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Polytype Selection and Structural Disorder Mediated by Intercalated Sulfate Ions Among the Layered Double Hydroxides of Zn with Al and Cr

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Received November 14, 2008; Revised Manuscript Received May 10, 2009

ABSTRACT: The stacking of metal hydroxide layers is mediated by intercalated anions. Thereby, anions of different molecular symmetries select for different polytypes. The sulfate ion (molecular symmetry T_d) intercalates with one of its axes of rotation parallel to the c -crystallographic axis, also the stacking direction. When the C_3 axis of the sulfate is parallel to the c -axis (coordination symmetry C_{3v}), the resulting solid crystallizes in the structure of the 1H or the $3R_1$ polytype. The coordination symmetry of the SO_4^{2-} ion (C_{3v}) is a subset of both O_h and D_{3h} , which are respectively the local symmetries of interlayer sites in the 1H and $3R_1$ polytypes. When the sulfate ion intercalates with one of its C_2 -axes parallel to the c -axis (coordination symmetry D_{2d}), the resulting solid has a faulted structure, and the local structure of the stacking faults resembles a crystal of monoclinic symmetry. When the sulfate retains the T_d symmetry in the interlayer, the LDH crystallizes with turbostratic disorder, which is a direct consequence of the mismatch between the interlayer site symmetry and that of SO_4^{2-} ion. This work demonstrates the correlation between the short-range interactions as shown by the local coordination symmetry of the anion and the long-range ordering reflected by the crystal symmetry.

Introduction

Layered double hydroxides (LDHs) belong to the class of layered materials having the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2](A^{n-})_{x/n} \cdot mH_2O$ ($M^{II} = \text{Mg, Fe, Ni, Co, Cu, Zn}$; $M^{III} = \text{Al, Cr, Fe}$; $0.2 \leq x \leq 0.33$).¹ We represent the LDH composition using the symbol $[M-M'-A]_x$. The structure of these materials can be derived from that of mineral brucite, $Mg(OH)_2$. Brucite comprises a hexagonal stacking of charge-neutral layers of the composition $[Mg(OH)_2]$.² When a fraction of Mg^{2+} ions is isomorphously substituted by a trivalent ion such as Al^{3+} , the metal hydroxide layer acquires a positive charge with the composition $[Mg_{1-x}Al_x(OH)_2]^{x+}$, leading to the incorporation of anions in the interlayer for charge neutrality.³ A variety of anions such as Cl^- , NO_3^- , CO_3^{2-} , SO_4^{2-} , polyoxometallates, carboxylates, sulphonates, phosphonates, and others, can be incorporated in the galleries between the metal hydroxide layers.

Like in other layered solids,⁴ among the LDHs too, the metal hydroxide layers can be stacked in different ways to obtain a variety of polytypes. For instance, among the $[Mg-Al-CO_3]_{0.33}$ LDHs, the mineral hydroxalite crystallizes in the rhombohedral symmetry (space group, $R\bar{3}m$) and manessite in the hexagonal symmetry (space group, $P6_3/mmc$).⁵ Bookin and Drits⁶ described all the theoretically possible polytypes among the LDHs and developed a simple nomenclature for the various stacking sequences. By this nomenclature, the minerals hydroxalite and manessite belong to the $3R_1$ and $2H_1$ polytypes, respectively. The rhombohedral cell comprises three metal hydroxide slabs, while the hexagonal cell comprises two. The suffix "1" stands for trigonal prismatic interlayer sites. The carbonate ion occupies prismatic sites in both these polytypes, as its molecular symmetry (D_{3h}) matches with the local symmetry of the trigonal prismatic interlayer site. The carbonate ions therefore select for polytypes with trigonal prismatic sites.⁷

There are other polytypes, for instance, the 1H, $2H_2$, and $3R_2$,⁶ which possess octahedral interlayer sites. For a given a -

parameter, the octahedral interlayer sites are smaller than the trigonal prismatic sites. In $Mg(OH)_2$, for instance, the interlayer sites are empty and the structure of the 1H polytype offers a close packing of metal hydroxide slabs, and thereby greater stability. Among the simple unitary hydroxides, other polytypes are not known.

When the interlayer is occupied, as in the LDHs, polytypes with prismatic sites are preferred. It would therefore be interesting to explore the possible synthesis of LDHs in different polytypes having octahedral interlayer sites, by using anions of the appropriate symmetry. One common anion is SO_4^{2-} , which has the T_d symmetry. Many SO_4^{2-} intercalated LDHs ($M^{II} = \text{Zn, Cu}$; $M^{III} = \text{Al, Cr}$) are reported in the literature.^{8,9} They vary considerably in the amount of intercalated water and consequently in their basal spacing. The basal spacing is sensitive to the environment as the SO_4^{2-} LDHs reversibly exchange their intercalated water content with the vapor phase. They also undergo structure changes in this process.¹⁰

On intercalation in the LDH galleries, the symmetry of the SO_4^{2-} ion is reduced to C_{3v} , if one of its S–O bonds is parallel to the stacking direction, also the c -crystallographic axis. The C_{3v} symmetry is a subset of both D_{3h} and O_h symmetries, and we surmised that the SO_4^{2-} must in principle mediate the ordered growth of polytypes with interlayer sites of both octahedral and trigonal prismatic symmetries. Additionally, the SO_4^{2-} ion could intercalate with its 2-fold axis parallel to the stacking direction. The coordination symmetry in this case would be D_{2d} . We ask the question if the D_{2d} -sulfate would mediate the growth of a polytype with monoclinic symmetry.

