

## Preparation and thermal decomposition of magnesium/iron(III) layered double hydroxide intercalated by hexacyanoferrate(III) ions

WEIQING MENG, FENG LI, DAVID G. EVANS, XUE DUAN

Education Ministry Key Laboratory of Science and Technology of Controllable Chemical Reactions,  
Beijing University of Chemical Technology, Beijing 100029, People's Republic of China  
E-mail: duanx@mail.buct.edu.cn

Spinel of the type  $M^{II}M^{III}_2O_4$  attract a great deal of interest because of their diverse practical applications [1]. The efficacy of the material depends on its microstructural properties which are sensitive to its mode of preparation [2–4]. To take magnesium ferrite,  $MgFe_2O_4$ , as an example, the conventional ceramic method of preparation [5] involves calcination of mixtures of precursors ( $MgO$  or  $MgCO_3$  and  $Fe_2O_3$ ) at temperatures of  $1100^\circ C$  or above. High temperatures are required to prepare a single homogeneous phase but if the temperature is too high there are problems with phase separation and non-stoichiometry [6]. Alternative wet chemical methods have been proposed including coprecipitation from aqueous solution [4], sol-gel synthesis [7] and use of micellar microemulsions [3, 8]. In these cases, it is difficult to prevent contamination of the product by cations from the precipitants or organic residues from the precursors [9]. In order to avoid compromising the purity and properties of magnesium ferrite and related materials it would be desirable to prepare them from a *single* solid precursor which can be prepared in a *pure* state.

We have recently demonstrated one such method starting from a layered double hydroxide (LDH) precursor [10]. LDHs, also known as hydrotalcite-like materials, are synthetic anionic clays whose structure can be described as containing brucite-like layers in which some of the divalent cations have been replaced by trivalent ions giving positively-charged sheets with anions between the layers [11, 12]. LDHs have the formula  $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}(A^{n-})_{x/n}\cdot yH_2O$  and the identities of  $M^{II}$ ,  $M^{III}$  and  $A^{n-}$  together with the value of the coefficient ( $x$ ) may be varied over a wide range. Calcination of LDHs above  $750^\circ C$  has long been known to give spinels, but these are mixed with the oxide of the divalent metal [13]. This reflects the fact that in LDHs, the ratio  $M^{II}/M^{III}$  is typically [12] in the range 2–4 whereas in a spinel the required ratio is  $M^{II}/M^{III} = 0.5$ . We have recently reported the preparation of LDHs of the type  $[Mg_{1-x}Fe^II_xFe^III_x(OH)_2]^{x+}(CO_3^{2-})_{x/2}\cdot yH_2O$  [10] and shown that when the  $Mg/(Fe^{II} + Fe^{III})$  ratio is 1:2, oxidation of  $Fe^{II}$  during calcination leads to the formation of a pure sample of  $MgFe_2O_4$  with excellent magnetic properties.

A potential alternative way of synthesizing LDHs with the required overall  $Mg/Fe$  ratio for formation of a pure spinel phase is by intercalation of anionic iron complexes in the interlayer region. For ex-

ample, intercalation of the well-known [14] hexanuclear iron carbido cluster  $[Fe_6(\mu_6-C)(CO)_{16}]^{2-}$  would give  $[Mg_4Fe_2(OH)_{12}]^{2+}[Fe_6(\mu_6-C)(CO)_{16}]^{2-}$ , where  $Mg/(Fe_{layer} + Fe_{interlayer})$  is 1:2. There exists the possibility however that segregation may occur during calcination, such that the layers decompose to give  $MgFe_2O_4$  and  $MgO$  in the usual way and the interlayer anions decompose to give an iron oxide phase such as  $Fe_2O_3$  or  $Fe_3O_4$ . Before setting out to prepare this and related materials, we intended to predict their likely thermal decomposition behavior by using the more readily available hexacyanoferrate(III) ion as a model for the clusters involved. Intercalation of hexacyanoferrate(III) in  $Mg/Al$  [13, 15–21] and  $Zn/Al$  [22, 23] LDHs has been reported previously, but there have been no reports of intercalation of this anion in  $Mg/Fe$  LDHs. In this paper we report the results of our preliminary study.

