Polytypism, Disorder and Anion Exchange Properties of Divalent Ion (Zn, Co) containing Bayerite-derived Layered Double Hydroxides

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Supporting Information

SI.1. The layer structure and the stacking vectors used in the simulation of the PXRD patterns of ordered polytypes

The DIFFaX code requires the stacking direction to be along the *c* crystallographic axis and the cell parameters to be defined as *a*, *b*, *c* and γ. The assumption is that $\alpha = \beta = 90^o$. Such a convention is suited for hexagonal and rhombohedral crystal systems. The nickelalumite structure crystallizes in the monoclinic crystal system. To make this structure compatible with the DIFFaX code, the cell was 'orthogonalized' as $a_o = a_m$, $b_o = b_m$, $c_o = c_m \text{Sin } \beta$, (o: orthogonalized cell parameter, m: monoclinic cell parameter), $\gamma_o = 90^o$. The stacking vector ($c_m/a_m \text{Cos } \beta$, 0, 1) generates the monoclinic symmetry. A single layer (stacking unit) is defined using the position coordinates taken from the model structure (space group: $P\ 12_1/n1$, a = 10.291 Å, b = 8.892 Å, c = 17.268Å, $\beta = 95.54^o$) with the following transformations for the orthogonalized cell: $x_0 = x_m + z_m(c_m/a_m \cos \beta)$, $y_o = y_m$, $z_o = z_m$. All the symmetry related atoms are explicitly defined and the point group is declared as 'unknown'. Such an option enables the DIFFaX code to evaluate the Laue symmetry. The computed symmetry is 2/*m*, compatible with the symmetry of the model structure.

Structure of Layer 1 used for the simulation of the PXRD patterns of the $2M_1$ and $2M_2$ polytypes

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LAYER 1  (Atom type, Atom label, x, y, z, B, S.O.F)

