Supplementary Information

SI.-I. DIFFaX Simulations

We summarize below some of the salient features relevant to the simulations used here.

The main brucite-like layer has the composition $(Zn_{1-x}Al_x)O_2$ (x=0.33). The atom positions are taken from the model structure corresponding to mineral hydrotalcite (ICSD No. 6296; Space group $R\text{-}3m$; $a = 3.054$ Å; $c = 22.81$ Å). In DIFFaX simulations we explicitly specify the coordinates of all symmetry related atoms for each layer and declare the point group symmetry of the crystal as unknown. The DIFFaX code, then computes the Laue symmetry. The cell parameters were obtained from the respective PXRD patterns ($a = 2$ d_{110} Å; $c = 6$ d_{006} Å). The calculated reflections were broadened using a Lorentzian line shape to account for instrumental factors. The full width at half maximum (FWHM) value chosen for the Lorentzian was obtained from the width of the 110 reflection. The 110 reflection remains unaffected by structural disorder.

Different LDHs investigated in this study vary in the structure and composition of the interlayer. The structure of the CO_3^{2-} containing LDH is described in detail elsewheres.[1] The structure model used for other anions is described below.

Cl^- ions

The crystal structure data for the DIFFaX simulation of the Zn-Al-Cl$^-$ LDH was obtained from the ICSD data (ICSD No. 91155 Space group $R\text{-}3m$; Space group $R\text{-}3m$; $a = 3.084$ Å; $c = 23.47$ Å). In this LDH, the interlayer composition is $[Cl_xO_z]$. The Cl$^-$ ions and the O atoms of the interlayer water occupy a single set of sites ($18h$) comprising six positions distributed around the three-fold axes.

For non-planar oxoanion, TO_4^{n-} (T = S, Cl)

There are several structures available in the ICSD database for the Zn-Al-SO_4^{2-} LDH of which CC No. 75542 (Space group $P6_3/mmc$; $a = 3.1202$ Å; $c = 17.844$ Å) is used for simulations reported here. This structure was preferred over the others as it corresponds to a hydrated phase and most laboratory-prepared LDHs incorporate interlayer water unless they are subjected to thermal dehydration. The same model was used for the LDHs containing other non-planar oxoanions.

In Zn-Al-SO_4^{2-} LDH, the sulfate anion is intercalated with one of the S-O bonds parallel to the c-crystallographic axis. This oxygen atom is referred to as the 'axial' O (O^a). The other three oxygen atoms are referred to as 'basal' O (O^b). The basal oxygen atoms of SO_4^{2-} tetrahedra and the oxygen atoms of water molecules share the same site (18h). The apical oxygen atom and the S atom occupy separate (6c) sites. The interlayer composition of Zn-Al-SO_4^{2-} LDHs can be written as $[S_{x/2}(O_{x/2})^a(O_{3x/2+z})^b]$. In 'b' site, 3x/2 represents the basal oxygen content of the SO_4^{2-} ions and the z corresponds to oxygen content of the interlayer water molecules. Hence the interlayer water content in sulfate containing LDHs depends on the occupancy of 'b' site. The same model is used to generate the interlayer structure of the ClO_4^- containing LDH. Using the above representation, interlayer composition of the LDHs with ClO_4^- ions can be written as $[Cl_x(O_x)^a(O_{3x+z})^b]$.

For BrO$_3^-$ ion

There is no structure data available in the ICSD database for LDHs containing BrO_3^- or any other anions with the C_{3v} symmetry. The BrO_3^- ion with its lone pair of electrons has a pyramidal structure. The only available interlayer structure with some resemblance to the structure of BrO_3^- ions, is that of the sulfate LDHs. Hence we used the

sulfate model for the simulation of the PXRD patterns of the bromate LDHs. The composition of bromate interlayer can be written as $[Br_x(O_{3x+z})^b]$ and is obtained by placing the Br and the oxygen atoms of the BrO_3^- ions in the S and the basal oxygen atom sites of the SO_4^{2-} tetrahedra respectively. The position of the apical O atom in SO_4^{2-} tetrahedra is left vacant and is presumably occupied by the lone pair on Br.