The  $Mg/Fe(III)/[Fe(III)(CN)_6]$ -LDH was prepared by the coprecipitation method [12]. A solution of  $Mg(NO_3)_2\cdot 6H_2O$  and  $Fe(NO_3)_3\cdot 6H_2O$  with an  $Mg^{2+}/Fe^{3+}$  ratio of 2 ( $[Mg^{2+}] + [Fe^{3+}] = 1 M$ ) was added dropwise under  $N_2$  to a vigorously stirred solution of  $NaOH$  and  $K_3[Fe(CN)_6]$  ( $\{[OH^-]/([Mg^{2+}] + [Fe^{3+}]) = 1.6, \{[Fe(CN)_6]^{3-}/[Fe^{3+}] = 3\}$ ) until the pH reached 9.5. The resulting suspension was aged at  $100^\circ C$  for 8 h under  $N_2$ . The mixture was filtered and the solid washed thoroughly with deionized water and dried at  $70^\circ C$  under vacuum for 24 h. The resulting solid (**I**) was characterized by elemental analysis, powder X-ray diffraction (PXRD), Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric (TGA) and differential thermal analysis (DTA). For comparison purposes (see below) a sample of an  $Mg/Fe(III)/CO_3$ -LDH was prepared in the same way substituting  $Na_2CO_3$  for  $K_3[Fe(CN)_6]$ .

Elemental analysis of the resulting hexacyanoferrate(III)-pillared LDH (**I**) was consistent with the formulation  $[Mg_{0.715}Fe_{0.285}(OH)_2][Fe(CN)_6]_{0.095}\cdot 0.92H_2O$ , with a  $Mg/Fe$  ratio of 1.88. Its PXRD pattern shown in Fig. 1a exhibits a single crystalline phase with the characteristic reflections [11, 12] of LDH materials with a series of (00 $l$ ) peaks appearing at low angle corresponding to the basal spacing of 1.076 nm and higher order reflections. Assuming a 3R stacking [24] of the layers the lattice parameters  $a$  and  $c$  for the LDH are 0.310 and 3.228 nm respectively. The gallery height (calculated from the  $d(003)$  spacing, 1.076 nm,

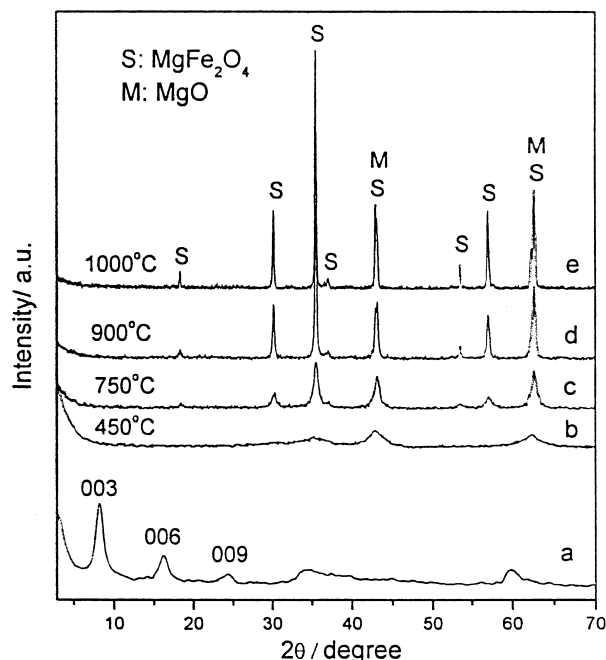


Figure 1 PXRD patterns for Mg/Fe(III)/[Fe(CN)<sub>6</sub>](III)-LDH (I) (a) and Mg/Fe(III)/[Fe(CN)<sub>6</sub>](III)-LDH after calcination at 450 (b)–1000 °C (e).

and the thickness of the brucite-like layers, 0.48 nm [12]) was 0.596 nm.

The size of the [Fe(CN)<sub>6</sub>]<sup>3-</sup> anion is close to 1.1 nm along the *C*<sub>4</sub> axis, 0.87 nm along the *C*<sub>2</sub> axis, and 0.651 nm along the *C*<sub>3</sub> axis [13]. This means that the anion in (I) is oriented with its *C*<sub>3</sub> axis perpendicular to the brucite-like layers. Similar interlayer spacings have been reported for the case of hexacyanoferrate(III) intercalated in Mg/Al [13, 15–21] and Zn/Al [22, 23] LDHs.

