Synthesis of the $3R_2$ polytype of a hydrotalcite-like mineral

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The direct synthesis is reported of a $3R_2$ polytype of a hydrotalcite-like mineral by the hydrothermal treatment of aluminium oxide and magnesium oxide.

Hydrotalcite-like materials [also known as layered double hydroxides (LDHs) and anionic clays] are of potential value in areas as diverse as catalysis, medicine and oil-field exploration.[1,2] Structurally they consist of stacks of brucite-like $M^{2+}(OH)_2$ layers in which a partial replacement of M^{2+} by M^{3+} occurs.[3] The resulting charge on the layers necessitates the incorporation of charge-balancing anions such as carbonate, sulfate and hydroxide within the interlayer.

The $M^{2+}(OH)_2$ layers consist of close-packed hydroxide ions, with cations occupying octahedral sites. Bookin and Drits[4] have reviewed the stacking sequences and possible polytypes that can theoretically exist for these layered materials. In summary, the hydroxyl sites in the plane of the layers can be described as A, B or C, and are related by hexagonal lattice translations in the ab-plane of (1/3, 2/3) or (2/3, 1/3). If it is assumed that the lower surface of a brucite-like layer is a hydroxyl sheet in which OH groups occupy A sites, and that the upper surface is formed by OH groups in C sites, then the cations must occupy octahedral positions in B sites. Such a layer can be symbolically represented as AC, since the position of the cation sites is entirely determined if the positions of the hydroxyl groups are known.[4]

Two direct layer-upon-layer arrangements may be considered. A prismatic (P-type, denoted by =) or octahedral (O-type, denoted by –) arrangement is distinguished depending on whether the opposing hydroxides of adjacent brucite-like layers lie vertically above one another (P) or are off-set by a lattice translation of (1/3, 2/3) or (2/3, 1/3) (O). In addition, different stacking sequences of O and P arrangements can then generate a range of polytypes. For example, the mineral with the approximate composition of $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ occurs as both the three-layer polytype hydrotalcite (the 3R polytype) and the two-layer polytype manasseite (the 2H polytype). The 3R polytype can have either all P-type interlayers or all O-type interlayers, designated by Bookin and Drits[4] as $3R_1$ or $3R_2$, respectively. These two polytypes will have the following stacking sequences:

$$AC=CB=BA=AC \qquad (3R_1)$$
$$AC–BA–CB–AC \qquad (3R_2)$$

Both have rhombohedral symmetry (space group $R\bar{3}m$) with cations homogeneously distributed over A, B and C sites. From single-crystal structure analysis, naturally occurring hydrotalcite belongs to the $3R_1$ class of polytype.[3]

As pointed out by Bookin and Drits,[4] most analysis of the X-ray patterns of hydrotalcite-like materials is primarily limited to the measurement of peak positions and to confirming formation of either the 2H or 3R polytype. Only by careful analysis of reflection intensities is it possible to distinguish, for example, $3R_1$ and $3R_2$. In a second paper, Bookin et al.[5] examined the available literature to determine which polytypes for hydrotalcite-like minerals had indeed been observed. They concluded that there was some evidence for the $3R_2$ and $3H_2$ polytypes for naturally occurring sulfate-bearing minerals (but only after ion-exchange and not by direct synthesis),[6] but with carbonate and hydroxide polytypes, formation was limited to $3R_1$ and possibly a 1H polytype.[7]

Given the interest in these materials, and the possibility that the $3R_1$ and $3R_2$ polytypes may have different physical as well as chemical properties, a synthetic strategy for forming $3R_2$ would be of considerable interest. We report here a simple and direct route to the $3R_2$ polytype.

MgO was obtained from Aldrich. Cp 1.5, which is a flash-calcined gibbsite (loss on ignition = 12.2 mass%), was obtained from Alcoa Chemicals. Deionised water was used for all preparations. Autogeneous hydrothermal preparations were carried out in stainless steel autoclaves with Teflon or glass linings. Non-hydrothermal treatments were typically performed using a covered 100 cm^3 conical flask heated on a hot-plate stirrer at ambient pressure. After reaction the samples were dried in air at 80 °C without filtering or washing. Powder X-ray diffraction (PXRD) patterns were recorded in reflection geometry using Cu Kα radiation (λ = 1.5418 Å). Data were collected from finely ground samples pressed into a glass sample holder.

