Synthesis and alteration of α-LiFeO₂ by mechanochemical processes

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The effects of grinding on a stoichiometric mixture of $LiOH \cdot H_2O$ and γ-FeOOH were studied. It was found that, in the course of grinding, losses of structural water occurred and a phase structurally related to disordered α-LiFeO₂ was formed. X-ray diffraction data suggest the occurrence of an ordered phase as intermediate and both γ-Fe₂O₃ and α-Fe₂O₃ were undetected during the comminution process. A prolonged mechanical treatment of this mixture originated an elimination of Li^+ from the α-LiFeO₂ structure and the appearance of the spinel phase, α-LiFe₅O₈. Additionally, the mechanical activation of a sample of α-LiFeO₂ prepared at high temperatures also leads to a similar rearrangement of cations. The structural transformation is explained with the help of a model in which the vacancies of Li^+ created during grinding promote the migration of the Fe^{3+} ions from octahedral to tetrahedral sites.

1. Introduction

The mechanical treatment of materials by grinding is now accepted as a common procedure for the increase in the reactivity of solids. Recent reports [1, 2] have shown that the ball milling of different crystalline powders has a pronounced effect on their surface and structural properties. Additionally, an extensive number of solid state reactions has been performed by grinding. These include examples which would require high temperatures to be performed under ordinary conditions.

In previous works various hydroxylated compounds of iron and cobalt were ground in a rotatory ball mill and studies were made of their structural and surface properties [3, 4]. These investigations were expanded to the Li–Co–O system [5] in which a phase structurally related to the layered structure LiCoO₂ (03) was obtained by milling stoichiometric mixtures of lithium and cobalt hydroxide for 10 h. Furthermore, it was shown that the mechanical activation of the LiCoO₂ phase enhances lithium mobility which accounts for the occurrence of the spinel Co₃O₄.

The present paper deals with the study of the mechanochemical reaction between γ-FeOOH (Lepidocrocite) and LiOH. The degradation of α-LiFeO₂ by grinding is also discussed for a better understanding of the phenomenological changes associated with the lithium diffusion through the oxygen cubic-close packing structure.

2. Experimental procedure

Powder γ-FeOOH samples were prepared by the method described by Giovanoli and Brutsch [6]. Intimate mixtures of 2 g γ-FeOOH and 0.944 g $LiOH \cdot H_2O$ (Merck, a.r.) were ground for different time intervals in a planetary ball mill (Retsch) equipped with a 250 ml agate jar and five balls of the same material, 1 cm in diameter. An α-LiFeO₂ sample was prepared by heating a mixture of reagent grade Li₂CO₃ and γ-FeOOH at 850° C. Grinding of this sample (2.0 g) was carried out under analogous experimental conditions.

Total lithium and iron contents were determined by atomic absorption spectrometry by using a Perkin Elmer 370 apparatus. The possible presence of Fe(II) was tested for by titration with potassium dichromate.

Powder X-ray diffraction spectra were recorded on a Siemens 501 Diffractometer provided with a curved graphite crystal to produce monochromatic Cu$K\alpha$ radiation. DSC curves were obtained with a Mettler TA 3000 apparatus and TG curves were recorded by using a Cahn 2000 electrobalance. All these measurements were carried out under static air atmosphere.