Zn      1       0.2498    0.0006  -0.00720   1.      1.0000
Zn      0       0.7501   -0.0006   0.00720   1.      1.0000
Al      0       0.4998    0.1714   0.00160   1.      1.0000
Al      1       0.5001    0.8286  -0.00160   1.      1.0000
Al      2      -0.0002    0.8259   0.00450   1.      1.0000
Al      2       0.0002    0.1741  -0.00450   1.      1.0000
Al      2       0.2511    0.6611   0.00240   1.      1.0000
Al      2       0.7489    0.3389  -0.00240   1.      1.0000
Al      2       0.2504    0.3394  -0.00010   1.      1.0000
Al      2       0.7496    0.6606   0.00010   1.      1.0000
S       3       0.4694    0.8906   0.25940   1.      1.0000
S       3       0.9499    0.3906   0.24060   1.      1.0000
O       4       0.0729    0.0029   0.05400   1.      1.0000
O       4       0.9271   -0.0029  -0.05400   1.      1.0000
O       1       0.5689   -0.0007   0.05730   1.      1.0000
O       0       0.4311    0.0007  -0.05730   1.      1.0000
O       0       0.8402    0.8211   0.06250   1.      1.0000
O       1       0.1598    0.1789  -0.06250   1.      1.0000
O       2       0.3381    0.1754   0.05670   1.      1.0000
O       2       0.6618    0.8246  -0.05670   1.      1.0000
O       2       0.5973    0.3062   0.05880   1.      1.0000
O       2       0.4027    0.0938  -0.05880   1.      1.0000
O       2       0.3079    0.4989   0.06240   1.      1.0000
O       2       0.6920    0.5011  -0.06240   1.      1.0000
O       3       0.8431    0.1824   0.05700   1.      1.0000
O       3       0.1569    0.8176  -0.05700   1.      1.0000
```

O	4	0.3409	0.8251	0.05590	1.	1.0000
O	4	0.6590	0.1749	-0.05590	1.	1.0000
O	1	0.5964	0.6949	0.05790	1.	1.0000
O	0	0.4035	0.3051	-0.05790	1.	1.0000
O	0	0.1003	0.6963	0.06290	1.	1.0000
O	1	0.8997	0.3037	-0.06290	1.	1.0000
O	2	0.0965	0.3055	0.05470	1.	1.000
O	2	0.9035	0.6945	-0.05470	1.	1.0000
O	2	0.8030	0.4984	0.05950	1.	1.0000
O	2	0.1970	0.5016	-0.05950	1.	1.0000
O	2	-0.0035	0.4748	0.17170	1.	1.000
O	2	0.4229	0.9748	0.32830	1.	1.000
O	3	0.8692	0.4892	0.28900	1.	1.000
O	3	0.5501	0.9892	0.21100	1.	1.000
O	4	0.0635	0.3363	0.28550	1.	1.000
O	4	0.3559	0.8363	0.21450	1.	1.000
O	1	0.8729	0.2607	0.21420	1.	1.0000
O	0	0.5464	0.7607	0.28580	1.	1.000
O	0	0.8112	0.7775	0.22250	1.	1.000
O	1	0.60820	0.27750	0.27750	1.	1.0000
O	2	0.1958	0.0981	0.19380	1.	1.000
O	2	0.2235	0.5981	0.30620	1.	1.000
O	2	0.4954	0.50650	0.18650	1.	1.000
O	2	0.9239	0.0065	0.31350	1.	1.000
O	6	0.1097	0.9500	0.25000	1.	1.000
O	6	0.3097	0.4500	0.25000	1.	1.000
O	6	0.1797	0.6000	0.25000	1.	1.000
O	6	0.2397	0.1000	0.25000	1.	1.000

LAYER 2 (Atom type, Atom label, x, y, z, B, S.O.F)

Zn	1	0.2498	-0.0006	-0.00720	1.	1.0000
Zn	0	0.7501	0.0006	0.00720	1.	1.0000
Al	0	0.4998	-0.1714	0.00160	1.	1.0000
Al	1	0.5001	-0.8286	-0.00160	1.	1.0000
Al	2	-0.0002	-0.8259	0.00450	1.	1.0000
Al	2	0.0002	-0.1741	-0.00450	1.	1.0000
Al	2	0.2511	-0.6611	0.00240	1.	1.0000
Al	2	0.7489	-0.3389	-0.00240	1.	1.0000
Al	2	0.2504	-0.3394	-0.00010	1.	1.0000
Al	2	0.7496	-0.6606	0.00010	1.	1.0000
S	3	0.4694	-0.8906	0.25940	1.	1.0000
S	3	0.9499	-0.3906	0.24060	1.	1.0000
O	4	0.0729	-0.0029	0.05400	1.	1.0000
O	4	0.9271	0.0029	-0.05400	1.	1.0000
O	1	0.5689	0.0007	0.05730	1.	1.0000
O	0	0.4311	-0.0007	-0.05730	1.	1.0000
O	0	0.8402	-0.8211	0.06250	1.	1.0000
O	1	0.1598	-0.1789	-0.06250	1.	1.0000
O	2	0.3381	-0.1754	0.05670	1.	1.0000
O	2	0.6618	-0.8246	-0.05670	1.	1.0000
O	2	0.5973	-0.3062	0.05880	1.	1.0000
O	2	0.4027	-0.0938	-0.05880	1.	1.0000
O	2	0.3079	-0.4989	0.06240	1.	1.0000
O	2	0.6920	-0.5011	-0.06240	1.	1.0000

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O       3       0.8431   -0.1824   0.05700   1.      1.0000
O       3       0.1569   -0.8176  -0.05700   1.      1.0000
O       4       0.3409   -0.8251   0.05590   1.      1.0000
O       4       0.6590   -0.1749  -0.05590   1.      1.0000
O       1       0.5964   -0.6949   0.05790   1.      1.0000
O       0       0.4035   -0.3051  -0.05790   1.      1.0000
O       0       0.1003   -0.6963   0.06290   1.      1.0000
O       1       0.8997   -0.3037  -0.06290   1.      1.0000
O       2       0.0965   -0.3055   0.05470   1.      1.000
O       2       0.9035   -0.6945  -0.05470   1.      1.0000
O       2       0.8030   -0.4984   0.05950   1.      1.0000
O       2       0.1970   -0.5016  -0.05950   1.      1.0000
O       2      -0.0035   -0.4748   0.17170   1.      1.000
O       2       0.4229   -0.9748   0.32830   1.      1.000
O       3       0.8692   -0.4892   0.28900   1.      1.000
O       3       0.5501   -0.9892   0.21100   1.      1.000
O       4       0.0635   -0.3363   0.28550   1.      1.000
O       4       0.3559   -0.8363   0.21450   1.      1.000
O       1       0.8729   -0.2607   0.21420   1.      1.0000
O       0       0.5464   -0.7607   0.28580   1.      1.000
O       0       0.8112   -0.7775   0.22250   1.      1.000
O       1       0.60820  -0.27750  0.27750   1.      1.0000
O       2       0.1958   -0.0981   0.19380   1.      1.000
O       2       0.2235   -0.5981   0.30620   1.      1.000
O       2       0.4954   -0.50650  0.18650   1.      1.000
O       2       0.9239   -0.0065   0.31350   1.      1.000
O       6       0.1097   -0.9500   0.25000   1.      1.000
O       6       0.3097   -0.4500   0.25000   1.      1.000
O       6       0.1797   -0.6000   0.25000   1.      1.000
O       6       0.2397   -0.1000   0.25000   1.      1.000
```