Fig. 1(a) is the simulated powder X-ray diffraction pattern of the $3R_1$ polytype of hydrotalcite. The pattern was simulated
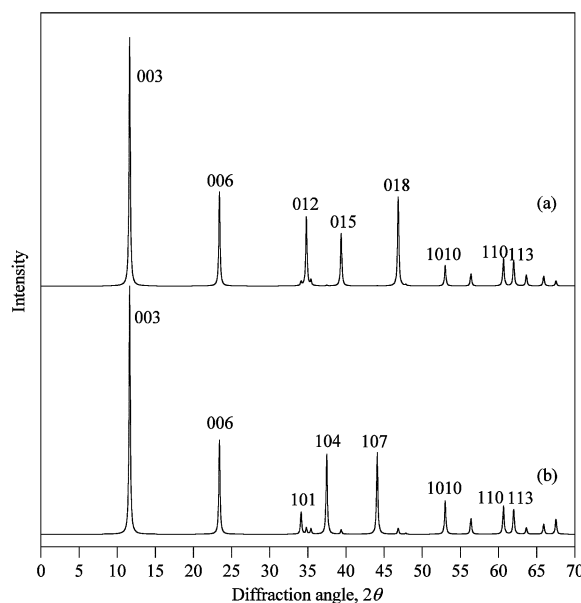

Fig. 1 Simulated PXRD patterns of the (a) $3R_1$ and (b) $3R_2$ polytypes of hydrotalcite.

from the crystal structure of hydrotalcite using the *Cerius²* software package.[3,8] Fig. 1(b) is the simulated PXRD pattern of the same material, but with the layers shifted by lattice translations of (1/3, 2/3) or (2/3, 1/3) to generate the $3R_2$ polytype. As expected the PXRD patterns are similar, except for the relative intensities of the 101, 012, 104, 015, 107 and 018 non-basal reflections. The predicted intensities are in good agreement with those of Bookin and Drits.[4] We note the important summary that:

for the $3R_1$ polytype, the 012, 015 and 018 reflections will be relatively strong;

for the $3R_2$ polytype, the 101, 104 and 107 reflections will be relatively strong.

Fig. 2 compares the PXRD patterns of products from a 20 wt% slurry of MgO and Cp in water, with a Mg : Al ratio of 2.0, treated for 24 h at 70 °C (atmospheric pressure, non-hydrothermal) or 180 °C (hydrothermal). Note that no anions were added to the system, thus the only sources of interlayer anions were CO_2 from the atmosphere or adsorbed on the reactants (giving CO_3^{2-} and/or HCO_3^{-}) and OH^{-} anions present in the slurry. Given that the hydrothermal synthesis was within a closed container it is believed that hydroxyl anions dominate during preparation, although during subsequent
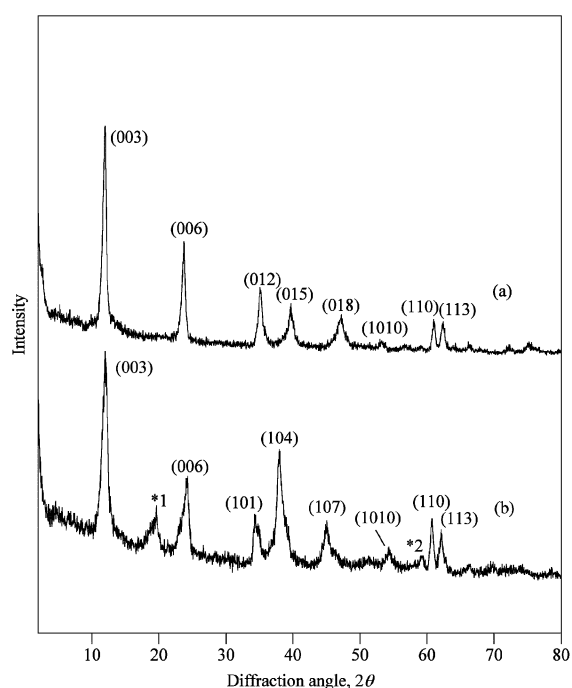
drying in air carbon dioxide uptake from the surrounding atmosphere will to some extent occur. For the non-hydrothermal preparation, CO_2 uptake will occur during synthesis leading to a carbonate-rich material compared to the hydrothermal product.