3. Results and discussion

The thermal evolution of stoichiometric 1 : 1 mixtures of γ-FeOOH and $LiOH \cdot H_2O$ was studied by analysis of the DSC and TG traces (Figs 1 and 2). The endothermal dehydration steps corresponding to the transformations: $LiOH \cdot H_2O \rightarrow LiOH$, γ-FeOOH → γ-Fe₂O₃ and $LiOH + \gamma$-Fe₂O₃ → α-LiFeO₂, were observed at 140, 220 and 430° C, respectively (Fig. 1a), and the different intermediate phases were identified by X-ray diffractometry. The exothermal effect found at 280° C can be ascribed to a surface reordering of the particles of ex-γ-FeOOH → γ-Fe₂O₃ [7]. The reaction at 430° C takes place at the melting point of LiOH. This temperature is virtually independent of the iron sesquioxide phase mixed with LiOH or the parent oxyhydroxide, as shown by the DSC traces of mixtures of LiOH with γ-Fe₂O₃, γ-FeOOH, δ-FeOOH. The reaction is developed without previous phase transition γ-Fe₂O₃ → α-Fe₂O₃. This fact may be interpreted by considering that the temperature of this transition is highly dependent on the crystallinity of γ-Fe₂O₃ [8]. Furthermore, it is known that the presence of lithium in the medium in which the mechanical treatment of γ-FeOOH is carried out affects the formation and thermal stability of γ-Fe₂O₃ [9].
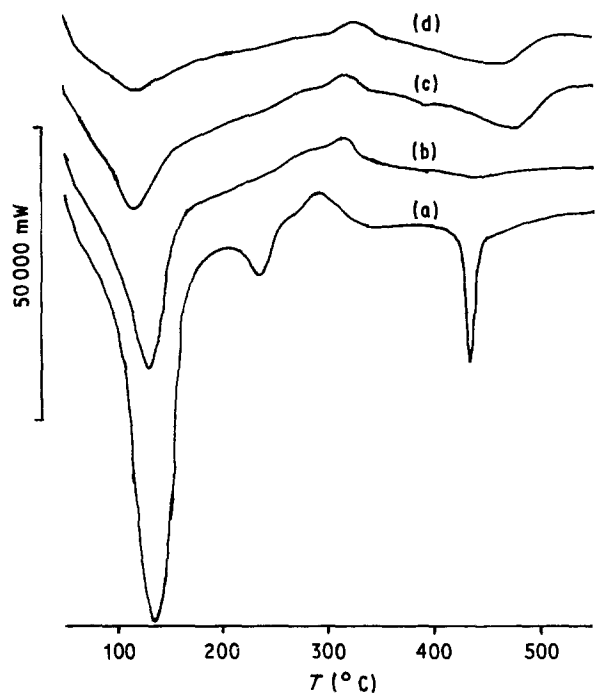
Figure 1 DSC traces of stoichiometric mixtures of LiOH · H₂O and γ-FeOOH ground for different periods of time: (a) 0 h, (b) 7 h, (c) 12 h, (d) 21 h.

For the sample ground for 7 h (Fig. 1b), special significance is attached to the disappearance of the endothermic peak located at 430° C and associated with the formation of LiFeO₂. Moreover, the magnitude of the remaining endothermic peaks and the weight loss decrease markedly with increasing grinding time. This indicates that the different hydroxylated compounds of lithium and iron undergo a progressive mechanical dehydration, that is accompanied by a structural rearrangement in which the increase in the mobility of Li⁺ ions caused by the shearing stress created under the impact of the balls inside the mill, plays a definite role.

The mechanical treatment of the original γ-FeOOH/LiOH · H₂O mixture was followed by X-ray diffraction (Fig. 3). The products at low grinding periods are characterized by a poor crystallinity shown by the highly broadened line profiles. Qualitative changes in phase composition have also taken place. Thus the
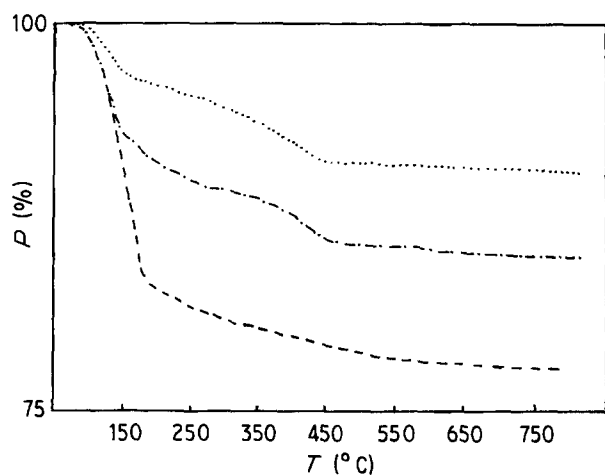

Figure 3 X-ray diffractograms of stoichiometric mixtures of LiOH · H₂O and γ-FeOOH: (a) ground for 7 h, (b) ground for 12 h, (c) ground for 21 h, (+) γ-FeOOH, (*) LiFeO₂, (○) LiFe₅O₈ exclusively.

