*Supporting Information*

# Synthesis, polytypism, and dehydration behaviour of nitrate-intercalated layered double hydroxides of Ca and Al

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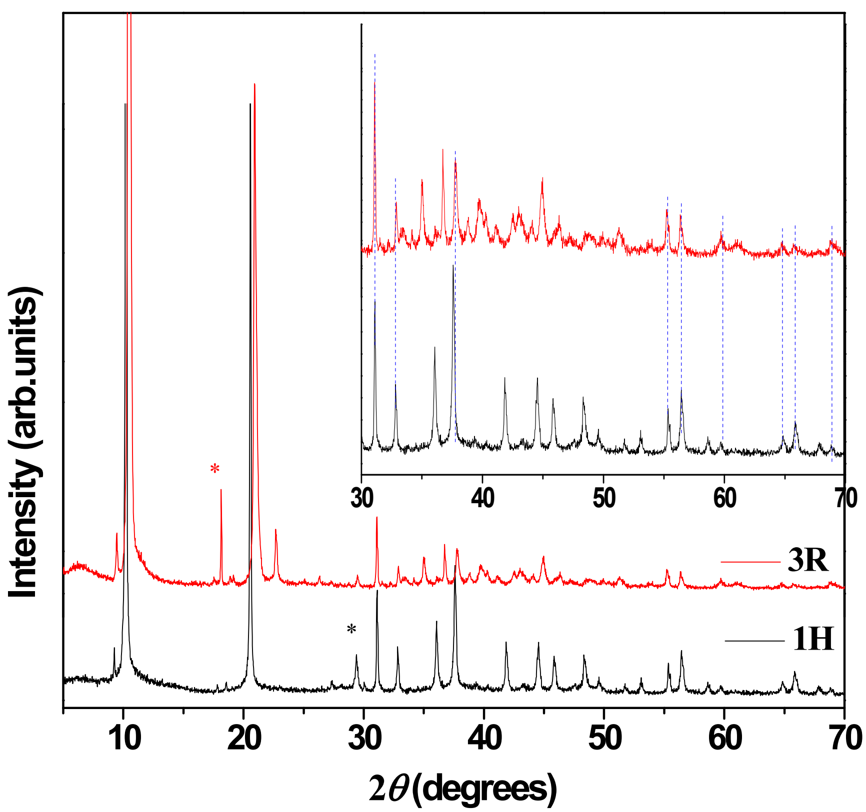
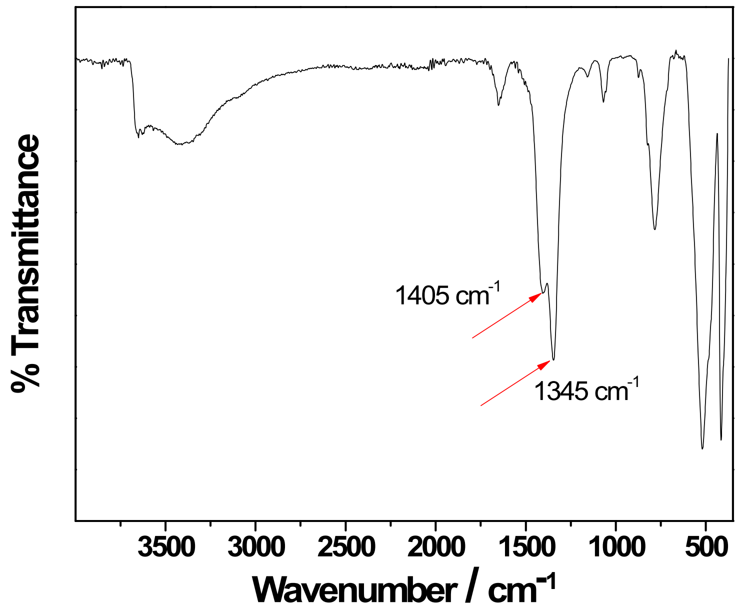



**Fig. S1** Comparison of PXRD patterns of as-prepared 1H and 3R polytypes of [Ca-Al-$NO_3$] LDH. Greater clarity arises from the expanded mid.- $2\theta$ region of the PXRD patterns in the inset. The Bragg angles marked in blue are common to both patterns. Peaks marked with the asterisk are due to $Ca(OH)_2$ (18.6° 2θ), and $CaCO_3$ (29.4° 2θ) impurities.



