

## Stoichiometric synthesis of a pure ferrite from a tailored layered double hydroxide (hydrotalcite-like) precursor

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Calcination of a layered double hydroxide precursor containing  $Mg^{II}$ ,  $Fe^{II}$  and  $Fe^{III}$  cations with an  $Mg^{2+}:(Fe^{II} + Fe^{III})$  ratio of 0.5 affords a pure ferrite spinel,  $MgFe_2O_4$ , which has a higher saturation magnetization than samples of the same material produced by conventional ceramic routes.

Spinel of the type  $M^{II}M^{III}_2O_4$  attract a great deal of interest because of their diverse practical applications. In the case of  $M^{III} = Fe$ , the resulting ferrites are amongst the most widely used magnetic materials.<sup>1</sup> The efficacy of the material depends on its microstructural properties which are sensitive to its mode of preparation.<sup>2–4</sup> To take magnesium ferrite,  $MgFe_2O_4$ , as an example, the conventional ceramic method of preparation<sup>5</sup> involves calcination of mixtures of precursors ( $MgO$  or  $MgCO_3$  and  $Fe_2O_3$ ) at temperatures of 1100 °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.<sup>6</sup> Alternative wet chemical methods have been proposed including coprecipitation from aqueous solution,<sup>4</sup> sol-gel synthesis<sup>7</sup> and use of micellar microemulsions.<sup>3,8</sup> In these cases, it is difficult to prevent contamination of the product by cations from the precipitants or organic residues from the precursors.<sup>9</sup> 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 in which the magnesium and iron cations are *uniformly distributed on an atomic level*. In this Communication, we show how synthesis of a layered double hydroxide (LDH) precursor with the correct stoichiometry allows this objective to be realized.

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clays whose structure can be described as containing brucite-like layers in which some of the divalent cations have been replaced by trivalent ions giving positively-charged sheets with anions between the layers.<sup>10</sup> 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. They are potential precursors for ferrite spinels since they are often formed with mixtures of the same cations and have been shown to have an absence of long-range cation ordering.<sup>11</sup> Calcination of LDHs at intermediate temperatures (450–600 °C) affords poorly crystalline mixed metal oxides.<sup>12</sup> Calcination above 750 °C is known to give spinels, but these are always mixed with the oxide of the divalent metal.<sup>13</sup> This reflects the fact that in LDHs, the ratio  $M^{II}/M^{III}$  is typically<sup>10</sup> in the range 2–4 whereas in a spinel the required ratio is  $M^{II}/M^{III} = 0.5$ .

Recently Refait *et al.* reported<sup>14</sup> a green rust mineral  $[Mg_{1-x-y}Fe^{II}_xFe^{III}_y(OH)_2]^{x+y}(CO_3^{2-})_{x/2} \cdot yH_2O$  having the LDH structure and some synthetic analogues. These are potential precursors to pure spinels since the  $Fe^{2+}$  ions will be oxidized on calcination in air to give  $Fe^{3+}$  ions, thus overcoming the deficiency of trivalent ions. We have prepared† LDHs I–III of the type  $[Mg_{1-x-y}Fe^{II}_xFe^{III}_y(OH)_2]^{x+y}(CO_3^{2-})_{x/2} \cdot yH_2O$  with three different molar ratios of cations by a modification of the literature procedure.<sup>14</sup> Compositions of the precursor mixtures

and elemental analysis results for the products are shown in Table 1. The  $Mg^{2+}:(Fe^{2+} + Fe^{3+})$  ratio in the final product is in each case significantly different from that in the corresponding synthesis mixture, but the values are reproducible within experimental error. The XRD patterns exhibit the characteristic reflections of LDH materials and no other crystalline phases are present. Fig. 1 shows the XRD patterns for the materials obtained by calcination in air of LDHs I–III at 1100 °C for 2 h. In each case the characteristic reflections of an  $MgFe_2O_4$  spinel are observed. Calcined LDH I also shows peaks due to an  $\alpha$ - $Fe_2O_3$  phase,<sup>6</sup> consistent with the low  $[Mg^{2+}:(Fe^{2+} + Fe^{3+})]$  ratio in the precursor. Although all of the main reflections of  $MgO$  coincide with those of  $MgFe_2O_4$ , the relatively high intensities of the peaks around  $2\theta$  values of 43° and 63° in the XRD pattern of calcined LDH III suggest that these are superpositions of reflections due to the spinel phase and magnesium oxide, consistent with the high  $[Mg^{2+}:(Fe^{2+} + Fe^{3+})]$  ratio in the precursor. The XRD pattern for calcined LDH II can be indexed to a pure spinel phase with  $a_0 = 0.8379$  nm, consistent with the  $[Mg^{2+}:(Fe^{2+} + Fe^{3+})]$  ratio of 1:2 in the