occurrence of crystalline modifications of LiFeO₂ is shown after 7 h grinding. Detailed study of the asymmetrically broadened profiles at ∼45° 2θ (Fig. 4), produced evidence of the presence of lines of the cubic modification as well as those of the tetragonal metastable phase β-LiFeO₂ [10]. However, the transformation is not complete as the diffraction 0 0 2 line of γ-FeOOH is still observed. A more prolonged mechanical treatment improves LiFeO₂ crystallinity and causes the mechanochemical phase transition β-LiFeO₂ → α-LiFeO₂, shown by the progressive disappearance of the asymmetrical broadening of the profiles. After 21 h grinding, the X-ray diffraction spectrum showed a predominance of the disordered
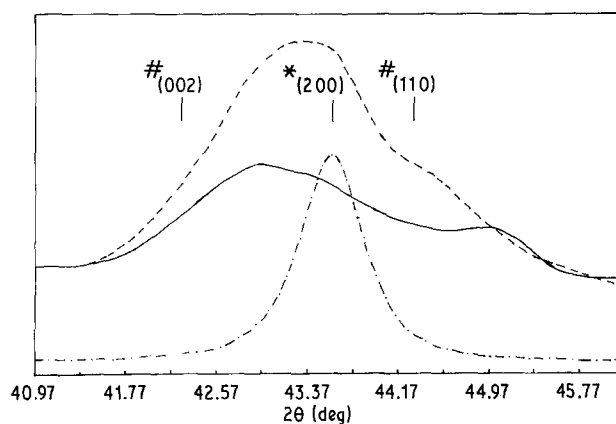

Figure 2 Thermogravimetric curves of stoichiometric mixtures of LiOH · H₂O and γ-FeOOH ground for different time intervals: (— — —) 7 h, (—·—·—) 12 h, (· · ·) 21 h.

Figure 4 X-ray diffractograms of stoichioimetric mixtures of LiOH · H₂O and γ-FeOOH performed with a step-scan of 0.002° 2θ/2 sec. (————) 7 h, (— — —) 12 h, (—·—·—) 21 h, (*) α-LiFeO₂, (#) β-LiFeO₂.
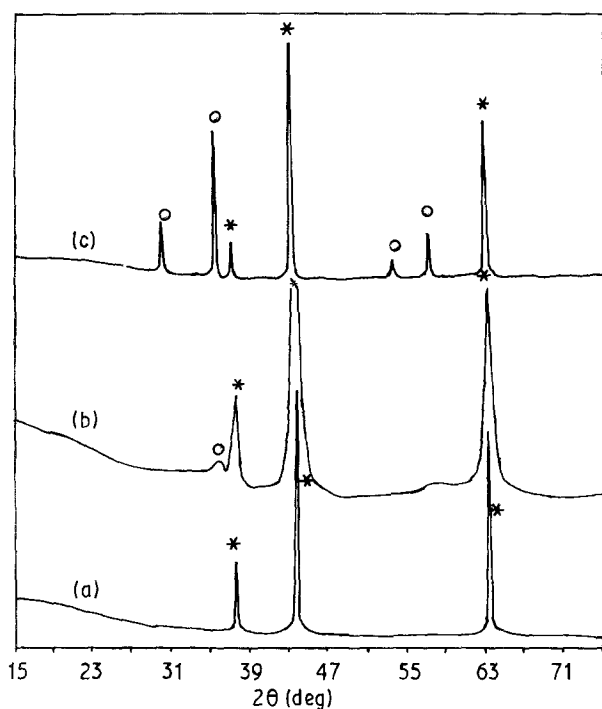
Figure 5 X-ray diffractograms of α-LiFeO$_2$ ground for different periods of time: (a) 0 h, (b) 7 h, (c) 7 h and heated at 750° C. (*) α-LiFeO$_2$, (O) α-LiFe$_5$O$_8$ exclusively.

cubic structure, α-LiFeO$_2$ and a small amount of unreacted particles of γ-FeOOH. Of additional interest is that the spectrum of this sample contained two peaks that correspond to the more intense reflections of the lithium ferrite, LiFe$_5$O$_8$.