All the reflections in the PXRD pattern of the non-hydrothermal product [Fig. 2(a)] may be indexed on the basis of a three-layer rhombohedral lattice with the hexagonal unit-cell parameters $a = 3.038$ Å and $c = 22.446$ Å (Table 1) The indexing (**1**) is consistent with a $MgAl(OH/CO_3)$ $3R_1$ hydrotalcite. For the hydrothermal product [Fig. 2(b)] the major reflections may again be indexed (**2**) on the basis of a three-layer rhombohedral lattice, with similar, although not exactly the same, hexagonal unit-cell parameters $a = 3.052$ Å and $c = 22.174$ Å (Table 1). In terms of reflection positions, therefore, both products index as 3R polytypes. Consideration of the intensities of the non-basal reflections, however, confirms that the hydrothermally-produced LDH belongs to the $3R_2$ rather than the $3R_1$ class of polytype. Indexing of the PXRD pattern of the hydrothermal product was also attempted on the basis of a hexagonal (2H) lattice, with, for example, $a = 3.048$ Å and $c = 14.72$ Å. Such indexing, however, was significantly less satisfactory than for the rhombohedral lattice. Other three-layer polytypes[3] were also considered (*i.e.* $3H_1$ and $3H_2$) but the absence of an expected (106) reflection indicated that these polytypes were not formed. An additional phase (**3**) could be identified in Fig. 2(b) and the positions of the reflections for this phase are also given in Table 1. These are in agreement with the formation of a small amount of $3R_1$, possibly formed during drying in air at atmospheric pressure. The parameters for this phase are very close to those for the ambient pressure preparation.

The non-indexed reflections *1 and *2 in Fig. 2(b) at 19.29° (2θ) (4.60 Å) and 59.20° (2θ) (1.56 Å) may be assigned tentatively to the presence of brucite as an impurity in the product. The assignment is only tentative because the observed reflections occur at lower *d*-spacings than reported data (4.77 and 1.57 Å, JCPDS number 83-0114). It should be noticed that the presence of brucite would also give rise to significant intensity at 37.98° (2θ) (2.37 Å), close to the expected position of a non-basal LDH (104) reflection. This may account for the high intensity of the reflection close to 37°. We note also that the reflection close to 19° has previously been assigned to a superlattice structure in LDHs – the theoretical value is given by $\sqrt{3}a\sin60$ which is equal to 4.57 Å. Its existence in the $3R_2$ polytype phase may point to the ordered arrangement of anions within the gallery. It is not possible to say whether this possible ordering may be the result of an ordered arrangement of cations in the octahedral sites. A similar ordered anion arrangement has been proposed[9,10] for the case of a benzoate-intercalated material and by Bookin *et al.* for a sulfate-containing material.[5] It was suggested that

Fig. 2 PXRD patterns of products from a 20 wt% slurry of MgO and Cp in water, with a Mg : Al ratio of 2.0, treated for 24 h at (a) 70 °C (atmospheric pressure) or (b) 180 °C (hydrothermal). *1 and *2 are non-indexed reflections (see text).

Table 1 PXRD data for the three phases discussed in the text. **1** refers to the ambient pressure product, **2** to the $3R_2$ product from hydrothermal synthesis and **3** the minor component present in the hydrothermal preparation. ($\lambda = 1.5418$ Å)

1				**2**				**3**			
$2\theta_{obs}$	d_{obs}	hkl	$d_{calc}{}^a$	$2\theta_{obs}$	d_{obs}	hkl	$d_{calc}{}^b$	$2\theta_{obs}$	d_{obs}	hkl	$d_{calc}{}^c$
11.873	7.454	003	7.489	11.931	7.418	003	7.391	11.931	7.418	003	7.506
23.650	3.762	006	3.744	24.167	3.683	006	3.696	23.428	3.797	006	3.753
35.122	2.555	012	2.562	34.277	2.616	101	2.625	34.843	2.575	012	2.573
39.648	2.273	015	2.270	37.932	2.372	104	2.386	38.852	2.318	015	2.280
47.054	1.931	018	1.920	44.962	2.016	107	2.029	46.282	1.962	018	1.927
53.320	1.718	1010	1.708	54.310	1.689	1010	1.699	—	—	1010	1.714
60.985	1.519	110	1.519	60.690	1.526	110	1.526	60.690	1.526	110	1.526
62.317	1.490	113	1.489	62.095	1.495	113	1.494	62.095	1.495	113	1.495