In this paper, we report the synthesis of sulfate intercalated LDHs in the Zn–M ($M = \text{Al, Cr}$) system having the structure of both 1H and $3R_1$ polytypes. We also introduce a new stacking disorder model having a monoclinic local symmetry within the matrix of rhombohedral symmetry.

Experimental Section

All the LDHs were prepared by coprecipitation. In a typical preparation, 50 mL of a mixed metal ($[Zn^{2+}]/[M^{3+}] = 2$; $M = \text{Al, Cr}$)

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Table 1. Precipitation Conditions Used for the Synthesis of LDH Samples and the Characterization Data of the Samples

LDH system	pH	T (°C)	cell parameters		SO ₄ ²⁻ content (mol)	water content (mol)
			<i>a</i> (Å)	<i>c</i> (Å)		
[Zn–Al–SO ₄] _{0.33}	8	65	~3.05	8.89	0.149	0.84
	9	65	3.064	32.67	0.142	0.96
	10	65	3.079	11.1	0.144	1.03
[Zn–Cr–SO ₄] _{0.33} as prepared	5	60	3.118	8.93	0.148	0.77
	5	60	3.123	32.82	0.149	1.4

salt solution was added dropwise to a reaction vessel containing 100 mL of a Na₂SO₄ salt solution, taken 10 times in excess of the stoichiometric requirement. A constant pH is maintained during preparation by simultaneous addition of 0.5 M NaOH using a Metrohm model 718 STAT Titrino, operating in the pH STAT mode. The temperature was kept constant at 60 °C, and nitrogen gas was bubbled continuously throughout the experiment. The resulting slurry was then aged for 15 h and separated by centrifugation. The precipitate obtained was washed with warm decarbonated water several times and finally with acetone and dried at 60 °C. The precipitation conditions are listed in Table 1. A well ground sample of the [Zn–Cr–SO₄]_{0.33} LDH obtained at pH 5 was then exposed to air at ambient conditions for 45 h to get the hydrated form having a basal spacing of 11 Å.

Characterization

All the samples were characterized by powder X-ray diffraction (PXRD) using a Bruker D8 Advance powder diffractometer (source Cu K α radiation, λ = 1.5418 Å). The powder patterns were indexed using the program *PROSZKI*¹¹ and the figure of merit was determined. For structure refinement by the Rietveld method, data were collected at a scan rate of 0.2° 2 θ min⁻¹ (step size of 0.02° 2 θ , counting time 6 s step⁻¹). IR spectra of the samples were recorded using a Nicolet model Impact 400D FTIR spectrometer (KBr pellets, 4 cm⁻¹ resolution, 400–4000 cm⁻¹). Thermogravimetric analysis (TGA) studies were carried out using a Mettler Toledo 851° TGA/SDTA system. The samples were dried at 100 °C for 30 min in the TG balance to expel the exchangeable water content and the temperature was ramped from 100–800 °C (5 °C min⁻¹; N₂ atmosphere). The sulfate content of the LDHs was estimated by wet chemical analysis. A previously weighed (1 g) amount of the LDH was dissolved in 1.5 mL of HCl (concentration 11 M) and diluted to 200 mL. Hot BaCl₂ solution was added to precipitate the dissolved sulfate and weighed as BaSO₄. The sulfate content present is listed in Table 1.

Computational Studies

The Rietveld technique was employed for structure refinement using the GSAS software.¹² Structure refinement of the [Zn–Cr–SO₄]_{0.33} LDH was carried out using the published structure models (Polytype 1H: CC No. 75542; Polytype 2H₁: CC No. 91860). DIFFaX (Version 1.807),^{13,14} a FORTRAN based computer program, was used for simulations of PXRD patterns of different polytypes as well as to quantify the structural disorder. Details of the use of these techniques in structure refinement of LDHs and simulation of structural disorder are described in detail in earlier papers and not repeated here.^{15–17} The new disorder model introduced here involves the growth of stacking disorders with a monoclinic local symmetry in the matrix of a crystal with rhombohedral symmetry. There are two ways of generating stacking faults of monoclinic symmetry: (i) by distortion of the coordination symmetry of the metal ion, (ii) by varying the stacking of metal hydroxide layers. In this paper, monoclinic faults are introduced by suitable translation of successive metal hydroxide layers

relative to one another. Two identical metal hydroxide layers defined by atomic position parameters of the model rhombohedral LDH structure (Polytype 3R₁: CC No. 91859) were used. Rhombohedral symmetry of the 3R₁ polytype (Laue symmetry 3/*m*) is generated by the relative translation of these layers by the stacking vector (2/3, 1/3, 1/3). A translation by the vector (1/2, 0, 1/3) or (0, 1/2, 1/3) destroys the 3-fold axis along the stacking direction while retaining the 2-fold symmetry. The DIFFaX code computes the Laue symmetry 2/*m* in keeping with the monoclinic symmetry. The simultaneous use of the two stacking vectors with different probabilities generates a hexagonal crystal with stacking faults having a local monoclinic symmetry.

