On the Thermal Stability and Structures of Layered Double Hydroxides Mg$_{1-x}$Al$_x$(OH)$_2$(NO$_3$)$_x$·mH$_2$O (0.18 ≤ x ≤ 0.38)


Keywords: Layered compounds / Double hydroxides / Magnesium / Aluminium

Introduction

The nanostructured character of layered double hydroxides (LDHs), their temperature-induced transformations into metastable oxide materials and their ability to reconstruct to the LDH state through the action of humidity or water lead to a range of applications within, for example, catalysis,[1,2] gas sorption[3,4] and drug delivery.[5,6] The currently investigated materials belong to the hydrotalcite class of layered compounds, M$^{II}_{x-n}$·M$^{III}_n$(OH)$_2$(A$^-$)$_n$vH$_2$O. These consist of brucite-like sheets with edge-shared octahedra of hydroxy-coordinated cations in the backbone. Their 2D layers, separated by anions and crystal water, are positively charged because 10–33% of the M$^{II}$ cations are substituted by M$^{III}$ cations. NMR and diffraction techniques proved that flat-lying water and nitrate become tilted towards [001] at higher nitrate concentrations, accompanied by expansion along the c-axis. The distribution of the molecular tilts is greatest for x = 0.25, which explains the extraordinary broad diffraction peaks. The unit cell volume was modified for all samples when subjected to moist air, most strongly for x = 0.25. On heating, in situ synchrotron diffraction data showed continuous changes along the c-axis during dehydration of samples with x = 0.20 and 0.33. For x = 0.25, an intermediate phase appeared. Dehydroxylation was initiated at the OH groups bonded to the cations MgAl$_2$Mg$_2$Al and Mg$_3$ (in said order), whereas complete nitrate loss occurred at higher temperatures for higher Al contents. Some aluminium simultaneously moved to tetrahedral sites, which, according to $^1$H–$^{27}$Al CP NMR spectroscopy, lack protons in their near neighbourhood. In contrast, octahedral aluminium remains surrounded by protons during decomposition. For the metastable oxide product, neutron diffraction indicated that 2/3 of aluminium reside in tetrahedral interstices. This oxide is defective, probably mimicking wüstite rather than a regular rock salt structure.

Nitrate-based layered double hydroxides, Mg$_{1-x}$Al$_x$(OH)$_2$(NO$_3$)$_x$·mH$_2$O, have been investigated to settle issues relating to stability towards humidity, dehydration and staging, nitrate group orientation, Al migration and crystal structure. Raman and IR spectroscopy together with modelling methods proved that flat-lying water and nitrate become tilted towards [001] at higher nitrate concentrations, accompanied by expansion along the c-axis. The distribution of the molecular tilts is greatest for x = 0.25, which explains the extraordinary broad diffraction peaks. The unit cell volume was modified for all samples when subjected to moist air, most strongly for x = 0.25. On heating, in situ synchrotron diffraction data showed continuous changes along the c-axis during dehydration of samples with x = 0.20 and 0.33. For x = 0.25, an intermediate phase appeared. Dehydroxylation was initiated at the OH groups bonded to the cations MgAl$_2$Mg$_2$Al and Mg$_3$ (in said order), whereas complete nitrate loss occurred at higher temperatures for higher Al contents. Some aluminium simultaneously moved to tetrahedral sites, which, according to $^1$H–$^{27}$Al CP NMR spectroscopy, lack protons in their near neighbourhood. In contrast, octahedral aluminium remains surrounded by protons during decomposition. For the metastable oxide product, neutron diffraction indicated that 2/3 of aluminium reside in tetrahedral interstices. This oxide is defective, probably mimicking wüstite rather than a regular rock salt structure.