For NO_3^- ions

The nitrate ions have planar geometry similar to carbonate ions but they intercalate with one of their N-O bonds parallel to the *c*-crystallographic axis. By Halford's rule,[2] the symmetry of coordination is C_{2v}. No structure data is available in the literature for NO_3^- containing LDHs. The nitrates in C_{2v} symmetry can be viewed as ions having two basal oxygen atoms and one apical oxygen atom. The atomic coordinates of the carbonate oxygen atoms are used for the basal oxygen atoms of the nitrate ions. The N and apical O atomic positions are taken from that of the S and apical O of the sulphate structure. The composition of the nitrate interlayer can be written as $[N_x(O_x)^a(O_{2x+z})^c]$; where superscript 'c' indicates the oxygen site of carbonate LDH.

Polytype simulations

In the LDH structure, the hydroxide layer together with the interlayer of the anions and water molecules constitutes a slab also called the building block. The PXRD patterns of different polytypes were simulated by stacking these slabs in different sequences using appropriate stacking vectors.

The stacking vector (0,0,1) simulates the simple 1H polytype. The PXRD patterns of the perfectly ordered $3R_1$ and $3R_2$ polytypes were simulated using stacking vectors (2/3,1/3,1/3) and (1/3,2/3,1/3) respectively. The pure $2H_1$ polytype is generated by

defining two different layers AC and CA and then stacking them one atop another using the stacking vector (0,0,1/2). The stacking faults are introduced by mixing two or more of these polytypic motifs in the LDH structure. A mixture of $3R_1$ and $3R_2$ motifs can be generated by the simultaneous use of the stacking vectors (2/3,1/3,1/3) and (1/3,2/3,1/3) with different probabilities. The use of the stacking vector (0,0,1/3) with one of the above stacking vector generates the mixtures of 1H with $3R_1$ or $3R_2$ motifs. A mixture of $3R_1$ and $2H_1$ motifs can be generated using AC and CA layers. Beginning with an AC layer, the $3R_1$ motif is generated by using the stacking vector (2/3,1/3,1/3). From a CA layer the $3R_1$ motifs are introduced using the (1/3,2/3,1/3) stacking vector.

Turbostraticity and Interstratification

Turbostraticity is another kind of disorder, which produces the random stacking sequences of the layers.[3] Turbostraticity is introduced into the structure by using a stacking vector (x, y, 1), where x and y are random numbers. Interstratification,[4] which leads to a poorly defined *c*-parameter, was used to simulate the PXRD pattern of the Zn-Al-NO_3^- obtained by the anion exchange reaction. To generate the interstratified phase, the building blocks of the Zn-Al-Cl^- and Zn-Al-NO_3^- LDHs were stacked one above the with stacking vector (2/3,1/3,k) with k = $c_{nitrate-}/c_{chloride}$; where $c_{nitrate-}$ and $c_{chloride}$ correspond to the *c*-parameters of the Zn-Al-NO_3^- and Zn-Al-Cl^- LDHs respectively.

Particle size effects

In layered materials, crystallite size along (*a-b*) plane is defined as 'disc diameter' and that along the stacking direction is given as thickness in number of layers. The broadening of the 110 reflection, beyond what is expected of instrumental factors is attributed to 'disc

diameter'. Similarly a broadening of the 00ℓ reflections upto a FWHM value of $0.6°$ in 2θ is attributed to particle thickness.[5]

Goodness of match

The DIFFaX formalism is qualitative in approach. The goodness of the visual match is based on obtaining an approximate match of the (1) peak positions (within $\pm\, 0.3°$ in 2θ), (2) FWHM values (within $\pm\, 0.1°$ in 2θ) and (3) intensities (within $\pm\, 5\%$) of the simulated peaks with those in the observed pattern. To facilitate this comparison, the experimental and simulated patterns are overlaid and the difference plotted.

SI.-II. DIFFaX simulations of polytypes of Zn-Al-CO$_3^{2-}$ LDH

In Figure S1 is shown a comparison of the DIFFaX simulated PXRD patterns of the $3R_1$ and $3R_2$ polytypes of the Zn-Al-CO$_3^{2-}$ LDH with the observed pattern. A visual inspection indicates that the Zn-Al-CO$_3^{2-}$ LDH crystallizes in the structure of the $3R_1$ polytype.