The FT-IR spectrum for (I) includes a strong band centered around 3449 cm<sup>-1</sup> which is a superposition of O–H stretching bands arising from metal-hydroxyl groups and hydrogen-bonded interlayer water molecules. The band corresponding to the vibration mode δ<sub>HOH</sub> appears at 1634 cm<sup>-1</sup> [11, 12]. The bands below 1000 cm<sup>-1</sup> are M–O vibration modes. The bands between 2200 and 2000 cm<sup>-1</sup> are due to the C–N stretching of cyanide groups. For hexacyanoferrates, the exact position of the band depends on the oxidation state of iron [17, 18]. The band at 2111 cm<sup>-1</sup> is attributed to the C–N stretching mode of hexacyanoferrate(III) and a weak band at 2034 cm<sup>-1</sup> is due to the C–N stretching mode of hexacyanoferrate(II), indicating that a small degree of Fe<sup>3+</sup> → Fe<sup>2+</sup> reduction has taken place in the LDHs. In the case of hexacyanoferrate(III) intercalated in Mg/Al LDHs, it has been reported that the stress exerted by the layers on the intercalated [Fe(CN)<sub>6</sub>]<sup>3-</sup> anion favors reduction to the smaller [Fe(CN)<sub>6</sub>]<sup>4-</sup> ion [17, 18] and a similar effect is presumably operating here.

As is usual for LDHs, the weight loss observed in the TGA of (I) occurs in two steps [11, 12]. The first one, up to ca. 220 °C, corresponds to removal of water physisorbed on the external surface of the crystallites as well as water intercalated in the interlayer galleries and corresponds to 16% of the total weight

of the sample. There is a corresponding endothermic event in the DTA at around 147 °C. The second weight loss for (I) involves dehydroxylation of the layers and loss of volatile species (CO<sub>2</sub> or NO<sub>2</sub>) arising from the interlayer anions ([Fe(CN)<sub>6</sub>]<sup>3-</sup>) [13]. There is an exothermic event at 270 °C, and an endothermic event at 364 °C in the DTA curve. The exothermic event is due to combustion of the cyanide ligands under the oxidizing atmosphere used during the DTA, and the endothermic event is due to dehydroxylation of the layers [13].

Calcination of (I) at 450 °C gives rise to formation of a poorly crystalline MgO phase as shown by the diffraction peaks at 0.210 and 0.148 nm (ca. 2θ = 43 and 63 ° respectively) [13] and a small amount of a spinel phase (Fig. 1b). When the calcination temperature is increased to 750 °C and above (Fig. 1c–f) the diffraction peaks due to the spinel become increasingly evident. From the positions of the diffraction peaks which are not coincident with those of MgO, the lattice parameter *a*<sub>0</sub> for the spinel phase can be calculated. The values do not vary significantly with calcination temperature and are close to 0.8390 nm in each case. The reported values for MgFe<sub>2</sub>O<sub>4</sub> (JCDPS file 36-398) and Fe<sub>3</sub>O<sub>4</sub> (JCDPS file 19-629) are 0.8387 and 0.8396 nm respectively. The similarity between their lattice parameters means that the observed diffraction peaks could arise from a mixture of these two phases. The apparent average crystallite size of the spinel phase may be estimated from the values of the full width at half maximum (FWHM) of the diffraction peaks which are not coincident with those of MgO by means of the Scherrer equation [ $L = 0.89\lambda/\beta(\theta) \cos \theta$ , where *L* is the crystallite size, λ is the wavelength of the radiation used, θ is the Bragg diffraction angle and β(θ) is the FWHM] [24]. The calculated crystallite size increases from 16.4 nm at 750 °C to 55.1 nm at 1000 °C. For the case of the Mg-Fe(III)-CO<sub>3</sub>-LDH (Mg/Fe = 2), the variation in PXRD pattern with calcination temperature is similar to both that observed for (I) and that for Mg-Fe(III)-CO<sub>3</sub>-LDH (Mg/Fe = 3) reported in the literature [13]. The apparent crystallite size of the resulting spinel phase however is considerably smaller than that of the spinel produced by calcination of (I) and increases from 11.6 nm at 750 °C to 35.3 nm at 1000 °C. This strongly suggests that calcination of (I) leads to pure MgFe<sub>2</sub>O<sub>4</sub> as the only spinel phase, since contamination by Fe<sub>3</sub>O<sub>4</sub> would presumably lead to either additional resolved peaks or a peak broadening and a decrease in apparent crystallite size. Furthermore, none of the characteristic peaks of α-Fe<sub>2</sub>O<sub>3</sub> (JCDPS file 05-0637) or γ-Fe<sub>2</sub>O<sub>3</sub> (JCDPS file 24-0081) can be observed in the PXRD patterns of (I) calcined at different temperatures.