Introduction

The nanostructured character of layered double hydroxides (LDHs), their temperature-induced transformations into metastable oxide materials and their ability to reconstruct to the LDH state through the action of humidity or water lead to a range of applications within, for example, catalysis,[1,2] gas sorption[3,4] and drug delivery.[5,6] The currently investigated materials belong to the hydrotalcite class of layered compounds, M$^{II}_{x-n}$·M$^{III}_n$(OH)$_2$(A$^-$)$_n$vH$_2$O. These consist of brucite-like sheets with edge-shared octahedra of hydroxy-coordinated cations in the backbone. Their 2D layers, separated by anions and crystal water, are positively charged because 10–33% of the M$^{II}$ cations are substituted by M$^{III}$ cations. NMR and diffraction techniques suggest frequent short-range ordering, and in certain cases long-range ordering.[7,8] M$^{III}$ contents above 33% are uncommon for crystal chemical reasons as neighbouring Al octahedra in non-defect brucite layers are discouraged (O bond strength).[9] The surplus positive charge arising from the heterovalent substitution is compensated by anions in the interlayer gallery. The quite spacious interlayer region allows uptake of guest molecules, normally water, which has a distinct effect on the layer-to-layer distance (c-axis) of these materials that ideally are based on AB or ABC stackings of brucite-like layers.

LDH materials have been intensively investigated, in particular, the carbonate-based Mg-Al system. Typically, their powder X-ray diffraction patterns show broad reflections, caused by stacking faults and disorder in the interlayer region, as well as by minute particle dimensions in the [001] stacking direction.[10] Their chemical behaviour depends on the method of synthesis (sample morphology, polytypism) and on the type of anions incorporated into the galleries. Carbonates appear as the most stable products.[11] It is generally accepted that once synthesized the stacking order of the A-, B-, and C-positioned double hydroxide slabs can hardly be interchanged by post-treatment, leaving only hydrothermal tuning of the crystallite size as an option.[12] Because one of our prime aims was to gain an in-depth understanding of the processes in which single nanosheets can be achieved in suspension by delamination, we have focused on phase-pure nitrate LDHs that represent the
most efficient anion choice when formamide is used as

dispersing solvent.\textsuperscript{[13]} We are currently focusing on phase-pure
$\text{Mg}_{x-\text{Al}}(\text{OH})_2(\text{NO}_3)_x \cdot m\text{H}_2\text{O}$ samples with predominantly
$R3\bar{m}$ crystal structure polytypes ($3R_1 + 3R_2$).\textsuperscript{[14,15]}

The layer charge correlates directly with Al concentration
and nitrate content. In carbonate LDHs, the charge-com-
penstate anions in the interlayers have their triangular
faces oriented parallel to the hydroxide layers, retaining $D_{3h}$
symmetry. However, at high layer charges the concentra-
tion of monovalent nitrate anions becomes too large to allow
these to be located in flat-lying positions. Two models have
been suggested for high nitrate contents:\textsuperscript{[15–22]} the “tilt-or-
ientation” and “stick-lying” models (see Figure 1). In the
“stick-lying” model proposed by Xu and Zeng,\textsuperscript{[16,17]} flat-
laying nitrate anions alternately stick to the top and bottom
layers of the same gallery. In the “tilt-orientation” model,
nitrate groups are inclined at a tilting angle to the brucite-
like layers.\textsuperscript{[15,18–22]} The recent modelling work of Li et al.
and Zhang et al. points to interlayer nitrate anions turning
from a horizontal, via a tilted orientation, to a vertical ar-
angement relative to the hydroxy groups as function of $x$.
\textsuperscript{[19,22]} The “stick-lying” model is not supported by mo-
-lecular dynamics simulations.\textsuperscript{[16,17,19,22]} In this work we
combined experimental Raman/IR spectroscopic data with
molecular dynamics (MD) and density functional theory
(DFT) calculations of Raman/IR spectra to settle the issue
on nitrate orientation in Mg-Al LDHs.