The mechanochemical transformation of α-LiFeO$_2$ into the spinel phase LiFe$_5$O$_8$ was also observed in a sample prepared by firing a stoichiometric mixture of lithium carbonate and iron oxyhydroxide in air at 850° C for 48 h (Fig. 5). The powder X-ray diffraction spectrum of a sample that has been ground for 7 h is shown in Fig. 5b. A noteworthy feature of this spectrum is the two-phase nature of the product resulting from the mechanochemical treatment. The characteristic reflections of the spinel phase LiFe$_5$O$_8$ become discernible and their intensities increase markedly with increasing annealing temperature.

The chemical composition given in terms of atomic ratio of lithium for both sets of samples is shown in Table I. The most relevant feature of these data is that the atomic ratio becomes smaller than unity as the griding time increases. Similar behaviour has recently been detected on a mechanically activated sample of LiCoO$_2$ [5]. In this case, it was found that the lithium migrated to the surface of the balls and the jar, and the concentration of the ion was higher in the particles stuck to these surfaces than in those belonging to the bulk of the material. This non-uniform distribution of the lithium ion produced by the mechanical activation was also confirmed in the system Li–Fe–O. Thus, for a sample of LiFeO$_2$ ground for 21 h, the Li/Fe ratio found in the solutions obtained by treating the balls and the jar with concentrated hydrochloric acid was 1.51, notably higher than unity.

The thermal behaviour of these systems deserves further comment. When the atomic ratio Li/Fe remains virtually unaltered (sample A$_7$ in Table I), the final

product after heating is only the disordered structure α-LiFeO$_2$ and therefore the firing temperature has litle influence on the formation of the LiFe$_5$O$_8$ phase (see curves of Fig. 6). If the lithium content decreases slightly, sample A$_{12}$) the diffractions corresponding to the spinel phase were observed only at temperatures above 750°C. In those samples in which a significant loss of lithium is present, the precipitation of the LiFe$_5$O$_8$ phase during grinding is observed at room temperature, and the intensity of its diffraction
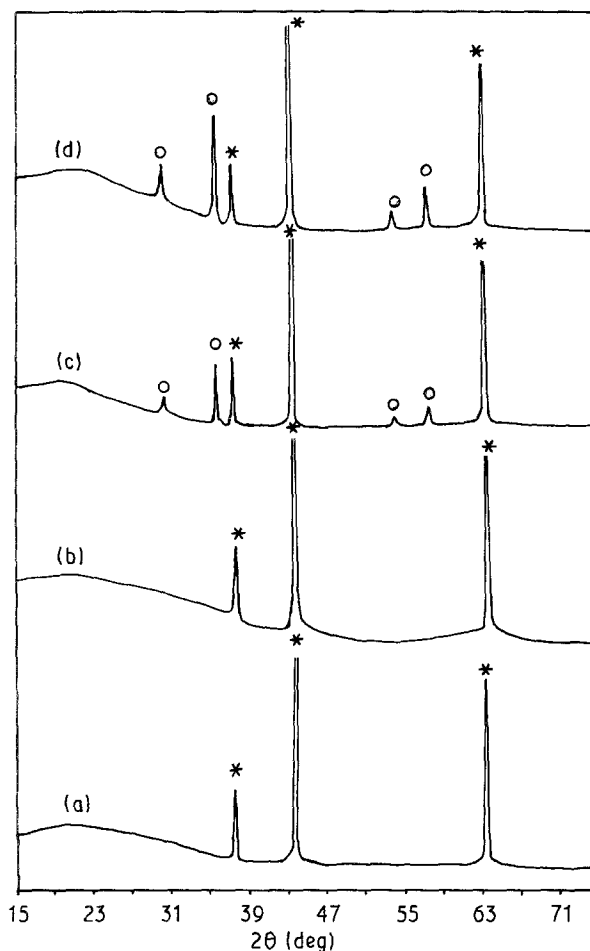

Figure 6 X-ray diffractograms of stoichiometric mixtures of LiOH · H$_2$O and γ-FeOOH: (a) 0 h and heated at 750° C, (b) 7 h and heated at 750° C, (c) 12 h and heated at 850° C, (d) 21 h and heated at 750° C. (*) LiFeO$_2$, (O) LiFe$_5$O$_8$ exclusively.