Stacking vectors used for ordered $2M_1$				
Transitions	Probabilities	Stacking vector		
		x	*y*	*z*
L1→L1	0.0	0	0	1
L1→L2	1.0	-0.5809	0.5	0.5
L2→L1	1.0	-0.5809	0.5	0.5
L2→L2	0.0	0	0	1
Stacking vectors used for ordered $2M_2$				
L1 →L1	0.0	0.0	0	1
L1→L2	1.0	-0.5809	0	0.5
L2→L1	1.0	-0.5809	0	0.5
L2→L2	0.0	0.0	0	1

SI.2. Stacking vectors and probabilities used for an illustrative DIFFaX simulation of the PXRD pattern of a faulted crystal

Layer 3 = 1
Layer 4 = 2

10% $2M_2$ motifs in $2M_1$ polytype

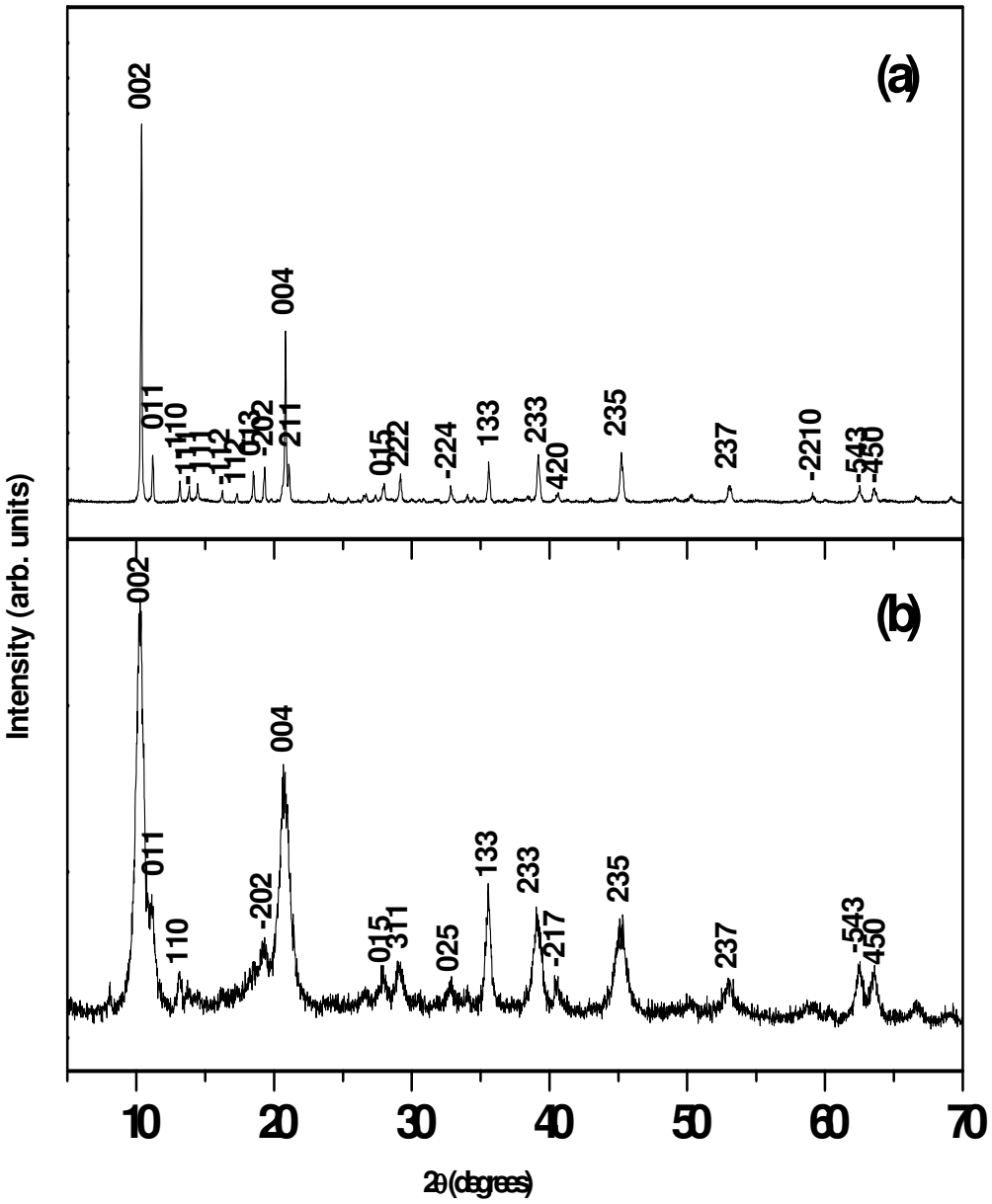
Transitions	Probabilities	Stacking vector *x*	*y*	*z*
L1→L1	0.0	0	0	1
L1→L2	0.9	-0.5809	0.5	0.5
L1→L3	0.0	0	0	1
L1→L4	0.1	-0.5809	0	0.5
L2→L1	0.9	-0.5809	0.5	0.5
L2→L2	0.0	0	0	1
L2→L3	0.1	-0.5809	0	0.5
L2→L4	0.0	0	0	1
L3→L1	0.0	0	0	1
L3→L2	0.1	-0.5809	0	0.5
L3→L3	0.0	0	0	1
L3→L4	0.9	-0.5809	0.5	0.5
L4→L1	0.1	-0.5809	0	0.5
L4→L2	0.0	0	0	1
L4→L3	0.9	-0.5809	0.5	0.5
L4→L4	0.0	0	0	1