In summary, we have demonstrated that layered double hydroxides containing Mg<sup>2+</sup> and Fe<sup>3+</sup> in the brucite-like layers and interlayer hexacyanoferrate(III) ions can be prepared through coprecipitation. Calcination of Mg/Fe/[Fe(CN)<sub>6</sub>]-LDH leads to a mixture of MgFe<sub>2</sub>O<sub>4</sub> and MgO. The iron from the interlayer ions is incorporated in the spinel phase along with the iron originally in the layers and is not converted

to a separate iron oxide phase. Indeed it appears that the presence of interlayer iron promotes the formation of the spinel phase, since the crystallite size is larger than that observed by calcination of an Mg/Fe/CO<sub>3</sub>-LDH with comparable Mg/Fe ratio in the layers. Encouraged by these results, we are currently investigating the intercalation of other iron-containing complex anions in Mg/Fe LDH hosts in order to obtain a precursor which, on calcination, will afford a pure single MgFe<sub>2</sub>O<sub>4</sub> spinel phase without any MgO being formed.

### Acknowledgments

The authors gratefully acknowledge financial support from the National Natural Science Foundation of China (Grant no. 20371006) and the Beijing Nova Program (Grant No. 2003B10).

### References

1. M. SUGIMOTO, *J. Amer. Ceram. Soc.* **82** (1999) 269.
2. S.-H. YU and M. YOSHIMURA, *Adv. Funct. Mater.* **12** (2002) 9.
3. M.-P. PILENI, *ibid.* **11** (2001) 323.
4. R. G. KULKARNI and H. H. JOSHI, *J. Solid State Chem.* **64** (1986) 141.
5. V. ŠEPALAK, D. BAABE, F. J. LITTERST and K. D. BECKER, *J. Appl. Phys.* **88** (2000) 5884.
6. H. ST. C. O'NEILL, H. ANNERSTEN and D. VIRGO, *Amer. Mineral.* **77** (1992) 725.
7. R. J. WILLEY, S. A. OLIVER, G. OLIVERI and G. BUSCA, *J. Mater. Res.* **8** (1993) 1418.
8. C. LIU, A. J. RONDINONE and Z. J. WANG, *Pure Appl. Chem.* **72** (2000) 37.
9. H. H. HAMDEH, Z. XIA, R. FOEHRWEISER, B. J. McCORMICK, R. J. WILLEY and G. BUSCA, *J. Appl. Phys.* **76** (1994) 1135.
10. J. LIU, F. LI, D. G. EVANS and X. DUAN, *Chem. Commun.* (2003) 542.
11. V. RIVES (ed.), "Layered Double Hydroxides: Present and Future" (Nova Science Publishers, New York, 2001).
12. A. VACCARI, *Catal. Today* **41** (1998) 53.
13. J. M. FERNÁNDEZ, M. A. ULIBARRI, F. M. LABAJOS and V. RIVES, *J. Mater. Chem.* **8** (1998) 2507.
14. O. ROSSELL, M. SECO, G. SEGALÉS, S. ALVAREZ, M. A. PELLIGHELLI, A. TIRIPICCHIO and D. DE MONTAUZON, *Organomet.* **16** (1997) 236.
15. J. W. BOCLAIR, P. S. BRATERMAN, B. D. BRISTER, Z. WANG and F. YARBERRY, *J. Solid State Chem.* **161** (2001) 249.
16. P. S. BRATERMAN, C. TAN and J. ZHAO, *Mater. Res. Bull.* **29** (1994) 1217.
17. H. NIJS, M. D. BOCK and E. F. VANSANT, *Micropor. Mesopor. Mater.* **30** (1999) 243.
18. M. J. HOLGADO, V. RIVES, M. S. SANROMAN and P. MALET, *Solid State Ionics* **92** (1996) 273.
19. H. CHRISTIAN, B. HANSEN and C. B. KOCH, *Clays Clay Miner.* **42** (1994) 170.
20. S. KIKKAWA and M. KOIZUMI, *Mater. Res. Bull.* **17** (1982) 191.
21. S. IDEMURAM, E. SUZUKI and Y. ONO, *Clays Clay Miner.* **37** (1989) 553.
22. I. CRESPO, C. BARRIGA, M. A. ULIBARRI, G. GONZÁLEZ-BANDERA, P. MALET and V. RIVES, *Chem. Mater.* **13** (2001) 1518.
23. I. CRESPO, C. BARRIGA, V. RIVES and M. A. ULIBARRI, *Solid State Ionics* **101-103** (1997) 729.
24. F. MILLANGE, R. I. WALTON and D. O'HARE, *J. Mater. Chem.* **10** (2000) 1713.

Received 13 January  
and accepted 9 March 2004