Results

[Zn–Al–SO₄] LDH. The PXRD pattern of the [Zn–Al–SO₄]_{0.33} LDH obtained by coprecipitation at pH 8 (Figure 1a) shows only four peaks: two low angle peaks are indexed to the basal reflections 001 and 002, respectively. The “sawtooth”-shaped reflections appearing above 30° 2 θ are characteristic of materials with turbostratic disorder and are therefore indexed to the two-dimensional reflections 10 and 11. The random translation of successive layers relative to each other destroys three-dimensional periodicity resulting in the extinction of all nonbasal reflections. The interlayer spacing estimated from the PXRD pattern is 8.81 Å corresponding to a monolayer of free sulfate ions.¹⁸ Because of excessive broadening of the peaks, the *a*-parameter cannot be reliably estimated. SO₄²⁻ incorporation is confirmed by wet chemical analysis as well as IR spectroscopy. SO₄²⁻ has *T_d* symmetry and only two IR active normal modes, ν_3 and ν_4 , which appear at 1105 and 613 cm⁻¹, respectively. The IR spectrum of this compound (Figure 2a) shows that the SO₄²⁻ ion retains its *T_d* symmetry, indicating a

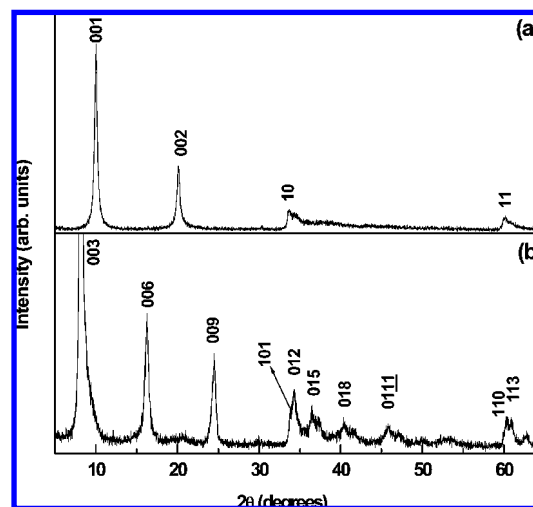


Figure 1. PXRD patterns of [Zn–Al–SO₄]_{0.33} LDH prepared at (a) pH 8, (b) pH 9.

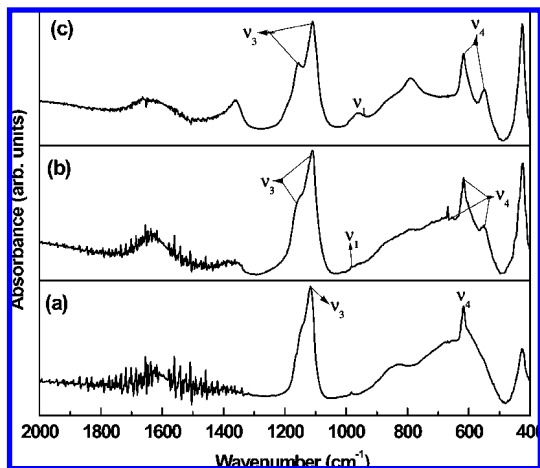


Figure 2. IR spectra of $[\text{Zn-Al-SO}_4]_{0.33}$ LDHs prepared at (a) pH 8, (b) pH 9, and (c) pH 10.

weak interaction with the host material. All the samples precipitated below pH 8 had similar characteristics. TGA (Supporting Information, SI.1) shows a four-step mass loss. The first mass loss corresponds to amount of exchangeable water in the interlayer and is removed isothermally at 100 °C. The second mass loss (100–200 °C) is due to the loss of nonexchangeable water from the interlayer. The broad peak in DTG at 200–400 °C is due to dehydroxylation of brucite-like sheets. The high temperature mass loss appearing above 650 °C is due to the decomposition of the sulfate ion. The water content estimated from the mass loss up to 200 °C was found to be 0.84 moles per formula unit. Combining this with the results of wet chemical analysis (Table 1) yields the approximate formula $[\text{Zn}_{0.667}\text{Al}_{0.33}(\text{OH})_2][(\text{SO}_4)_{0.15}(\text{CO}_3)_{0.016}] \cdot 0.84\text{H}_2\text{O}$.