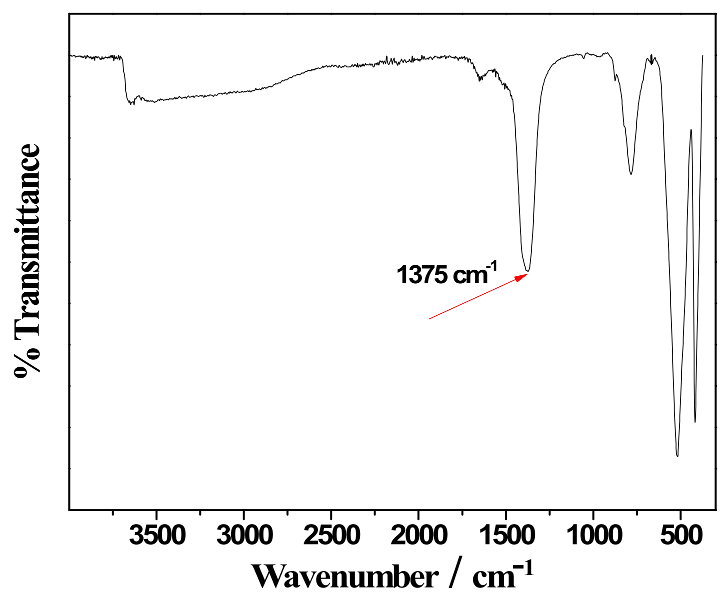




**Fig. S2** Infrared spectra of the as-prepared 1H (upper panel) and 3R (lower panel) polytypes of the [Ca-Al-$NO_3$] LDH.