SI. 3. Observed and Calculated *d* – spacings of the ZA-1 LDH.

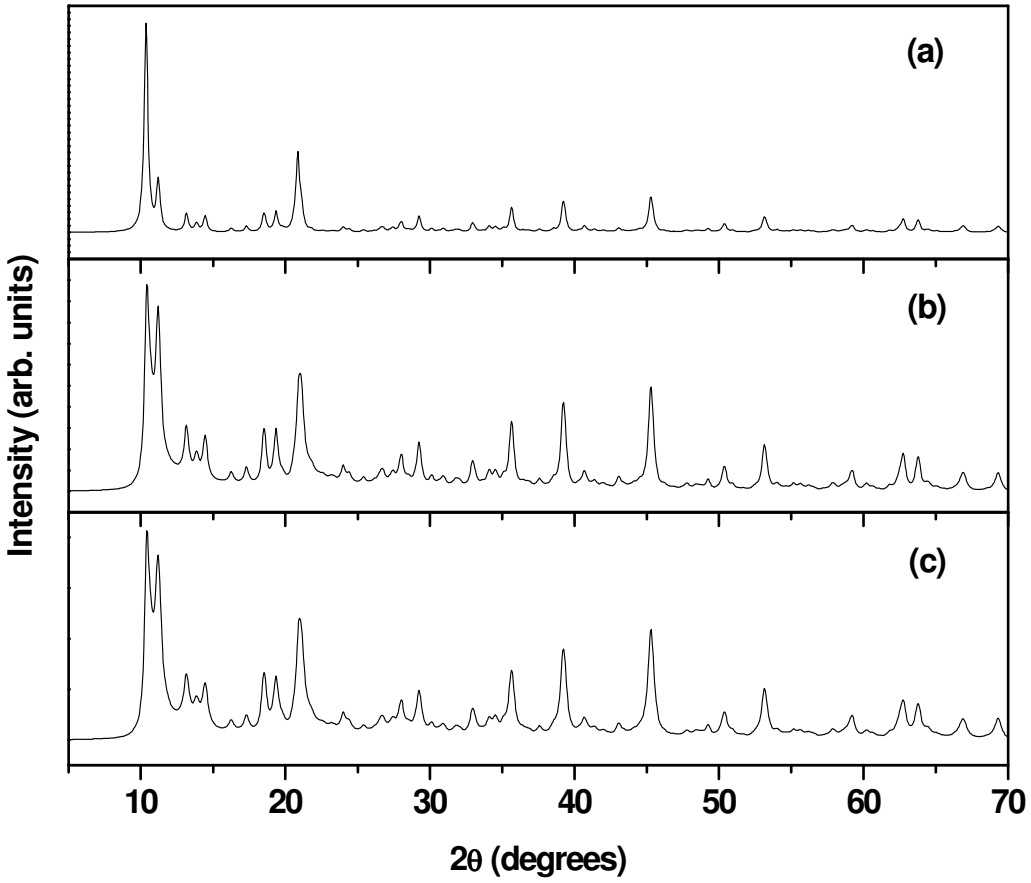
d (obs) Å	*d* (calc) Å	*hkℓ*
8.541	8.528	002
7.902	7.898	011
6.723	6.726	-110
6.401	6.401	-111
6.125	6.123	111
5.453	5.456	-112
5.116	5.122	112
4.797	4.793	013
4.599	4.600	-202
4.267	4.264	004
4.212	4.213	211
3.709	3.712	-114
3.361	3.363	-220
3.341	3.341	-221
3.256	3.258	123
3.186	3.186	015
3.062	3.062	222
2.728	2.728	-224
2.599	2.600	215
2.521	2.522	133
2.300	2.299	233
2.223	2.222	420
2.005	2.005	235
1.814	1.814	-237
1.726	1.726	237
1.563	1.563	-2210
1.485	1.485	-543
1.463	1.463	-450

