

## Ageing behaviour of unary hydroxides in trivalent metal salt solutions: Formation of layered double hydroxide (LDH)-like phases

MICHAEL RAJAMATHI\* and P VISHNU KAMATH

Department of Chemistry, Central College, Bangalore University, Bangalore 560 001, India

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**Abstract.** The hydroxides of Mg, Ni, Cu and Zn transform into layered double hydroxide (LDH)-like phases on ageing in solutions of Al or Cr salts. This reaction is similar to acid leaching and proceeds by a dissolution–reprecipitation mechanism offering a simple method of LDH synthesis, with implications for the accepted theories of formation of LDH minerals in the earth's crust.

**Keywords.** Hydroxides; hydrotalcites; layered double hydroxides.

### 1. Introduction

Layered double hydroxides (LDHs) are modeled on the structure of  $\text{Mg}(\text{OH})_2$  (mineral brucite) and consist of a stacking of positively charged layers of the composition  $[\text{M}_{1-x}^{\text{II}} \text{M}_x^{\text{III}}(\text{OH})_2]^{x+}$  with anions  $[\text{A}^{n-}]$  intercalated in the interlayer region for charge neutrality (Carrado *et al* 1986). The LDHs are useful as anion exchange resins (Ookubo *et al* 1993), catalysts (Cavani *et al* 1991) and as electrodes for alkaline secondary batteries (Bauer *et al* 1990; Kamath *et al* 1994). While a variety of LDHs containing different combinations of divalent and trivalent cations have been synthesized, LDHs of some combinations form easily compared to others. Mg and Ni form LDHs easily with both Al and Fe by simple coprecipitation (Reichle 1986), but require prolonged hydrothermal treatment to form LDHs with Cr (Kooli *et al* 1995). On the other hand, ZnO readily reacts with a  $\text{Cr}(\text{NO}_3)_3$  solution to yield the Zn–Cr LDH within minutes (Boehm *et al* 1977). Mg forms a LDH with  $\text{V}^{3+}$  on hydrothermal treatment (Rives *et al* 1993), whereas with Ga, simple precipitation yields a crystalline LDH (Lopez-Salinas *et al* 1997). The LDHs of Cu present a special problem, as cupric hydroxide is structurally different from other divalent hydroxides and  $\text{Cu}^{2+}$  being a Jahn-Teller ion is not well suited to occupy the octahedral sites in the LDH structure. Nevertheless, the LDH of Cu with Al has been obtained by the addition of strong alkali to a cuprammine sulphate solution containing  $\text{Al}^{3+}$  ions (Park *et al* 1990). After an extensive examination of all the parameters that influence the outcome of a precipitation reaction, Grosso *et al* (1992) synthesized a Cu–Cr LDH, although not in a pure form. Other reports indicate single phase Cu–Cr

LDH formation when precipitation is carried out at a constant low (5.5) pH (Depege *et al* 1994, 1996). Such a technique has also been employed for the synthesis of LDHs of Co with Fe at pH 6.5 (Hansen *et al* 1994). While it is believed that coprecipitation at a constant low pH improves crystallinity, it has been observed that systems such as those of Cd with Al require a high pH (> 13) for LDH formation (Vichi and Alves 1997). There appears to be no single preparative technique for LDH synthesis and minor variations in the experimental protocol are required for different systems.

In this paper, we report the formation of LDH-like phases on ageing the solid divalent hydroxides in an aqueous solution of a salt of a trivalent metal such as Al or Cr. Aqueous solutions of the salts of Al and Cr are highly acidic (pH 0–1) and these reactions are somewhat similar to acid leaching. Treatment with acidic solutions of salts instead of pure acids can, in principle, go beyond proton insertion and cation exchange for protons and lead to incorporation of different metal ions (such as Al or Cr) into the solid. Moreover the observation of mineral LDH bands in brucite deposits outside the hydrothermal belt (Mondal and Baidya 1996) point to the possible formation of the LDH minerals by this process.