Table 1 Analytical properties of LDHs

Sample	I	II	III
Initial $Mg^{2+}:Fe^{2+}:Fe^{3+}$	1:2:1	2:1:1	8:1:3
Initial $(Mg^{2+} + Fe^{2+}):Fe^{3+}$	3.000	3.000	3.000
Initial $Mg^{2+}:(Fe^{2+} + Fe^{3+})$	0.333	1.000	2.000
$Mg^{2+}:(Fe^{2+} + Fe^{3+})$ in LDH <sup>a</sup>	0.325	0.505	2.120

<sup>a</sup> Solid dissolved in dil. nitric acid and ratio determined by ICP

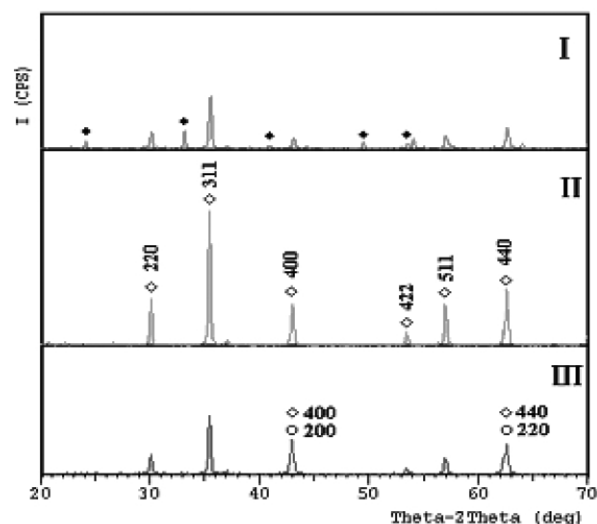


Fig. 1 Powder XRD peaks and corresponding Miller indices for LDHs I–III (see Table 1) calcined at 1100 °C for 2 h. The characteristic reflections of  $MgFe_2O_4$  are observed in each case ( $\diamond$ ). II is a single phase since the  $Mg:Fe$  ratio in the precursor has the same value (0.5) as that in  $MgFe_2O_4$  itself. I also shows peaks due to  $\alpha$ - $Fe_2O_3$  ( $\blacklozenge$ ) since the  $Mg:Fe$  ratio in the precursor is less than 0.5. III also shows peaks due to  $MgO$  ( $\circ$ ) since the  $Mg:Fe$  ratio in the precursor is greater than 0.5.

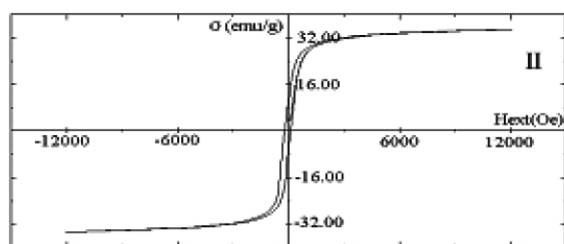
LDH precursor. The average crystallite size, estimated using the Scherrer equation,<sup>15</sup> is about 85 nm.

The Mössbauer spectra for calcined LDHs I – III are consistent with the literature<sup>4,5</sup> for MgFe<sub>2</sub>O<sub>4</sub>. The spectrum of calcined LDH I also shows lines which can be assigned<sup>9</sup> to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, consistent with the XRD data discussed above. The structural formula of magnesium ferrite is usually written as (Mg<sup>2+</sup><sub>1-c</sub>Fe<sup>3+</sup><sub>c</sub>) [Mg<sup>2+</sup><sub>c</sub>Fe<sup>3+</sup><sub>2-c</sub>]{O<sup>2-</sup>}<sub>4</sub>, where the round and square brackets denote sites of tetrahedral (A) and octahedral [B] coordination respectively and where *c* represents the degree of inversion which can be calculated<sup>5</sup> from the relative areas of the Mössbauer subspectra. Assuming the ratio of the recoilless fraction *f<sub>B</sub>/f<sub>A</sub>* is 0.94 at room temperature,<sup>5</sup> the structural formulae of the spinels obtained by calcination of LDHs I–III are (Mg<sub>0.19</sub>Fe<sub>0.81</sub>)[Mg<sub>0.81</sub>Fe<sub>1.19</sub>]O<sub>4</sub>, (Mg<sub>0.29</sub>Fe<sub>0.71</sub>)[Mg<sub>0.71</sub>Fe<sub>1.29</sub>]O<sub>4</sub> and (Mg<sub>0.18</sub>Fe<sub>0.82</sub>)[Mg<sub>0.82</sub>Fe<sub>1.18</sub>]O<sub>4</sub> respectively. The Mössbauer parameters are given in Table 2.