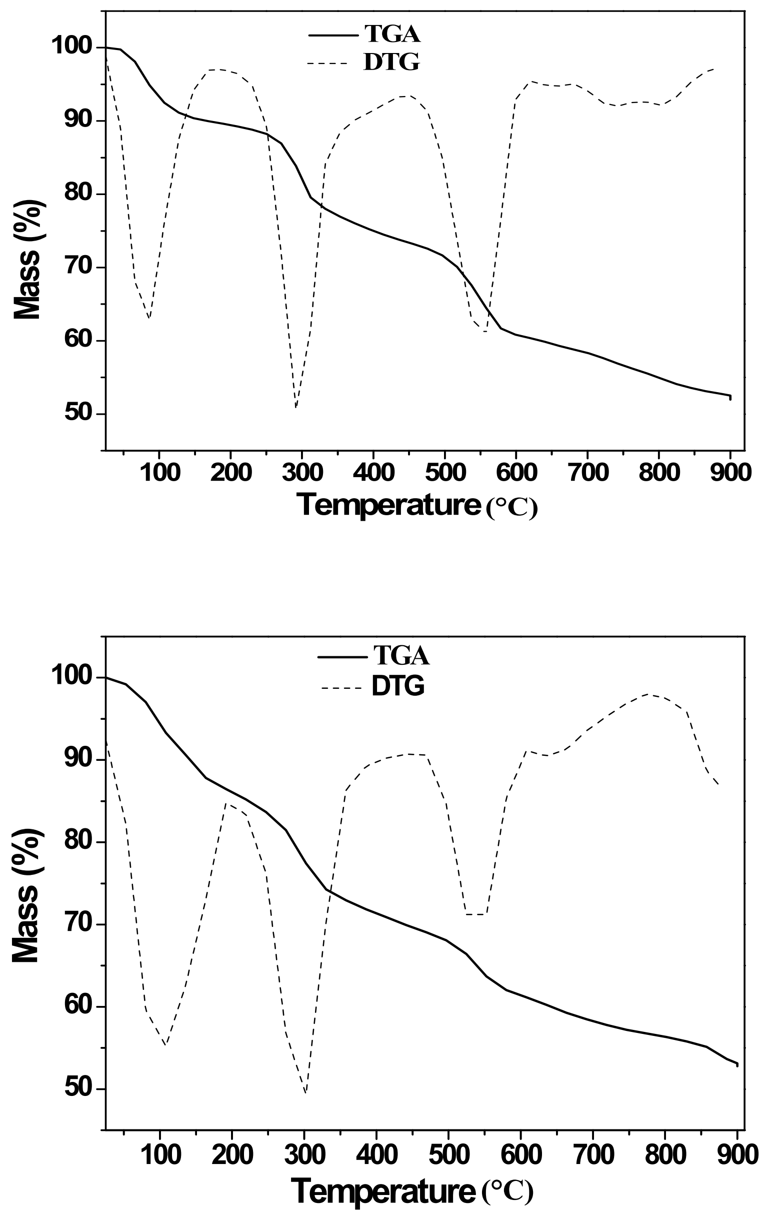
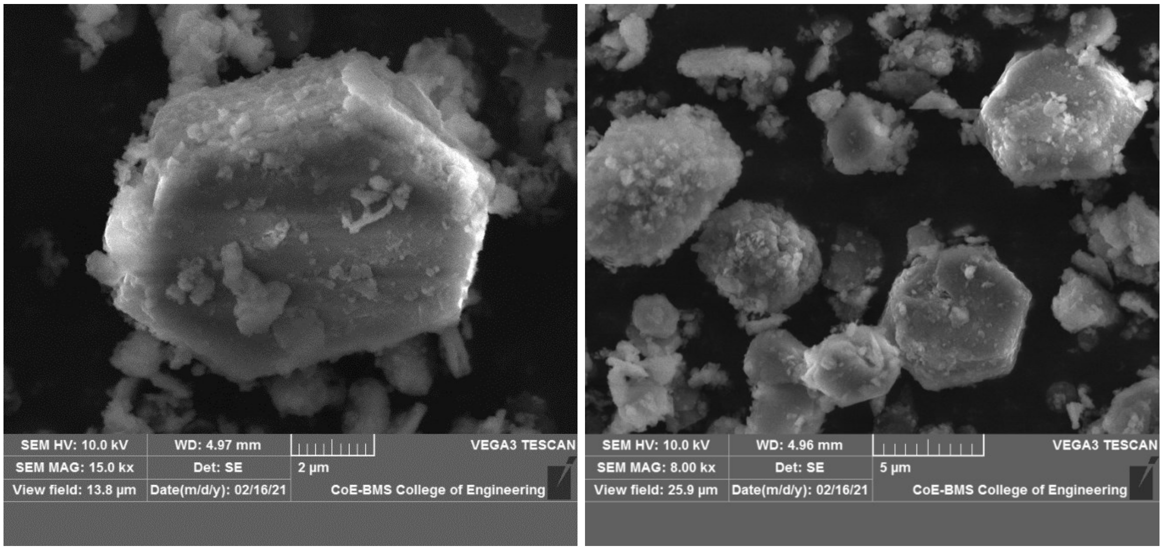
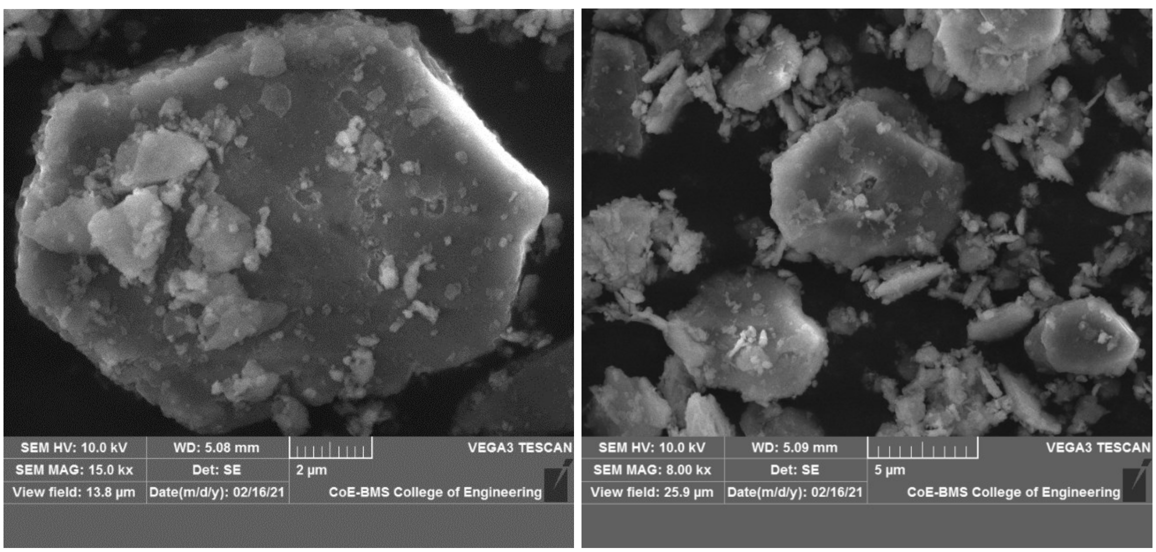



**Fig. S3** TG and DTG profiles of 1H (upper panel) and 3R (lower panel) polytypes of [Ca-Al-$NO_3$] LDH in flowing $N_2$.