### 2. Experimental

Magnesium, nickel and cupric hydroxides, cupric oxide and zinc oxide were prepared by standard methods (Brauer 1965). 0.5 to 1 g of the unary hydroxide/oxide was made into a slurry in 5 ml of distilled water and aged in 10 ml of 0.5–1 mol  $\text{dm}^{-3}$  Al (or Cr) salt (nitrate, sulphate or chloride) solutions at 65°C for 2 to 4 days. These salt solutions were highly acidic (pH 0–1). The solid after ageing was filtered, washed free of anions and dried to constant weight at 100°C.

\*Author for correspondence

The products were characterized by X-ray diffractometry (JEOL JDX8P powder X-ray diffractometer, CuK $\alpha$  radiation) and infrared spectroscopy (Nicolet Impact 400D FTIR spectrometer, KBr pellets, 4 cm<sup>-1</sup> resolution).

### 3. Results and discussion

Table 1 shows the results of the ageing experiments. A majority of these experiments yielded single phase, although poorly ordered products. Figure 1 shows the powder X-ray diffractograms of the samples obtained by the ageing of copper(II) hydroxide in solutions of chromium nitrate and chloride. The prominent *d*-spacings are listed in table 2. The patterns are completely different from that of the starting material and can be indexed on a hexagonal cell similar to the assignment made by other authors (Depege *et al* 1994, 1996). The LDHs of Cu could also be obtained by the ageing of CuO. Figure 2 shows representative results of the ageing of CuO in a solution of aluminium nitrate. After 48 h of ageing, a highly ordered phase atypical of LDHs was obtained at the ambient temperature. This pattern corresponds to the

hydroxysalt, Cu<sub>3</sub>(OH)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> (JCPDS PDF No. 45-0594). On further ageing, a new phase with a larger inter-layer spacing corresponding to the Cu–Al LDH was observed.

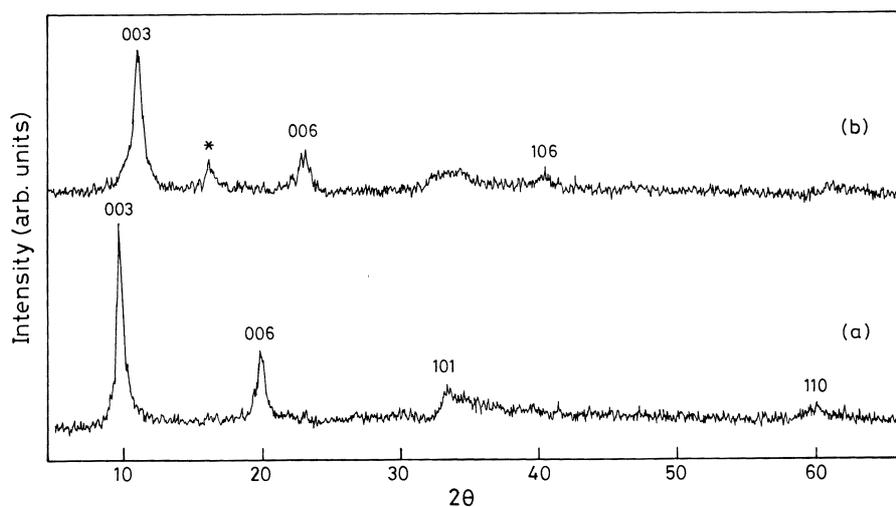
Similar results were also obtained in the Mg and Ni systems. Figure 3 shows the powder X-ray diffractograms of the as-prepared nickel hydroxide and the samples obtained by ageing it in Al chloride, nitrate and sulphate solutions. Before ageing, the highest *d*-spacing observed for nickel hydroxide is at 4.6 Å due to its (001) reflection. The diffraction patterns of the aged samples are completely different, with a new peak arising at around 8.0 Å followed by another around 4.0 Å. The patterns of the aged samples are similar to those of the mineral takovite, as well as the Ni–Al LDH obtained by conventional methods (Bish and Brindley 1977). Similar results were obtained for the ageing of magnesium hydroxide which yielded hydrotalcite-like LDHs.

