and was similar to the result observed in the non-milled mixture following calcination at 700°C. The X-ray powder diffraction patterns recorded from the pre-milled mixture following heating at 800°C and 900°C and subsequently quenched in air showed the α-$LiFeO_2$ phase to remain unchanged as was also observed when the non-milled mixture was rapidly cooled from similar temperatures (Fig. 1f). However, when the pre-milled mixture was slowly cooled in the furnace following calcination at 800°C and 900°C (Fig. 4d) the formation of a very small amount of $LiFe_5O_8$ was observed. This may be clearly seen in the inset to Fig. 4 where the arrows indicate the peaks characteristic of spinel-related $LiFe_5O_8$ in the X-ray powder diffraction pattern of the material slowly cooled from 800°C. The result contrasts with that recorded from the non-milled mixture following slow cooling from elevated temperatures (Fig. 1e) where only polymorphs of $LiFeO_2$ were obtained. The result also contrasts with the work of others [5] who reported that quenching was required for the formation of $LiFe_5O_8$.

4. Conclusion

Pre-milling of a mixture of α-Fe_2O_3 and Li_2CO_3 lowers the temperature at which $LiFeO_2$ is formed by ca. 200°C. A thermally stable γ-$LiFeO_2$ phase is formed at temperatures below 500 and 600°C. The slow cooling of the pre-milled mixture which had been calcined at elevated temperatures resulted in the formation of some $LiFe_5O_8$.

Acknowledgement

We thank the Gordon Memorial College Trust Fund, the Swedish International Co-operation and Development Agency (SIDA) and the Abdus Salam ICTP for financial and research support to HMW.

References

1. Y. SAKURAI, H. ARAI and J. YAMAKI, *Solid State Ionics* **113–115** (1998) 29.
2. T. SHIRANE, R. KANNO, Y. KAWAMOTO, Y. TAKEDA, M. TAKANO, T. KAMIYAMA and F. IZUMI, *ibid.* **79** (1995) 227.
3. M. TABUCHI, K. ADO, H. SAKAEBE, C. MASQUELIIER, H. KAGEYAMA and O. NAKUMURA, *ibid.* **79** (1995) 220.
4. N. RAMACHANDRAN and A. B. BISWAS, *J. Solid State Chem.* **30** (1979) 81.
5. G. A. EL-SHOKABI and H. A. IBRAHIM, *Thermochim. Acta* **118** (1987) 151.
6. V. BERBENNI, A. MARINI and D. CAPSONI, *Z. Naturforsch* **30** (1998) 997.

7. A. ARCOS, R. VALENZUELA, M. VAZQUEZ and M. VALLET-REGI, *J. Solid State Chem.* **141** (1998) 10.
8. S. BEGIN-COLIN, T. GIROT, G. L. CAER and A. MACELLIN, *ibid.* **149** (2000) 41.
9. T. A. HEWSTON and B. L. CHAMBERLAND, *J. Phys. Chem. Solids* **48** (1987) 97.
10. J. C. ANDERSON and M. SCHIEBER, *ibid.* **25** (1964) 961.

Received 25 October 2001
and accepted 2 July 2002