The PXRD pattern of the sample precipitated at pH 9 (Figure 1b) shows three basal reflections with an interlayer spacing 11 Å, corresponding to the inclusion of a water molecule in addition to the sulfate in a bilayer arrangement.¹⁸ Although the features appearing above 30° 2θ have a “sawtooth” envelope, individual peak maxima can be discerned indicative of a more ordered structure. However, the peaks are nonuniformly broadened. An indication of the nature of disorder responsible for the broadening is obtained from the splitting of lines in the IR spectrum of the sample in the 1200–400 cm^{-1} region (Figure 2b), indicating the reduced symmetry of the SO_4^{2-} ion in the interlayer. The triply degenerate ν_3 mode splits into two peaks at 1114 cm^{-1} and 1160 cm^{-1} corresponding, respectively, to the A_1 and E modes, and the ν_4 mode splits into three peaks at 669 cm^{-1} (A_2), 615 cm^{-1} (B_1), and 550 cm^{-1} (B_2). The ν_2 mode which is expected to be at 440 cm^{-1} is not seen as a separate band due to its overlap with O–M–O bending mode of metal-hydroxide sheet at 450 cm^{-1} .¹⁹ The above data indicate that the symmetry of SO_4^{2-} is reduced to D_{2d} . TGA (Supporting Information SI.1) shows a four-step mass loss. The water content estimated from the mass loss up to 200 °C was found to be 0.96 moles per formula unit. Combining this with the results of wet chemical analysis (Table 1) yields the approximate formula $[\text{Zn}_{0.667}\text{Al}_{0.33}(\text{OH})_2][(\text{SO}_4)_{0.142}(\text{CO}_3)_{0.02}] \cdot 0.96\text{H}_2\text{O}$.

The question arises as to how a sulfate ion in the D_{2d} coordination symmetry is accommodated in the interlayer region. A polytype with a 2-fold symmetry along the stacking direction can be envisaged having the monoclinic symmetry. The DIF-FaX-simulated PXRD pattern expected of such a polytype is compared with that of the $3R_1$ polytype (Figure 3). While some of the observed reflections in Figure 1b match with those

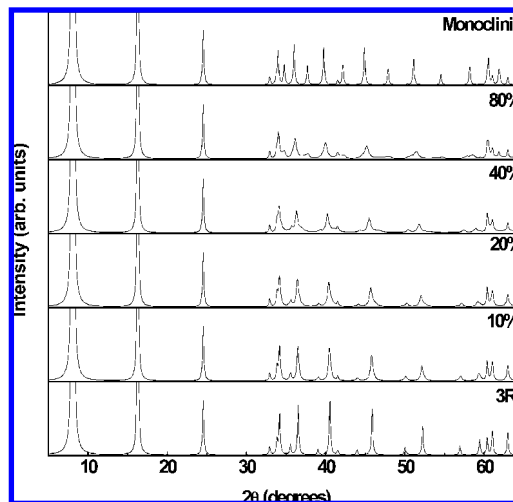


Figure 3. Model simulations of the PXRD patterns of the $3R_1$ polytype containing different proportions of stacking faults of monoclinic local symmetry.

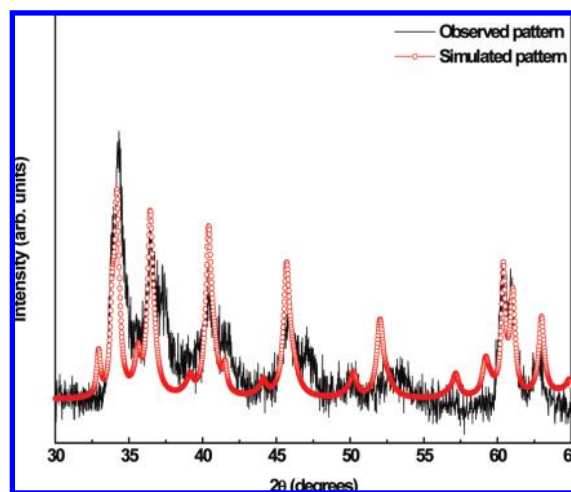


Figure 4. PXRD pattern of the LDH $[\text{Zn-Al-SO}_4]_{0.33}$ prepared at pH 9 overlaid with the simulated pattern of $3R_1$ polytype with 20% monoclinic fault. Basal reflections are deleted for clarity.

expected of a structure with rhombohedral symmetry the whole pattern could not be indexed to either a rhombohedral or a monoclinic cell. We therefore conclude that the material obtained at pH 9 is a faulted structure.

The rhombohedral and monoclinic polytypes differ only slightly from one another. While the successive layers in the $3R_1$ polytype are translated by $(2/3, 1/3)$ in the a – b plane, the monoclinic symmetry is generated using the translation $(0, 1/2)$ or $(1/2, 0)$. Since different translations differ only slightly in energy,²⁰ it is not difficult to conceive the intergrowth of regions belonging to the two different symmetries within a faulted crystal. The DIF-FaX-simulated PXRD patterns expected of faulted crystals having different proportions of monoclinic faults within a matrix of the $3R_1$ polytype are given in Figure 3. It is seen that the incorporation of stacking faults leaves the basal reflections unaffected, whereas the peaks due to the $0kl$ reflections are broadened. The experimentally observed broadening in Figure 1b was simulated (Figure 4) by incorporating 20% monoclinic stacking faults within the matrix of the $3R_1$ polytype. There is an overall match of the intensity envelope.