One of the characteristic features of the LDHs is the presence of anions intercalated between the layers. Infrared spectra have been used for the characterization of intercalated anions. In figure 4 the infrared spectrum of as-prepared magnesium hydroxide is compared with the spectrum of the sample obtained after ageing it in a solution of aluminium sulphate. Mg(OH)<sub>2</sub> shows a sharp peak at 3650 cm<sup>-1</sup> due to the OH stretch followed by a broad band characteristic of the brucite lattice in the low frequency region (800–400 cm<sup>-1</sup>). The aged sample on the other hand shows a broad band in the 3600–3300 cm<sup>-1</sup> region due to OH groups hydrogen bonded to the intercalated water molecules. Further, strong vibrations are seen in the 1500–1000 cm<sup>-1</sup> region due to the intercalated sulphate (1124 cm<sup>-1</sup>). Magnesium hydroxide aged in aluminium nitrate shows peaks at 1420, 1387 and 1350 cm<sup>-1</sup> respectively, which are characteristic of nitrate

**Table 1.** A summary of the results of ageing unary hydroxides in solution of salts of trivalent metals.

	AlCl <sub>3</sub>	Al(NO <sub>3</sub> ) <sub>3</sub>	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	CrCl <sub>3</sub>	Cr(NO <sub>3</sub> ) <sub>3</sub>
Mg(OH) <sub>2</sub>	–	HT + Br	HT	AS	AS
Ni(OH) <sub>2</sub>	HT	HT	HT	AS	AS
Cu(OH) <sub>2</sub>	–	HT	–	HT	HT
CuO	–	HT	–	HT	HT
ZnO	–	HT	–	HT	HT

HT: Hydrotalcite-like LDH; Br: brucite; AS: amorphous solid.



**Figure 1.** Powder X-ray diffraction pattern of copper (II) hydroxide aged in chromium (III) nitrate (a) and chloride (b) solutions. Feature marked by asterisk is due to impurities.

ions intercalated in the  $C_{2v}$  symmetry (Portemer *et al* 1992). The presence of intercalated anions, as seen from the infrared spectra is consistent with the increase in interlayer spacing observed by diffraction studies.

Chemical analyses of the LDH samples were done by a combination of gravimetric and complexometric techniques. Except for the Cu–Cr LDH which answered to the formula  $Cu_2Cr_{1.1}(OH)_{6.3}(NO_3)_{1.1} \cdot 2H_2O$ , analyses of other LDHs did not lead to any consistent results. An excess of Al was found in most samples, probably due to the presence of X-ray amorphous  $Al(OH)_3$  and  $AlO(OH)$  phases.

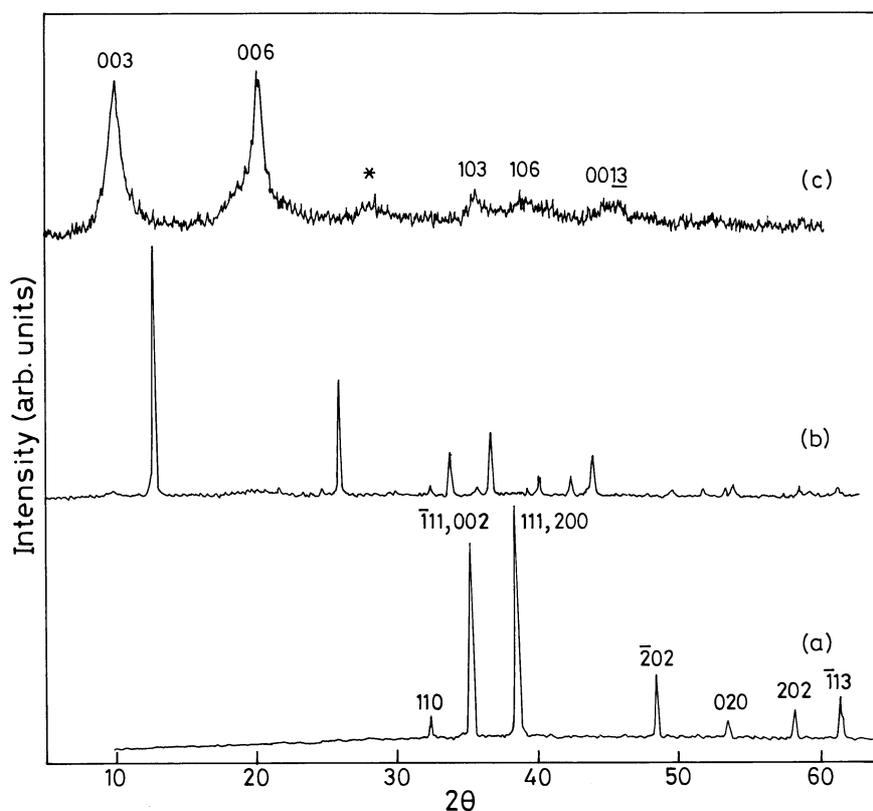
Chemical coprecipitation of  $Al^{3+}$  (or  $Cr^{3+}$ ) with divalent metals at high pH leads to the formation of carbonate intercalated LDHs. Special precautions have to be taken to obtain LDHs containing other anions such as chloride or nitrate (Wang *et al* 1992). In the present instance the LDHs are formed at a low pH which preclude carbonate incorporation and thereby LDHs containing nitrate, chloride and sulphate ions having their own characteristic interlayer spacings have been obtained.