(a)




(b)

**Fig. S4** SEM images of 1H, and (b) 3R polytpes.

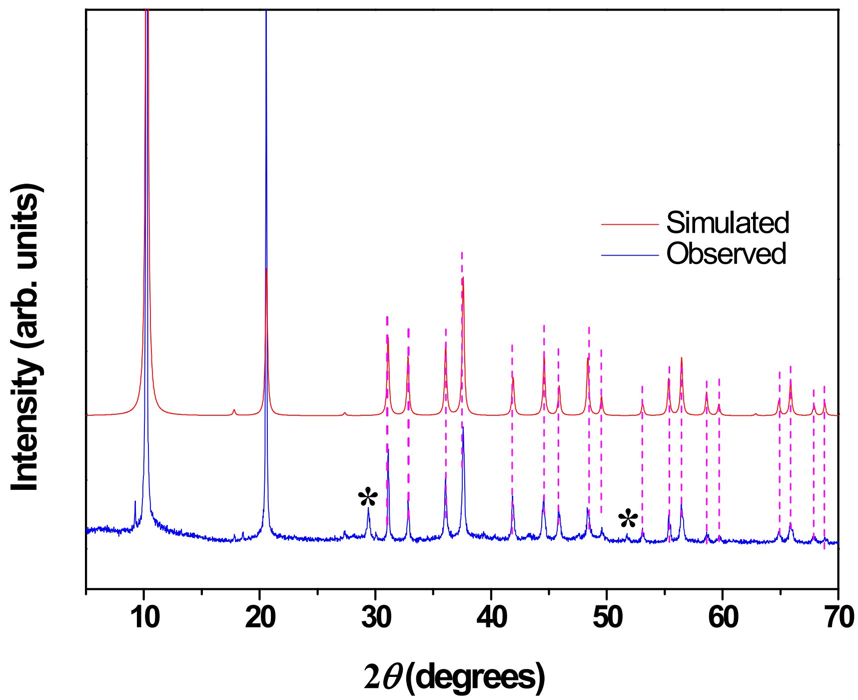



**Fig. S5** Observed PXRD pattern of the [Ca-Al-$NO_3$] LDH (1H polytype) compared with the DIFFaX simulated pattern for the stacking vector (0, 0, 1). Reflections marked with the asterisk correspond to $CaCO_3$ impurity.