a = 10.305(3) Å, b = 8.911(2) Å, c = 17.141(2) Å, β = 95.68(2)°

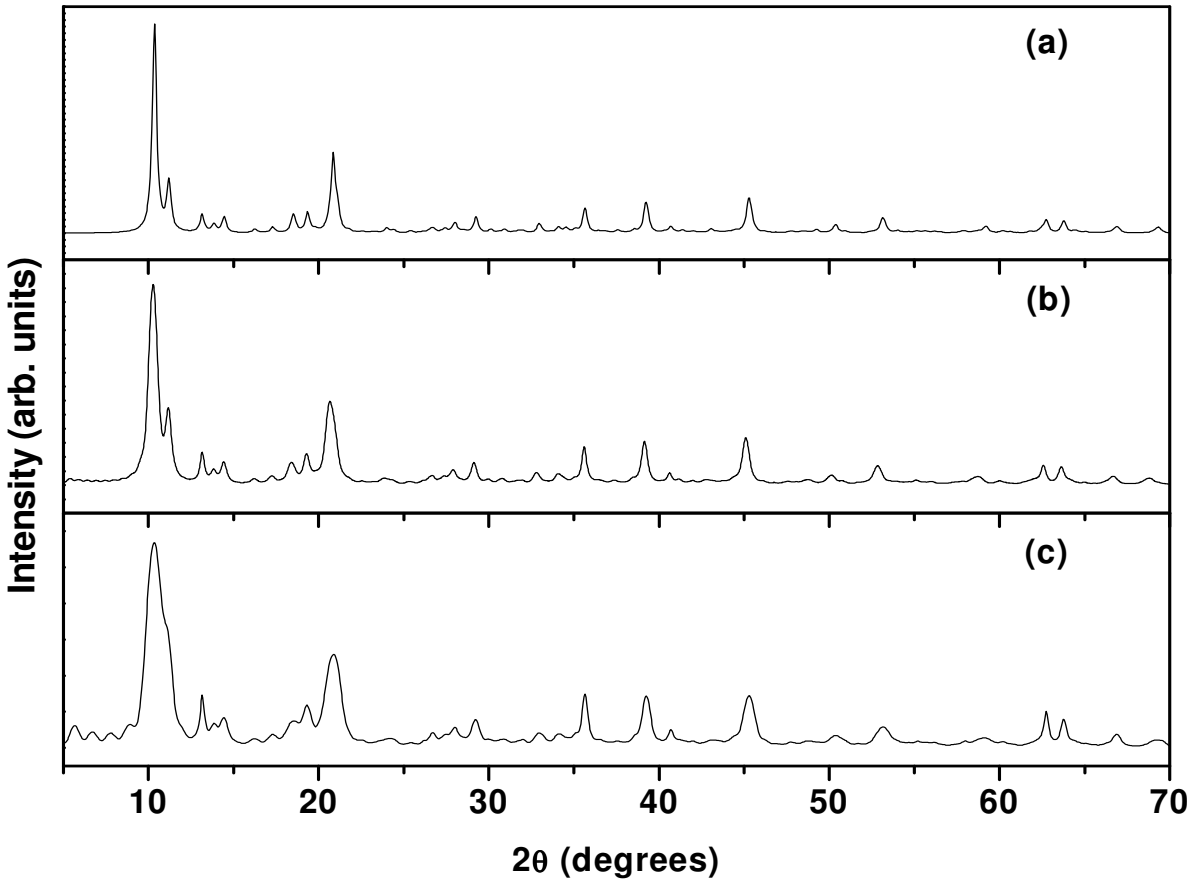
SI. 4. PXRD pattern of LDH prepared from (a) bayerite (ZA-1) and (b) by ageing ZnO in $Al_2(SO_4)_3$ (ZA-2).