The PXRD pattern of the LDH obtained at pH 10 (Figure 5) contains many sharp reflections whose Bragg angles match with

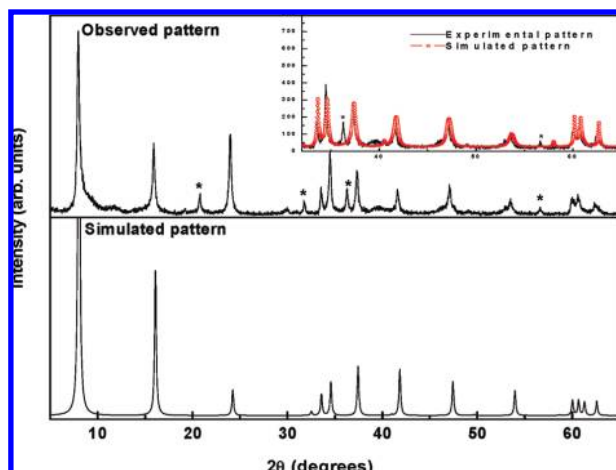


Figure 5. PXRD pattern of $[\text{Zn-Al-SO}_4]_{0.33}$ LDH prepared at pH 10 compared with the DIFFaX-simulated pattern of the 1H polytype. Inset is an overlay of the two in the region $32\text{--}65^\circ$ 2θ . Peaks marked by asterisk are due to an impurity.

those expected of the 1H polytype. The pattern was indexed to a single layered hexagonal cell ($a = 3.079 \text{ \AA}$; $c = 11.1 \text{ \AA}$; figure of merit: 28.6, Table 2). There is however a mismatch between the relative intensities of some of the reflections, which could be accounted for by the inclusion of a nominal 10% stacking faults having the $3R_1$ motifs. The match between the observed and simulated patterns is given in the inset to Figure 5.

The IR spectrum (Figure 2c) shows that the ν_3 and ν_4 absorptions are split into two each. The two doublets appear at 1160 and 1109 cm^{-1} and 550 and 619 cm^{-1} , respectively. The ν_1 mode is activated and appears at 960 cm^{-1} . All these are characteristic of SO_4^{2-} in the C_{3v} coordination symmetry. Thermogravimetric analysis (Supporting Information SI.1) shows a four-step mass loss. The water content (1.03 per formula unit) and sulfate content (0.144 per formula unit) yield the approximate formula $[\text{Zn}_{0.667}\text{Al}_{0.33}(\text{OH})_2][(\text{SO}_4)_{0.144}(\text{CO}_3)_{0.02}]\cdot 1.03 \text{ H}_2\text{O}$.

[Zn-Cr-SO₄] LDH. In the Zn-Cr system, LDHs were prepared at three different pH values of 5, 5.5, and 6. A highly ordered sample was obtained only at pH 5. The structure of this phase was refined by the Rietveld method and was found to belong to the 1H polytype (Figure 6a). The fit is satisfactory and the results are given in Tables 3 and 4. Although the structure of the 1H polytype differs considerably from that of the 2H polytype, the PXRD patterns of the two differ only slightly from one another since the distribution of cations in the brucite like layers is similar. The presence of weak 103 and 105 reflections are the only distinguishing features of the $2H_1$ polytype.²¹ To confirm that the observed pattern is of the 1H polytype, a Rietveld refinement was also carried out using the $2H_1$ structure model (Supporting Information SI.2). The goodness of fit parameters obtained for the latter fit were inferior to those obtained for the former (Table 3).

In the 1H structure, one of the S-O bonds is parallel to the c -crystallographic axis. This oxygen (O3) is referred to as apical oxygen. The other oxygens are called equatorial oxygens (O2). The site of the equatorial oxygen is shared by the oxygen of the intercalated water molecules as well. The O-S-O angles do not depart much from the tetrahedral value (109°), but the S-O3 bond length is significantly shorter than the S-O2 generating the C_{3v} symmetry (see Table 4).

The IR spectrum (Figure 6b) shows different vibrational modes of sulfate where ν_3 splits at 1114 and 1130 cm^{-1} , ν_4 at

570 and 617 cm^{-1} , and ν_1 appearing at 984 cm^{-1} indicating distortion of T_d symmetry of sulfate to C_{3v} . ν_2 overlaps with the lattice vibrations and appears at 514 and 410 cm^{-1} . TG studies (Supporting Information SI.3) of the sample show the four-step mass loss as in the earlier cases. The approximate formula determined from TG data and wet chemical analysis is $[\text{Zn}_{0.667}\text{Cr}_{0.33}(\text{OH})_2][(\text{SO}_4)_{0.148}(\text{CO}_3)_{0.018}]\cdot 0.77 \text{ H}_2\text{O}$.