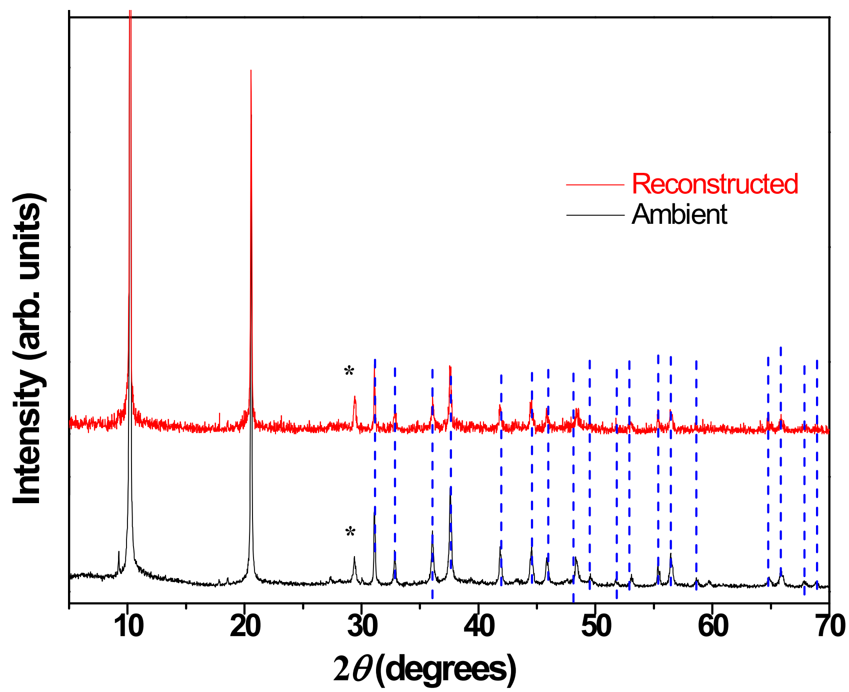



**Fig. S6** The reconstructed PXRD pattern compared with the reconstructed pattern obtained at ambient conditions. Reflection at 29.4º 2$\Theta$ marked with an asterisk corresponds to $CaCO_3$ impurity.

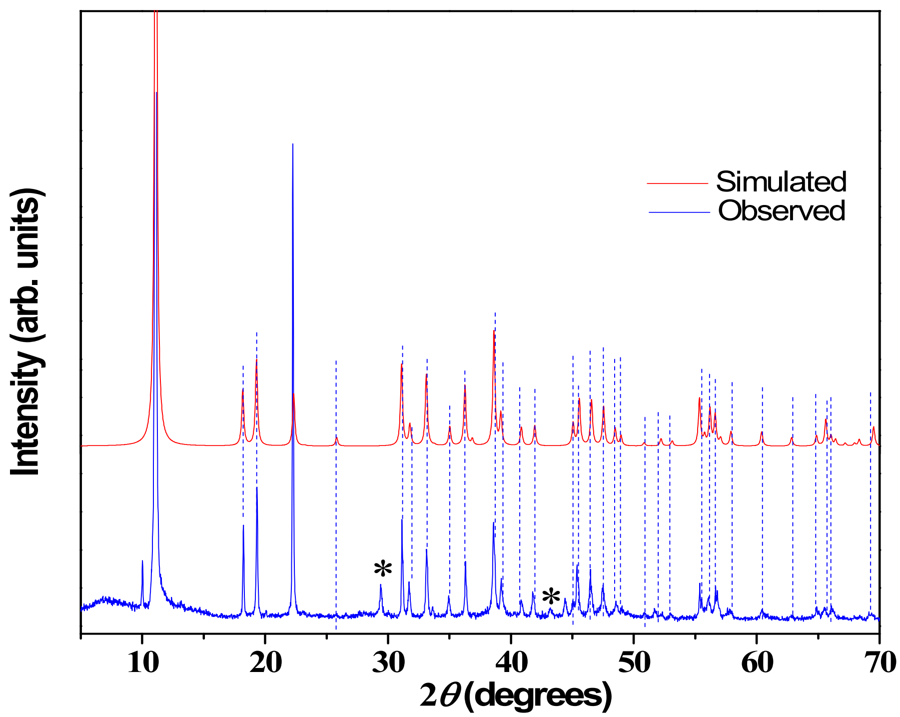



**Fig. S7** Observed PXRD pattern of the dehydrated [Ca-Al-$NO_3$] LDH (3R polytype) compared with the DIFFaX simulated pattern for the stacking vector (1/3, 2/3, z). Reflections marked with an asterisk (*) corresponds to $CaCO_3$ impurity.