The magnetic properties of calcined LDHs I–III were investigated using a vibrating sample magnetometer (VSM). The hysteresis curve for calcined LDH II is shown in Fig. 2. The saturation magnetization has a much higher value ( $\sigma_s = 34.6$  emu g<sup>-1</sup>) than that of MgFe<sub>2</sub>O<sub>4</sub> produced by conventional ceramic methods<sup>16</sup> (26.4 emu g<sup>-1</sup>). LDHs possess several advantages as a precursor to ferrite spinels which lead to enhanced saturation magnetization. Use of a single precursor with the cations randomly distributed with no long range order<sup>11</sup> facilitates the synthesis of a homogeneous spinel phase. The close structural relationship between the LDH precursor and its calcination products is also a key factor. Rebours *et al.* have shown<sup>17</sup> that collapse of the layered structure on heating an LDH at around 400 °C gives a poorly crystalline mixed metal

**Table 2** Mössbauer parameters measured at room temperature for materials produced by calcination of LDHs I – III at 1100 °C for 2 h. (A): tetrahedral Fe<sup>3+</sup> in MgFe<sub>2</sub>O<sub>4</sub>; [B] octahedral Fe<sup>3+</sup> in MgFe<sub>2</sub>O<sub>4</sub>;  $\delta$  (mm s<sup>-1</sup>): isomer shift relative to sodium nitroprusside;  $\Delta E$  (mm s<sup>-1</sup>): quadrupole splitting; RA (%): relative intensity of peak areas.

		(A)	[B]	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>
LDH I	$\delta$	0.023	0.102	0.040
	$\Delta E$	0.120	0.003	0.153
	RA	34.84	48.54	16.62
LDH II	$\delta$	0.035	0.151	
	$\Delta E$	0.129	0.023	
	RA	36.79	63.21	
LDH III	$\delta$	0.040	0.155	
	$\Delta E$	0.127	0.019	
	RA	42.61	57.39	



**Fig. 2** Hysteresis curve of spinel phase produced by calcination of LDH II at 1100 °C for 2 h. Its saturation magnetization is much higher than that of a spinel phase produced by conventional ceramic methods.

oxide which can best be described as a spinel-like phase. This phase preserves the particle morphology of the LDH,<sup>18</sup> suggesting a topotactic transformation. In this case the (110) reflection of the LDH transforms to the (440) spinel reflection. Furthermore the fact that the spinel is produced from a single solid precursor rather than a mixture means that the calcination process requires a much shorter time, leading to a lower chance of side-reactions occurring. The high saturation magnetization observed for the spinel obtained by calcination of LDH II is also a function of the low degree of inversion obtained using this method (0.71). This is lower than the values for MgFe<sub>2</sub>O<sub>4</sub> produced by ceramic methods, although the value can be reduced by high-energy milling after calcination.<sup>5</sup>

A wide variety of LDHs with three and four different cations in the layers can be prepared.<sup>10</sup> Further work on the synthesis of LDH precursors of the type [M<sup>II</sup><sub>1-x-y</sub>Fe<sup>II</sup><sub>y</sub>Fe<sup>III</sup><sub>x</sub>(OH)<sub>2</sub>]<sup>x-</sup>(CO<sub>3</sub><sup>2-</sup>)<sub>x/2-y</sub>H<sub>2</sub>O with compositions appropriate for the synthesis of a range of ferrite spinels of commercial importance such as zinc ferrite and (Ni,Zn) and (Mn,Zn) ferrite is currently underway in our laboratory.

## Notes and references

† *Synthesis of LDHs I–III*: A mixture of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, FeCl<sub>2</sub>·4H<sub>2</sub>O and Fe(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was dissolved in N<sub>2</sub>-saturated deionized water {[Mg<sup>2+</sup>] + [Fe<sup>2+</sup>] + [Fe<sup>3+</sup>] = 0.66 M}. A mixed base solution ([NaOH] = 1.5 M, [Na<sub>2</sub>CO<sub>3</sub>] = 0.7 M) in N<sub>2</sub>-saturated deionized water was added dropwise to the stirred mixture at 25 °C until the pH reached 11. The resulting suspension was aged for 15 h in an N<sub>2</sub> atmosphere. The mixture was cooled by adding N<sub>2</sub>-saturated deionized water at 0 °C, filtered and washed with N<sub>2</sub>-saturated deionized water at 0 °C and then N<sub>2</sub>-saturated ethanol at 0 °C. The resulting solid was dried at room temperature and stored at 0 °C under N<sub>2</sub>.

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