Further when this sample was exposed to air at ambient conditions for a period of 45 h, a hydrated phase with an elongated basal spacing of 10.80 \AA was obtained. The PXRD pattern of the LDH sample thus obtained (Figure 7) matches well with that simulated for the $3R_1$ polytype. The SO_4^{2-} ion retains its C_{3v} symmetry in the transformed sample. The TG data (Supporting Information SI.4) reveals the water content present in the sample to be 1.4 moles per formula unit.

Discussion

Polytypism is one-dimensional polymorphism.²⁰ In the specific context of layered hydroxides, all polytypes have a common metal hydroxide slab, whose structure can be represented as AbC, or more simply as AC.⁶ Here the upper case symbols stand for the hydroxyl ion positions and the lower case symbols for the cation positions, which correspond to the octahedral interstitials.

In the $3R_1$ polytype the metal hydroxide stacking sequence is AC CB BA AC..., each underlined pair of upper case symbols representing one metal hydroxide slab. It is clear that the hydroxyl ions of the successive slabs face each other generating prismatic interlayer sites, having the local symmetry, D_{3h} . CO_3^{2-} ions, also of D_{3h} symmetry, occupy these sites and mediate the ordered growth of crystallites, resulting in highly ordered $[\text{M-M}'\text{-CO}_3]$ LDHs ($\text{M} = \text{Zn, Co, Mg}$; $\text{M}' = \text{Al}$).^{17,22} These materials have been used for structure refinement by the Reitveld method.

There is another class of polytypes having sequences of the type:



These polytypes differ from $3R_1$ in that they incorporate octahedral interlayer sites. There have been suggestions in the literature of the existence of carbonate containing LDHs in the structure of the $3R_2$ polytype.²³ But the evidence is not unequivocal, and no structure refinements have been reported.

The following questions arise:

(1) What if any are the factors responsible for polytype selection?

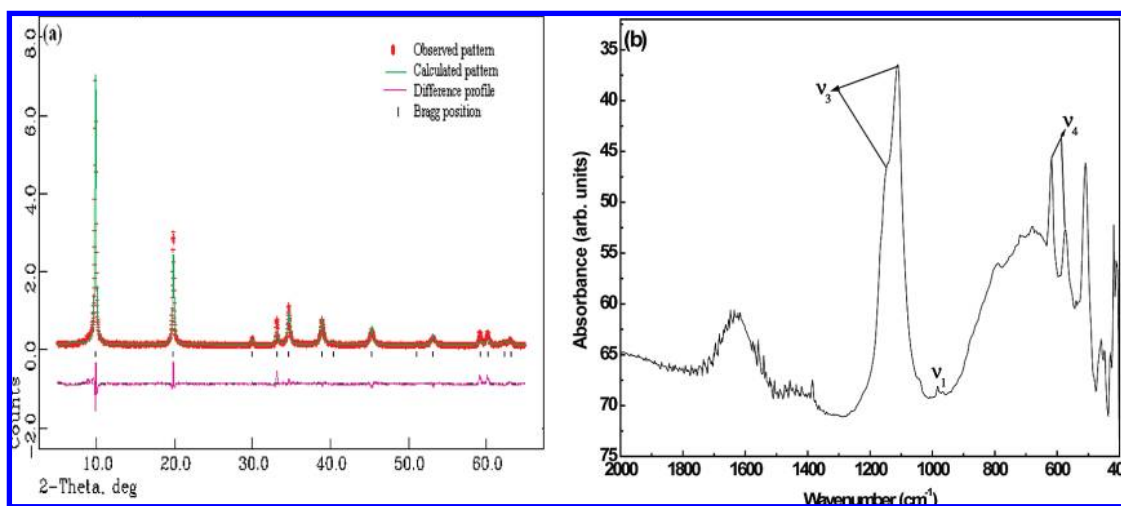
(2) How do we engineer the synthesis of a polytype with octahedral interlayer sites?

Polytype selection is mediated by the anions.⁷ Anions select for the polytype, whose interlayer site symmetry best matches their own symmetry. The symmetry of the anion, should however be computed with caution. According to Halford's rule,²⁴ for a "molecule" in a solid, the principal axis of symmetry is the crystallographic axis of the host material. In the present instance, most relevant is the c -crystallographic axis, which is also the stacking direction. In the context of Halford's rule, the anion best suited to select for polytypes with both prismatic and octahedral interstitial sites is the sulfate ion.