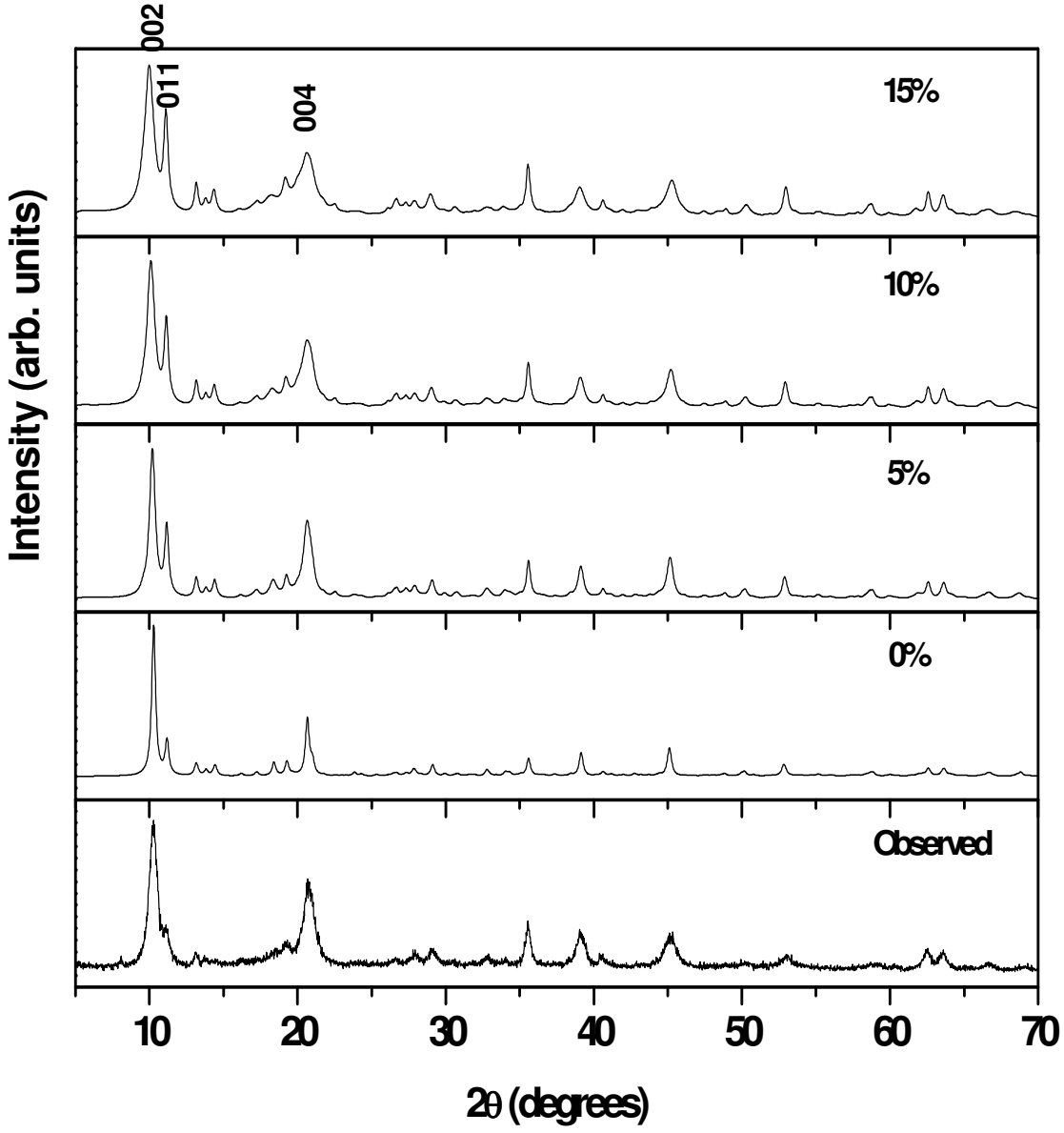
SI. 5. Simulated PXRD patterns of the bayerite-based LDH with different disc diameters (R) (a) R = ∞, (b) R = 2000 Å, (c) R = 1000 Å (Line shape: Lorentzian broadening of 0.3° 2θ).