DIFFaX also yields the assignments of the Bragg reflections. In Table S1 the observed Bragg angles are compared with the Bragg angles calculated for the $3R_1$ polytype.
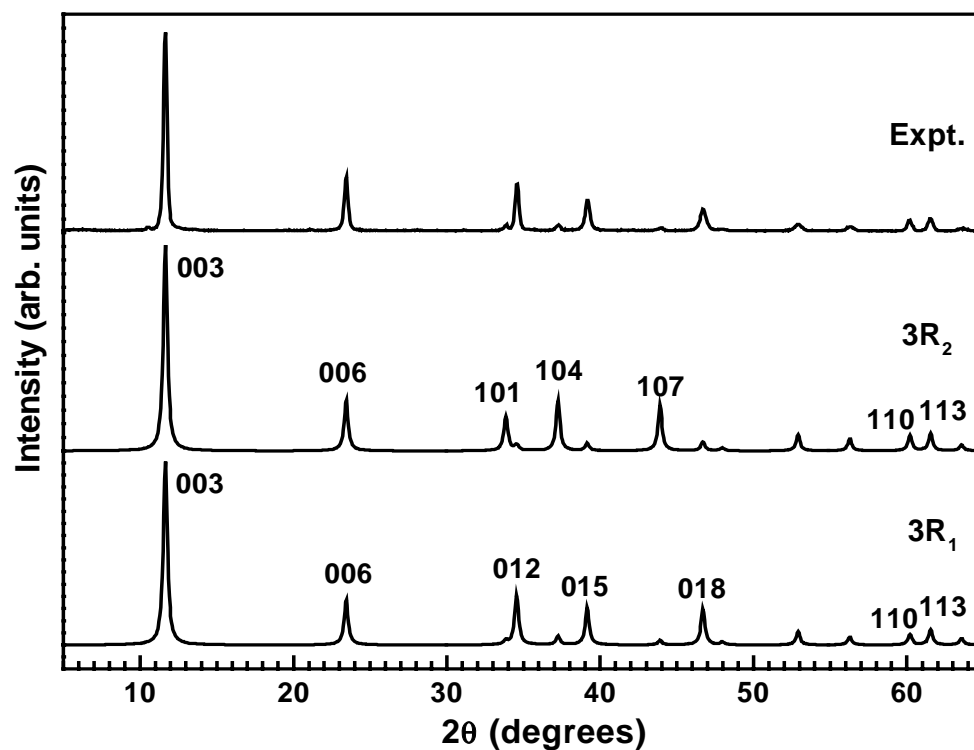
Figure S1. DIFFaX simulated PXRD patterns of the $3R_1$ and $3R_2$ polytypes compared the observed PXRD pattern of the Zn-Al-CO_3^{2-} LDH.

Table S1. Bragg angles of reflections observed in Zn-Al-A^{n-} LDHs compared with the Bragg angles calculated for the $3R_1$ polytype

$hk\ell$	CO_3^{2-} (2θ in °)		Cl^-	
	Calculated	Observed	Calculated	Observed
003	11.65	11.65	11.35	11.35
006	23.45	23.45	22.8	22.81
012	34.55	34.6	34.48	34.53
015	39.15	39.15	38.86	38.93
018	46.7	46.7	46.06	46.11
110	60.2	60.2	60.08	60.09
113	61.55	61.55	61.36	61.33