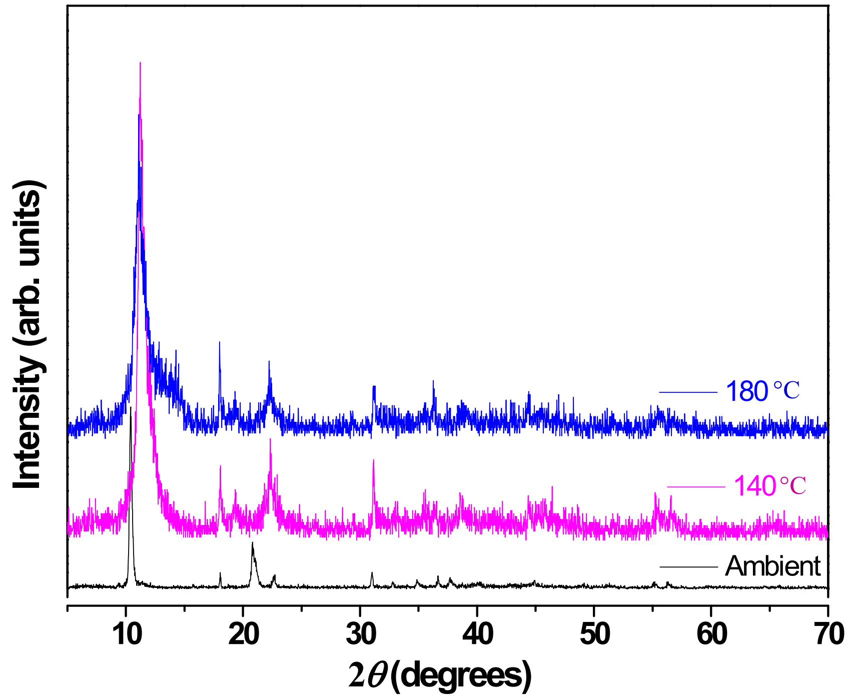



**Fig. S8** Variable temperature PXRD patterns of the as-prepared 3R polytype of [Ca-Al-$NO_3$] LDH.

**Table S1** Observed 2$\theta$ values and corresponding indices of the as-prepared [Ca-Al-$NO_3$] LDHs.

| 1H polytype<br>*a* = 5.75 Å *c* = 8.62 Å<br>FM (Mn) = 46.50 | | 3R polytype<br>*a* = 5.75 Å *c* = 25.44 Å<br>FM (Mn) = 8.0 | |
|---|---|---|---|
| ***hkl*** | **2$\theta$** | ***hkl*** | **2$\theta$** |
| *0 0 1* | 10.3 | *0 0 3* | 10.4 |
| *0 0 2* | 20.6 | *1 0 1* | 18.1 |
| *0 0 3* | 31.1 | *1 0 4* | 22.7 |
| *1 11* | 32.9 | *2 -1 0* | 31.1 |
| *1 0 3* | 36.1 | *2 -1 3* | 32.9 |
| *1 1 2* | 37.6 | *1 -1 8* | 33.5 |
| *0 0 4* | 41.9 | *1 1 4* | 34.2 |
| *1 1 3* | 44.6 | *2 -2 1* | 36.1 |
| *1 0 4* | 45.9 | *2 0 2* | 36.8 |
| *2 0 3* | 48.4 | *2 -1 6* | 37.8 |
| *2 1 1* | 49.6 | *2 -2 4* | 38.8 |
| *2 1 2* | 53.1 | *1 0 <u>10</u>* | 39.7 |
| *3 0 0* | 55.4 | *2 0 5* | 40.3 |
| *3 0 1* | 56.5 | *1 0 <u>11</u>* | 43.1 |
| *2 1 3* | 58.6 | *2 -2 7* | 44.1 |
| *3 0 2* | 59.7 | *11 9* | 44.9 |
| *2 2 0* | 64.9 | *2 0 8* | 46.3 |
| *2 2 1* | 65.9 | *2 -3 2* | 48.8 |
| *3 1 0* | 67.9 | *2 -2 <u>10</u>* | 51.3 |
| *2 2 2* | 68.9 | *3 0 0* | 55.2 |
| *1 1 6* | 73.8 | *3 -3 3* | 56.4 |
| *2 1 5* | 74.6 | *3 0 6* | 59.8 |
| *4 0 0* | 76.5 | *1 0 <u>16</u>* | 61.2 |
| *4 0 2* | 80.2 | *4 -2 0* | 64.8 |
| | | *2 2 6* | 68.9 |

**Table S2** Refined bond lengths and bond angles of 1H polytype of [Ca-Al-$NO_3$] LDH.

(a) As-prepared phase

| Bond lengths [Å] | | Bond angles [°] | |
|---|---|---|---|
| Ca–Oh | 2.3953(1), 2.5042(0) | Oh-Ca-Oh | 116.09, 88.761(1), 147.269(1), 64.36(1) |
| Ca-Ow | 2.5633(1) | Oh-Al-Oh | 92.174(2), 87.826(2) |
| Al–Oh | 1.8823(0) | Oh-Ca- Ow | 78.428(1), 129.971(1) |
| $O_{N3}$-Ow | 2.3584(0), 2.6868(0) | $O_{N1}$-N- $O_{N3}$ | 116.131(1) |
| $O_{N2}$- Oh | 2.5956(1), 3.1477(0) | $O_{N3}$-N- $O_{N2}$ | 124.754(1) |
| $O_{N3}$- Oh | 2.6616(1), 3.2469(1) | $O_{N2}$-N- $O_{N1}$ | 119.109(1) |
| N-$O_{N1}$ | 1.2032(1) | | |
| N-$O_{N2}$ | 1.3225(0) | | |
| N-$O_{N3}$ | 1.3187(0) | | |