Solid state transformations by acid leaching can take place topotactically or by a dissolution–reprecipitation mechanism. In the former case, the structure of the

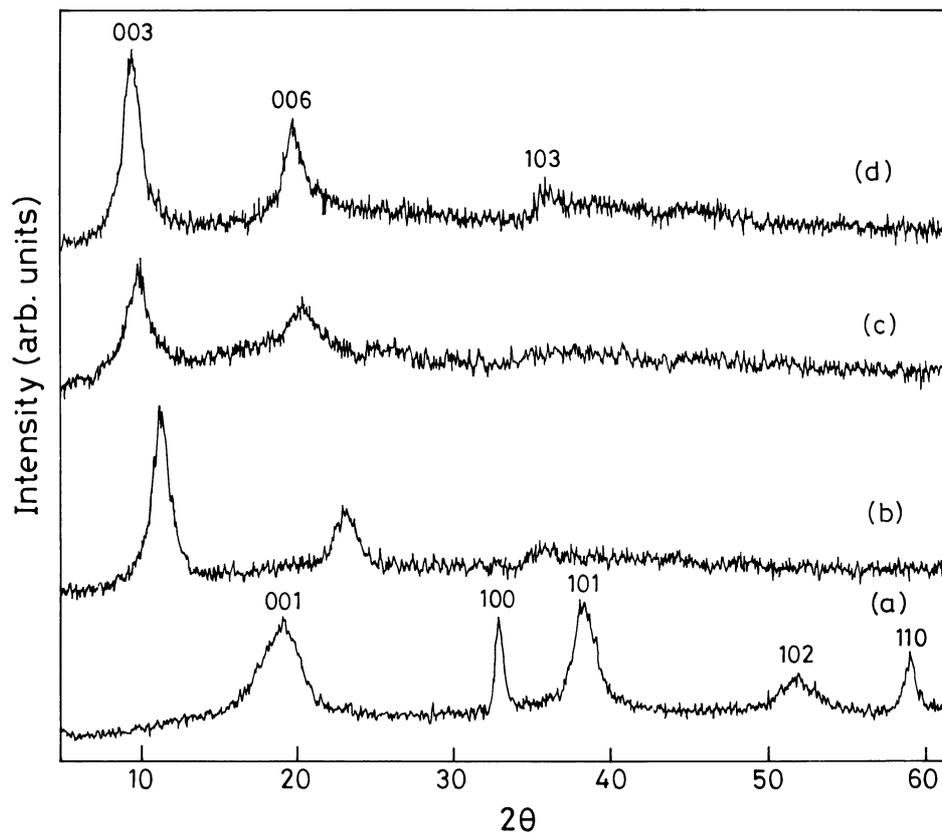
**Table 2.** Powder X-ray diffraction data of layered double hydroxides obtained by the ageing of unary hydroxides in Al (or Cr) salt solutions.