SI.-III. DIFFaX simulations of different polytypes of Zn-Al-SO$_4^{2-}$ LDH
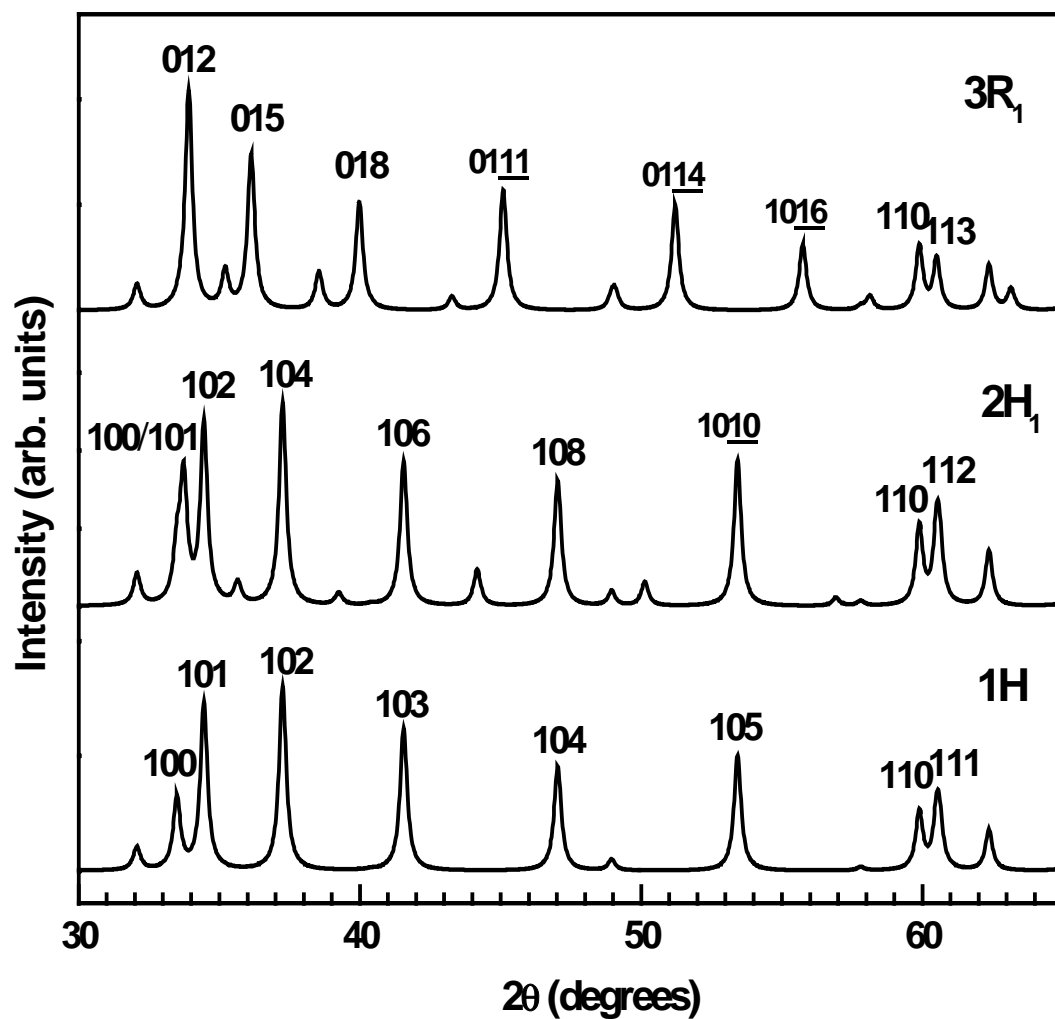

Figure S2. DIFFaX simulated PXRD patterns in the mid.-2θ region of the 1H, 2H$_1$ and 3R$_1$ polytypes of the Zn-Al-SO$_4^{2-}$ LDH.

Table S2. 2θ values of the most intense lines observed in mid.-2θ region of different polytypes of the Zn-Al-SO$_4^{2-}$ LDH

hkℓ	2θ in °			
	3R$_1$	2H$_1$	1H	Expt.(Cp)
100	-	33.51	33.49	33.56
101	-	33.73	34.45	34.5
102/012	33.91	34.45	37.25	37.32
103	-	-	41.55	41.68
104	-	37.25	47.03	47.06
105/015	36.13	-	53.43	53.52
106	-	41.55	-	-
108/018	39.97	47.03	-	-
10$\underline{10}$	-	53.43	-	-
01$\underline{11}$	45.09	-	-	-
01$\underline{14}$	51.21	-	-	-
10$\underline{16}$	55.75	-	-	-

References

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(5) Ramesh, T.N.; Jayashree, R.S; Kamath, P.V. *Clays Clay Minerals* **2003,** *51*, 570.