(b) Dehydrated phase (3R polytype)

| Bond lengths [Å] | | Bond angles [°] | |
|---|---|---|---|
| Ca–Oh | 2.4611(0), 2.4448(1) | Oh-Ca-Oh | 65.075(1), 88.958(1), 115.959(1), 146.890(1) |
| Al–Oh | 1.9099(0) | Oh-Al-Oh | 87.361(2), 92.639(2) |
| Ca-$O_{N3}$ | 2.3444(0) | $O_{N1}$-N- $O_{N2}$ | 120.53(2) |
| N-$O_{N1}$ | 1.3373(1) | $O_{N2}$-N- $O_{N3}$ | 116.48(2) |
| N-$O_{N2}$ | 1.2017(0) | $O_{N3}$-N- $O_{N1}$ | 120.83(2) |
| N-$O_{N3}$ | 1.2053(0) | | |
| $O_{N1}$- Oh | 2.9695(0), 2.9804(0) | | |
| $O_{N2}$- Oh | 3.1697(0) | | |
| $O_{N3}$- Oh | 2.6046(0), 2.9973(0) | | |

**Table S3** Observed 2$\theta$ values and corresponding indices of the 1H polytype of [Ca-Al-$NO_3$] LDH obtained from temperature-induced dehydration.

| **Dehydrated phase (3R) of 1H polytype**<br>$a$ = 5.76 Å, $c$ = 23.98 Å, FM (Mn) = 9.73 | |
|---|---|
| ***hkl*** | **2$\theta$** |
| *0 0 3* | 11.1 |
| *1 0 1* | 18.2 |
| *1 0 2* | 19.3 |
| *0 0 6* | 22.3 |
| *1 1 0* | 31.1 |
| *1 0 7* | 31.7 |
| *1 1 3* | 33.1 |
| *1 0 8* | 34.9 |
| *2 0 1* | 36.3 |
| *1 1 6* | 38.6 |
| *2 0 4* | 39.2 |
| *2 0 5* | 40.8 |
| *1 0 10* | 41.8 |
| *2 0 7* | 45.0 |
| *0 0 12* | 45.4 |
| *1 1 9* | 46.5 |
| *2 0 8* | 47.5 |
| *2 1 1* | 48.5 |
| *2 1 4* | 50.9 |
| *3 0 0* | 55.4 |
| *3 0 1* | 55.5 |
| *2 0 11* | 56.1 |
| *3 0 3* | 56.7 |
| *3 0 6* | 60.5 |
| *2 2 0* | 64.9 |
| *2 1 11* | 65.5 |
| *2 2 3* | 66.1 |
| *1 0 17* | 69.2 |
| *3 1 7* | 74.1 |
| *2 1 14* | 75.0 |
| *2 2 12* | 82.7 |
| *4 1 3* | 91.5 |
| *1 0 22* | 92.7 |
| *2 1 19* | 94.7 |

**Table S4** Refined bond lengths and bond angles of as-prepared 3R polytype of [Ca-Al-$NO_3$] LDH.

| Bond lengths [Å] | | Bond angles [°] | |
|---|---|---|---|
| Ca–Oh | 2.4651(1), 2.3020(2) | Oh-Ca-Oh | 117.902(1), 91.962(6), 148.729(2), 56.965(4) |
| Ca-Ow | 2.3599(1) | Oh-Al-Oh | 97.662(4), 82.338(5) |
| Al–Oh | 1.7302(0) | Oh-Ca- Ow | 81.574(1), 125.980(3) |
| $O_{N2}$-Ow | 2.9525(1) | $O_{N1}$-N- $O_{N3}$ | 123.245(5) |
| $O_{N1}$- Oh | 3.2696(1) | $O_{N2}$-N- $O_{N1}$ | 115.783(4) |
| $O_{N3}$- Oh | 3.1775(1) | $O_{N3}$-N- $O_{N2}$ | 117.882(4) |
| N-$O_{N1}$ | 1.1813(0) | | |
| N-$O_{N2}$ | 1.2773(0) | | |
| N-$O_{N3}$ | 1.1981(2) | | |