$hkl^a$	$d/\text{\AA}$								
	Mg–Al <sup>b</sup> $NO_3^-$	Mg–Al $SO_4^{2-}$	Ni–Al $NO_3^-$	Ni–Al $SO_4^{2-}$	Ni–Al $Cl^-$	Cu–Al $NO_3^-$	Cu–Cr $NO_3^-$	Cu–Cr $Cl^-$	Zn–Al $NO_3^-$
003	7.83	8.76	8.76	8.59	7.66	8.60	8.93	7.79	9.12
006	3.93	4.46 <sup>c</sup>	4.38	4.31	3.85	4.33	4.48	3.91	4.53
103	–	–	2.50	–	2.51	2.51	2.67	–	–
104	–	–	2.43	–	–	–	2.45	–	–

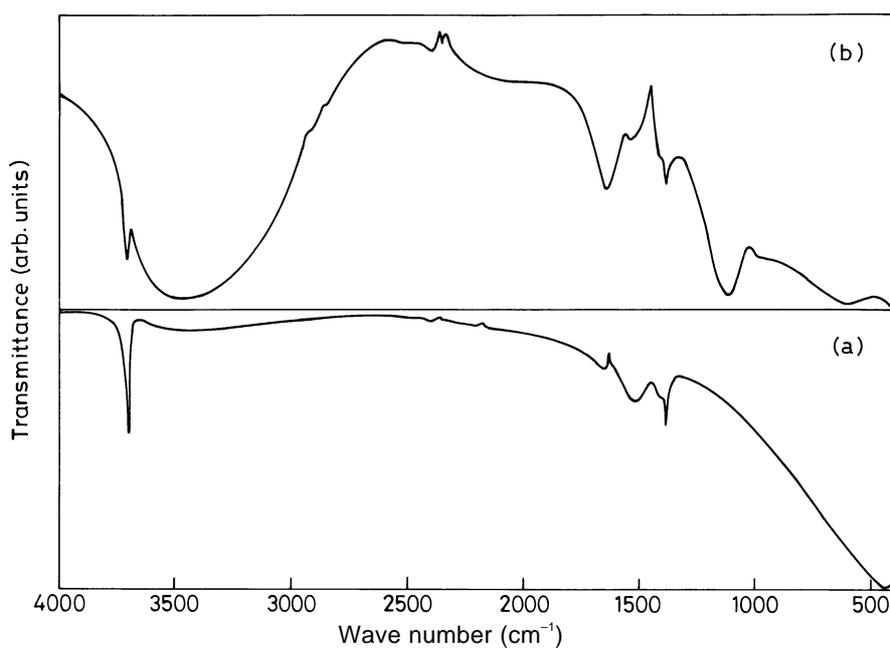
<sup>a</sup>For phases showing only two lines, assignment has been done by comparison with the diffraction patterns of model compounds taken from the literature. For others a hexagonal cell has been used; <sup>b</sup>weak lines due to starting materials persist even after prolonged ageing and are not listed here; <sup>c</sup>broad.



**Figure 2.** Powder X-ray diffractogram of CuO (a) compared with those of CuO aged in aluminium nitrate for 2 days (b) and 4 days (c). Feature marked by asterisk is due to impurities.



**Figure 3.** Powder X-ray diffraction pattern of nickel hydroxide (a) compared with those of nickel hydroxide aged in aluminium chloride (b), sulphate (c) and nitrate (d) solutions.



**Figure 4.** Infrared spectrum of magnesium hydroxide (a) compared with that of magnesium hydroxide aged in an aluminium sulphate solution (b).

product phases are related to the structure of the reactant. In the present instance, both cupric hydroxide as well as CuO and ZnO, all of which differ in their structures lead to isostructural LDH-like phases. Clearly the structure of the product formed is independent of the structure of the starting materials, indicating that this ageing reaction proceeds via the dissolution–reprecipitation mechanism.

These observations have important implications for the current understanding of the formation of mineral LDH deposits in the earth's crust. LDHs are mainly known to occur within the hydrothermal belt leading to the assumption that hydrothermal conditions are essential for the formation of LDH deposits. But the observation of mineral LDH bands in brucite deposits outside the hydrothermal belt is yet to be explained. It is well known that the pH of open and closed water bodies in nature can vary significantly in the range 2–9 depending upon the conditions. Ageing of brucite deposits in water bodies containing dissolved Al could easily explain these observations.

#### 4. Conclusions

In this study we have demonstrated the formation of layered double hydroxide-like phases by the ageing of solid unary hydroxides in solutions of Al or Cr salts at temperatures close to the ambient (< 65°C).

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