Table 2. Observed and Calculated 2θ Values of $[\text{Zn-M-SO}_4]_{0.33}$ (M = Al, Cr) LDHs

$[\text{Zn-Al-SO}_4]_{0.33}$ (pH 10) ^a			$[\text{Zn-Cr-SO}_4]_{0.33}$ (pH 5) ^b			$[\text{Zn-Cr-SO}_4]_{0.33}$ (pH 5) ^c		
			as prepared			exposed to air for 45 h		
<i>d</i> (obs) (Å)	<i>d</i> (calc) (Å)	<i>hkl</i>	<i>d</i> (obs) (Å)	<i>d</i> (calc) (Å)	<i>hkl</i>	<i>d</i> (obs) (Å)	<i>d</i> (calc) (Å)	<i>hkl</i>
11.05	11.06	001	8.93	8.93	001	10.82	10.84	003
5.52	5.53	002	4.46	4.46	002	5.41	5.42	006
3.69	3.68	003	2.97	2.97	003	3.61	3.61	009
2.66	2.66	100	2.69	2.70	100	2.68	2.68	101
2.59	2.59	101	2.58	2.58	101	2.66	2.66	012
2.40	2.40	102	2.31	2.31	102	2.56	2.56	104
2.15	2.16	103	2.0	2.0	103	2.49	2.50	015
1.92	1.91	103	1.72	1.72	104	2.32	2.32	107
1.70	1.70	105	1.56	1.55	110	2.24	2.24	018
1.54	1.53	110	1.53	1.53	111	1.99	1.99	0111
1.52	1.52	111				1.56	1.56	110
						1.54	1.54	113
						1.50	1.50	116

^a $a = 3.0795(9)$ Å, $c = 11.032(7)$ Å, FOM = 28.68. ^b $a = 3.119(1)$ Å, $c = 8.931(6)$ Å, FOM = 28.79. ^c $a = 3.119(2)$ Å, $c = 32.521(4)$ Å, FOM = 11.14.

**Figure 6.** (a) Rietveld fit of the PXRD pattern of the $[\text{Zn-Cr-SO}_4]_{0.33}$ LDH coprecipitated at pH-5, (b) IR spectrum of the sample.**Table 3.** Comparison of the Results of the Rietveld Refinement of $[\text{Zn-Cr-SO}_4]_{0.33}$ LDH Structure with 1H and 2H₁ Structure Models

polytype	1H	2H ₁
space group	$P\bar{3}$	$P6_3/mmc$
cell parameters		
<i>a</i> (Å)	3.1144(10)	3.1139(19)
<i>c</i> (Å)	8.92412(19)	17.851(16)
goodness of fit		
R_{wp}	0.13	0.156
R_F^2	0.11	0.38
R_p	0.107	0.135
χ^2	0.033	0.058

Many sulfate intercalated LDHs are reported,^{8,25,26} and sulfate is known to intercalate with one of its S–O bonds parallel to the *c*-crystallographic axis, the coordination symmetry of such bonding being C_{3v} . Such LDHs have been shown to crystallize in 3R₁ polytype. This is understandable as the coordination symmetry C_{3v} is a subset of D_{3h} , the local symmetry of the interlayer site. As C_{3v} is also a subset of O_h , it was felt that under appropriate synthetic conditions, SO_4^{2-} ions must also select for polytypes with octahedral interstitial sites. Among various possible structures, it is customary to select the one with the smallest unit cell as the model, in the absence of overwhelming evidence of the existence of larger cells. So, we select for our consideration the 1H polytype. There are references in earlier literature to

Table 4. Position Parameters Obtained from the Rietveld Refinement of $[\text{Zn-Cr-SO}_4]_{0.33}$ LDH Structure Using the 1H Structure Model

polytype	atom	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>
1H	Zn	1 <i>a</i>	0.000	0.000	0.000
	Cr	1 <i>a</i>	0.000	0.000	0.000
	O1	2 <i>d</i>	0.3333	0.6666	0.10471(9)
	S	2 <i>c</i>	0.000	0.000	0.469(6)
	O2	6 <i>g</i>	0.243(5)	0.725(5)	0.418(1)
	O3	2 <i>c</i>	0.000	0.000	0.5909(61)
distances (Å)			angles (°)		
(Zn,Cr)–O1			O1–Zn–O1		
O1–O1			O1–Zn–O1		
S–O2			O2–S–O3		
S–O3			O2–S–O2		

the existence of mineral forms of SO_4^{2-} LDHs in the structure of the 1H polytype.²¹

In this work, we see a good correlation between the crystal symmetry of the polytype and the coordination symmetry of the SO_4^{2-} ion. When for instance, the LDH is turbostratically disordered, and the crystallographic axes are ill-defined, the SO_4^{2-} ion is found to behave as a free molecule in the T_d symmetry. It could in fact be conversely argued that the lack of orientational order among the SO_4^{2-} ions in this high symmetry is responsible for the random stacking of the metal hydroxide slabs resulting in a material with turbostratic disorder.

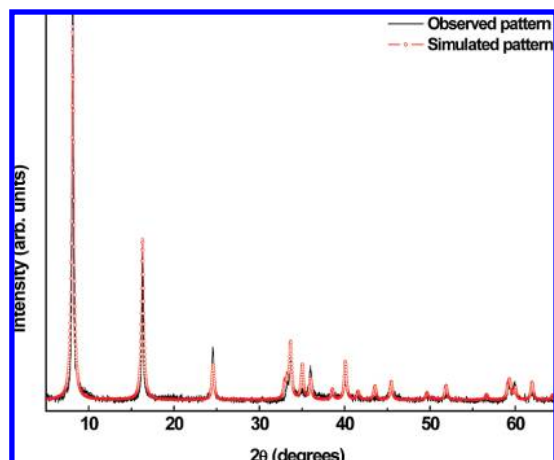


Figure 7. PXRD pattern of the $[\text{Zn-Cr-SO}_4]_{0.33}$ sample prepared at pH 5 and exposed to air for 45 h overlaid with its DIFFaX simulation.