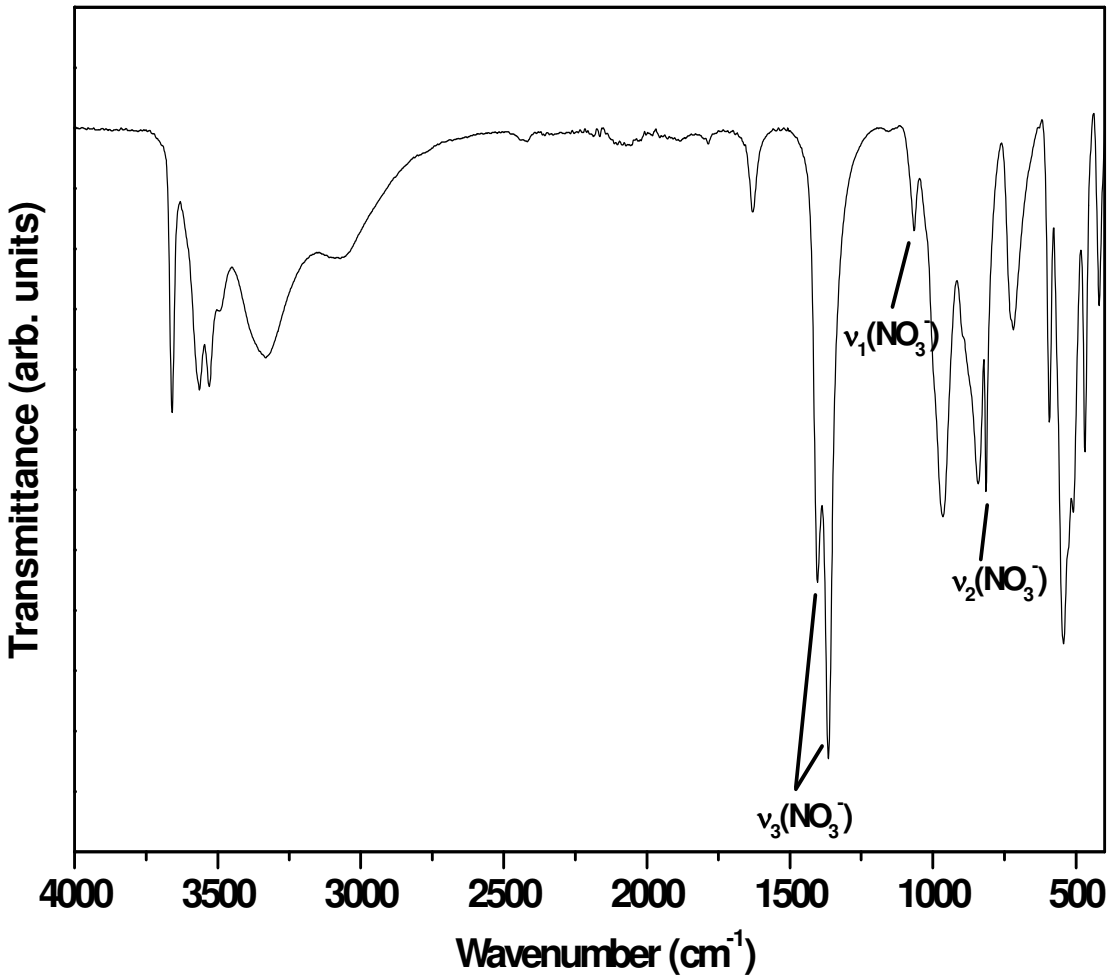
SI. 6. Simulated PXRD patterns of the bayerite-based LDH with different crystallite thickness (n, number of layers) (a) n = ∞, (b) n = 20, (c) n = 10. (Line shape: Lorentzian broadening of 0.3° 2θ).