$^a a = 3.038$, $c = 22.466$: 101, 2.613; 104, 2.383; 107, 2.035 Å – a $3R_1$ polytype. $^b a = 3.052$, $c = 22.174$ Å: 012, 2.571; 015, 2.270; 018, 1.913 Å – a $3R_2$ polytype. $^c a = 3.052$, $c = 22.517$ Å: 101, 2.625; 104, 2.393; 107, 2.042 Å – a $3R_1$ polytype.
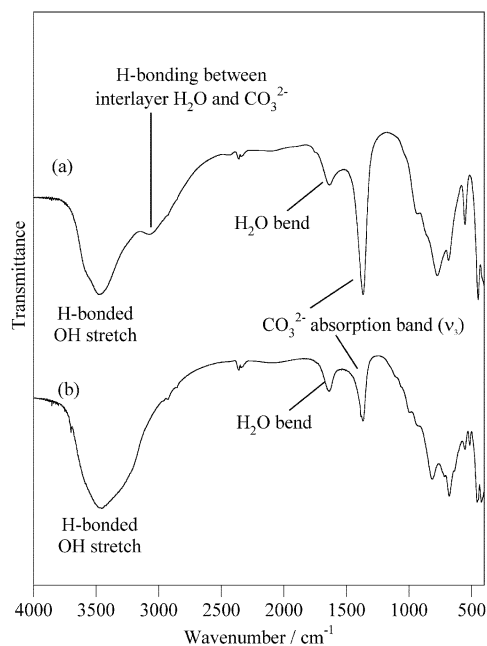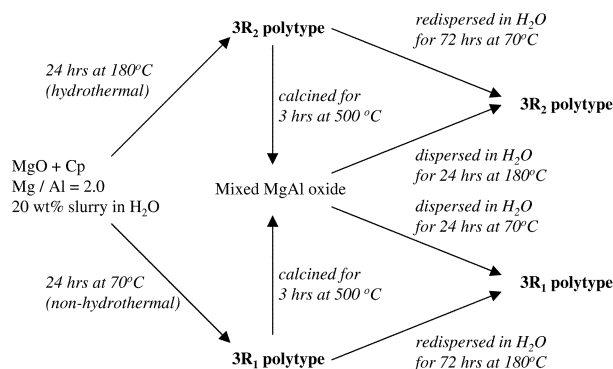
Fig. 3 FTIR spectra of representative samples of (a) $3R_1$ and (b) $3R_2$ polytypes of hydrotalcite-like LDHs.

Scheme 1 Formation and interconversion of hydrotalcite-like $3R_1$ and $3R_2$ LDH polytypes.

the anion ordering might be reflecting an ordering of the Al^{3+} cations within the hydroxide sheet.[9]

Fourier-transform infrared (FTIR) spectra of representative examples of the $3R_1$ and $3R_2$ polytypes are compared in Fig. 3. Although generally similar, it is noticeable that the carbonate absorption bands are significantly weaker for the $3R_2$ polytype. The obvious conclusion is that there is less interlayer carbonate present in the $3R_2$ polytype compared with the $3R_1$. It is probable, therefore, that hydroxide is the principal anion introduced during hydrothermal synthesis.

The Mg : Al ratio of the representative examples of the $3R_1$ and $3R_2$ polytypes can be estimated by comparing the measured a-parameter with literature values.[11] The results suggest that the ratio in the LDH phase is close to 2.6 and 2.1, respectively, for the $3R_1$ and $3R_2$ forms. These values indicate that the polytypes, in particular the $3R_1$ form, are Mg-rich compared with the starting materials, and that an impurity Al-containing phase is present in the products, which was not washed away or filtered post-reaction.

Dispersion in deionised water of the $3R_1$ polytype and hydrothermal treatment at 180 °C for 72 h does not generate the $3R_2$ polytype (Scheme 1). Similarly, redispersing the $3R_2$ polytype in deionised water or 1 M Na_2CO_3(aq) and treatment at 70 °C for 72 h does not generate the $3R_1$ polytype, which suggests that, once formed, the $3R_2$ polytype is stable under such conditions. It is interesting to note, however, that calcination of the $3R_2$ polytype at 500 °C for 3 h generates a poorly crystalline mixed Al and Mg oxide which upon rehydration in deionised water at 70 °C for 24 h generates the hydrotalcite-like $3R_1$ polytype. Hydrothermal rehydration at 180 °C

re-generates, however, the $3R_2$ polytype. Calcination and rehydration of the $3R_1$ polytype at 70 °C for 24 h re-generates the hydrotalcite-like $3R_1$ whilst hydrothermal rehydration at 180 °C generates, however, the $3R_2$ polytype.

In summary, we have demonstrated that the hitherto theoretical $3R_2$ polytype of a hydrotalcite-like LDH can be prepared by hydrothermal treatment of a calcined LDH precursor or a mixture of MgO and a flash-calcined gibbsite. Once formed, the $3R_2$ polytype is relatively stable in air and in water.

We are currently undertaking a systematic investigation to determine the conditions under which the $3R_2$ polytype offers enhanced physical and chemical properties compared to the well-known $3R_1$ polytype of hydrotalcite.

Acknowledgements

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