When, on the other hand, the SO_4^{2-} orientation could be fixed in the C_{3v} symmetry, the structure of the 1H polytype was stabilized at pH 10. Under other conditions a faulted $3R_1$ polytype was stabilized. For instance, the sample prepared at pH 9 has SO_4^{2-} in D_{2d} symmetry and results in a faulted $3R_1$ polytype. In order to simulate the observed pattern, we introduce a new structural disorder model that of the intergrowth of a phase of monoclinic symmetry within the rhombohedral $3R_1$ polytype. The fact that the SO_4^{2-} ion in this particular sample is in D_{2d} symmetry made us surmise that the layers could slide with respect to each other in such a way that a local 2-fold symmetry, characteristic of a monoclinic crystal is generated. The translation vector used to obtain the monoclinic fault is $(a/2, 0)$ or $(0, b/2)$. Since relative translations obtained from crystal chemistry are energetically more feasible compared to turbostratic disorder,²⁰ the monoclinic disorder model is reasonable from a crystal chemical perspective. Nevertheless, we provide in Supporting Information SI.5 a DIFFaX simulation based on the more conventional stacking fault model for comparison.

In the $[\text{Zn-Cr-SO}_4]_{0.33}$ system also, the material obtained at pH 5 crystallizes in the structure of the 1H polytype. In fact, the materials were adequately well ordered to facilitate structure refinement by the Reitveld method. In this case too the SO_4^{2-} ion is in C_{3v} symmetry. The sample when exposed to air for 45 h was transformed into $3R_1$ polytype wherein the sulfate ion retains its C_{3v} symmetry. Thus, in the $[\text{Zn-Cr}]$ LDH system too, the 1H and $3R_1$ polytypes were obtained wherein the sulfate ion is present in two different interstitial sites.

In addition to symmetry considerations, it is evident that pH has an important role in polytype selection. This is particularly true in the present instance as the same polytype (1H) with SO_4^{2-} ions in the same coordination (C_{3v}) is obtained at completely different pH values in the Zn-Cr and Zn-Al systems. The formation pH of the 1H polytype in the Zn-Al system is 10, which is higher than the precipitation pH of the two unitary hydroxides $[\text{Zn}(\text{OH})_2]$ pH 6–7; $[\text{Al}(\text{OH})_3]$ pH 4–5 suggesting that the 1H polytype is a product of coprecipitation. In the Zn-Cr system, the 1H polytype forms at pH 5, which is less than the precipitation pH of $\text{Zn}(\text{OH})_2$. Variation of pH affects the synthesis in two ways: (a) by bringing about a change in the $[\text{SO}_4^{2-}]/[\text{OH}^-]$ ratio and (b) by generating different reactive species as a result of the hydrolysis of cations.²⁷ Cr^{3+} is known to form many

oligomeric species in the pH range 6–8 which adversely affect the formation of ordered LDH phases.¹⁸ In the Zn-Al-Cl system, ordered LDHs belonging to the $3R_1$ polytype are obtained in the pH range 7–10.¹⁸ Within the Zn-Al- SO_4^{2-} system, we show that the 1H polytype forms at the higher end of this pH range, while at the lower end, faulted structures are obtained. There are many intangibles in polytype selection and it is difficult to quantify all of them. What this work attempts to do is to focus on the role of anion symmetry as a possible determining factor in polytype selection.

Conclusion

In conclusion, the $[\text{Zn-Al-SO}_4]$ LDHs could be crystallized in both $3R_1$ and 1H polytypes. In the former the intercalated SO_4^{2-} ion (coordination symmetry C_{3v}) occupies a trigonal prismatic site while in the latter it occupies an octahedral interlayer site. When the coordination symmetry of the SO_4^{2-} changes to D_{2d} , the resulting solid is faulted, and the local structure of the stacking faults has a 2-fold symmetry reminiscent of a possible monoclinic polytype. The $[\text{Zn-Cr-SO}_4]$ LDH also crystallizes in 1H and $3R_1$ structures indicating that the observations are general to SO_4^{2-} -containing LDHs.

Acknowledgment. Authors thank the Department of Science and Technology (DST), Government of India, for financial support. P.V.K. is a recipient of the Ramanna Fellowship of the DST.

Supporting Information Available: TG-DTG curves of all the samples, Rietveld refinement of $[\text{Zn-Cr-SO}_4]_{0.33}$ LDH with 2H structure model, and the DIFFaX simulation of the $[\text{Zn-Al-SO}_4]$ LDH (pH 9). This information is available free of charge via the Internet at <http://pubs.acs.org>.

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