Temperature	$LiFe_5O_8$ (%)
0	–
550	–
590	9
640	10
750	14

profiles increases with increasing annealing temperature. A quantitative evaluation of the composition was carried out by applying the autoflusing method of Chung [11] to the reflections 1 1 1 and 3 1 1 corresponding to the $LiFeO_2$ and $LiFe_5O_8$ phases, respectively. The values found are shown in Table II. It is noteworthy that the percentage of the spinel phase, $LiFe_5O_8$ at 750° C is in agreement with that calculated from the value of the atomic ratio Li/Fe referred to in the presence of two phases.

The increase in the Li^+ ion mobility within the solid as a consequence of the stress conditions created during the mechanical treatment probably allows the extrusion of the ion according to a reaction such as

$$LiFeO_2 \rightarrow Li_{1-x}FeO_{2-(x/2)} + x/2\ Li_2O \qquad (1)$$
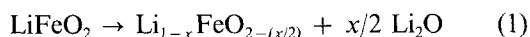
For $0.1 < x < 0.2$, the new phase of spindel structure probably occurs through a reaction that involves the decomposition of the defective rock salt structure

$$Li_{1-x}FeO_{2-(x/2)} \rightarrow x/4\ LiFe_5O_8 + (4 - 5x)/4\ LiFeO_2 \qquad (2)$$
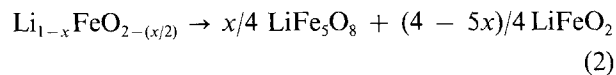
This process is also favoured by heat treatment, even for a loss of lithium of less than 10%.

It can be concluded that the mechanical stress applied to a mixture of reagent γ-FeOOH and LiOH · H_2O in a stoichiometric molar ratio 1 : 1, induces the formation of an oxygen cubic close-packing framework with the cationic species located on the octahedral holes of the structure. In this atomic rearrangement the water molecules produced during the mechanical dehydration of lepidocrocite facilitate the lithium mobility in a similar way to that found when the lithium hydroxide melts and reacts with Fe_2O_3. This inference is supported by the fact that a stoichiometric powdered mixture of α-Fe_2O_3 + LiOH · H_2O ground for 14 h remains unaltered and no sign of a new phase was detected in the X-ray diffraction patterns.

It seems that in the first stage of the mechanical activation the lithium ions have a tendency to adopt an ordered distribution leading to the low-temperature stable ordered form β-$LiFeO_2$. Further action of the mechanical operation transforms this latter phase into the stable disordered form α-$LiFeO_2$, that can also be accomplished by heating a mixture of the original reagents at high temperatures. However, this structure with high thermal stability can easily be degraded by the effects of the external forces exerted during grinding in a process that involves at least two steps. Firstly, there is a release of Li^+ from the structure apparently without altering the cubic close packing. As a con-

sequence of this deficiency, this phase becomes metastable and by means of heat treatment or by a more drastic mechanical activation, its decomposition is easily achieved.

The understanding of the structural transformation described by Reaction 2 can be facilitated by considering the ideal spinel structure $A_t(B_2)_oO_4$ with the symmetry Fd3m. B refers to the cations in octahedral holes (16d), A to the cations in tetrahedral holes (8a) and the oxygens located at 32e positions. The empty positions are octahedral (16c) and tetrahedral (8b and 48f) positions. According to this model, the ferrite $LiFe_5O_8$ is equivalent to $Fe_t(Li_{0.5}Fe_{1.5})_oO_4$.

Previous studies have reported that lithium can be inserted into spinel leading to phases of nominal composition $Li_xA(B_2)O_4$ [12, 13] in which lithium ions occupy the 16c vacant positions and tetrahedral A cations are cooperatively displaced to the 16c octahedral sites. In this way a cubic rock salt structure can be achieved, in which the 16c and 16d octahedral holes are indistinguishable vgr. α-$LiFeO_2$.

Thus, the above results can be interpreted by considering that the vacant positions created by the release of Li^+ ions favour the promotion of Fe^{3+} ions to the tetrahedral 8a positions. The energy required for this cationic redistribution must be low taking into account that the octahedral 16c and tetrahedral 8a share a common face that enables a possible diffusion pathway 16c $\rightarrow$ 8a through the oxide lattice. Finally there is direct evidence that the cubic close-packed array of oxygen does not alter under the stress conditions operating during grinding.

Acknowledgement

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