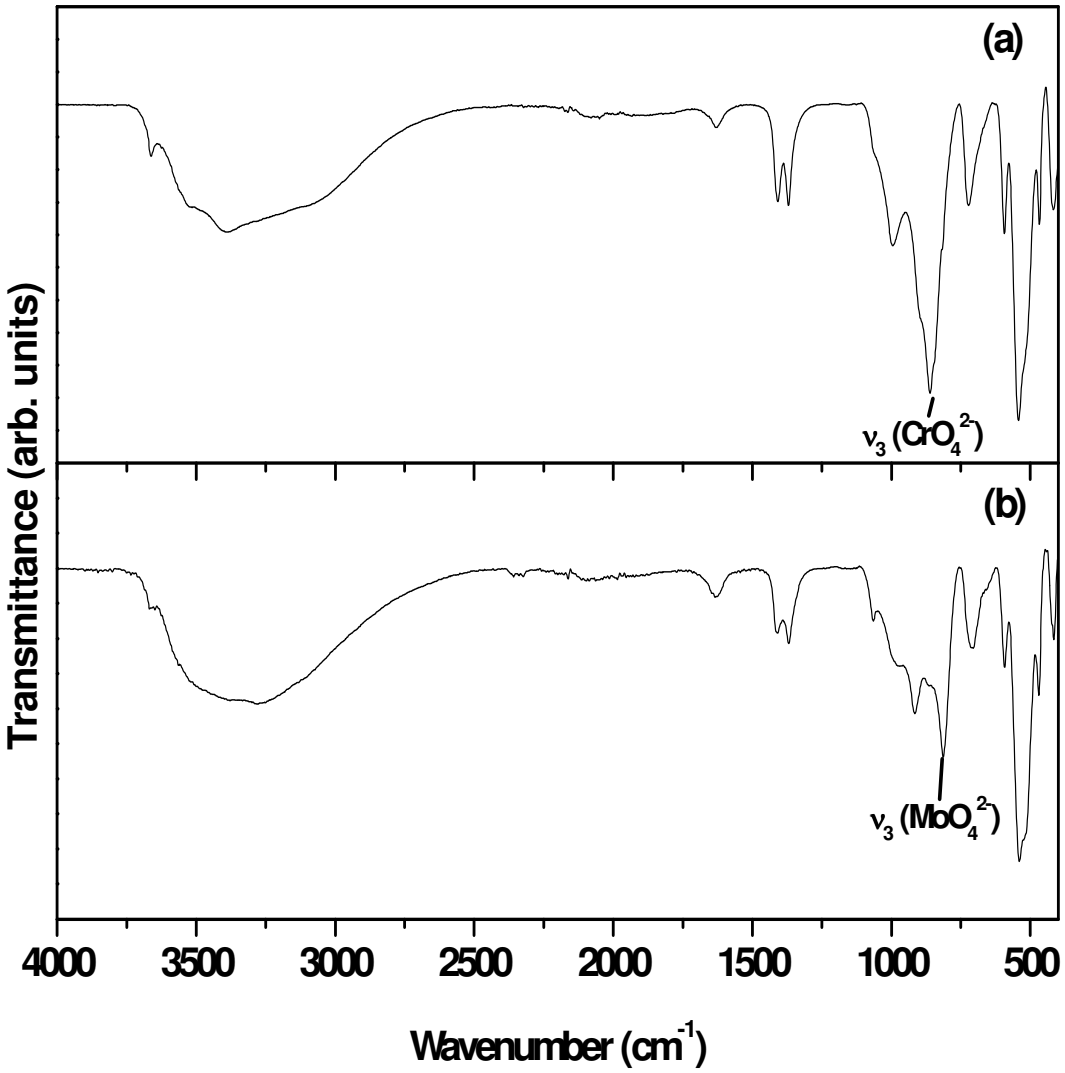
SI. 7. PXRD pattern of the ZA-2 LDH and the DIFFaX simulations obtained by the interstratification of different proportions of the hydrated phase (*d*-spacing, 10.7 Å).



SI. 8. IR spectrum of product obtained on hydrothermal treatment of bayerite in $Zn(NO_3)_2$ solution.



SI. 9. IR spectrum of product obtained on exchange of NO_3 with (a) CrO_4^{2-} and (b) MoO_4^{2-} from solution.



SI. 10. PXRD pattern of the (a) bayerite-based Zn-Al-NO_3 LDH and the product obtained after exchange of NO_3 for (b) Cl^- and (c) CO_3^{2-}. Features marked by the asterisk correspond to $Al(OH)_3$.