Water and humidity play major roles in interlayer gallery
chemistry,\textsuperscript{[23]} decomposition and LDH reconstruction. The
unit cell dimensions are good indicators of the structural
details of LDHs, and the interlayer gallery spacing ($c$-axis)
depends strongly on the loading of water, which further-
more influences the nitrate group orientation. We address
open issues and complement literature data with the goal of
providing a more complete understanding of hydration ef-
fects. Concretely, we show how the storage and treatment
of samples in humidity may influence the interlayers and
nitrate orientation. The dehydration of nitrate LDHs may
occur by routes different to the carbonate analogues;
hydrated phases with fixed overall compositions that have
a range of crystal water contents can transform, continu-
ously or via intermediate stages, to a water-free variant. We
provide a new insight based on in situ decomposition stud-
ies by synchrotron powder diffraction.

The thermal stability of LDHs is moderate. The litera-
ture on the thermal decomposition and structural aspects
of phase-pure nitrate LDHs is limited compared with car-
bonate analogues. To the best of our knowledge only a few
studies on the thermal decomposition of nitrate-based
LDHs are available.\textsuperscript{[17,24]} MAS NMR\textsuperscript{[25]} and EXAFS\textsuperscript{[26]}
studies have revealed that the thermal stability of carbonate
LDHs depends on the local structures of cations surround-
ing the OH groups within the 2D brucite-like layers, that is,
on whether the hydroxy groups are of the type Mg$_3$-OH,
Mg$_2$Al-OH or MgAl$_2$-OH (Figure 1), with decreasing ther-
mal stability in the said order. For $x \approx 0.33$, all Al atoms
have six Mg atoms as nearest-neighbour cations, possibly
with long-range order for $x = 0.33$. Tricoordinate hydroxy
groups have either Mg$_3$-OH or Mg$_2$Al-OH configurations.
In this work we have extended beyond the traditional com-
positions to include one high-content Al sample in which
the MgAl$_2$-OH arrangement ought to prevail in a measur-
able amount.

The thermal decomposition products are highly relevant
for applications in heterogeneous catalysis. The as-synthe-
sized LDHs, typically substituted with Fe, Co or Ni transi-
tion-metal ions, are calcined and subjected to reducing at-
mospheres to partly decompose the material into minute
support particles with cluster islands or nanoparticles of
reduced 3d metal.\textsuperscript{[1]} Notably, nanocomposites based on de-
laminated and restacked LDH nanosheets represent novel
types of catalysts.\textsuperscript{[26]} The required temperature for acti-
vation (decomposition, reduction) depends on the 3d LDH
system. At high temperatures the dehydroxylation is fol-
lowed by nitrate decomposition and a high surface area
(metastable) oxide is formed at around 400–600 °C.\textsuperscript{[24]} Ulti-
ately, a thermodynamically stable situation is achieved as
a mixture of spinel and MO (rock salt or wurtzite)-type
oxides. MAS NMR spectroscopic data show that Al$^{III}$
is partly moved from octahedral to tetrahedral sites during
the stepwise thermal treatments. A recent pair distribution
function (PDF) study of Mg$_{1+x}$Al$_{1-x}$(OH)$_2$(CO$_3$)$_{1+x/2}$
$\cdot $mH$_2$O by using X-ray and neutron scattering data indicated that the
cationic backbone is maintained during the conversion of
LDHs into metastable rock salt like oxides.\textsuperscript{[27]} It was further
concluded that locally adjacent layers are not covalently
connected at 460 °C although layer–layer correlations have
disappeared from the patterns. It remains open how PDF
and NMR spectroscopic data together may explain the
atomic arrangements in the metastable oxide and account
for small amounts of carbon and hydrogen species iden-
tified through PDF characteristics.\textsuperscript{[27]} Little is known about
the chemistry of the different types of aluminium species
appearing during the transformations, and the mechanism
proposed by Perez-Ramirez et al.\textsuperscript{[28]} has been debated, for
example, by Mourad et al.\textsuperscript{[27]} Yet, these Al species and their
mobility are likely keys to the so-called reconstruction of
the LDH from the metastable oxide in water/humidity at
close to ambient temperatures. The current combination of
Raman, NMR, TGA, XRD and powder neutron diffrac-

Figure 1. Left: schematic drawing of “stick-lying” (left) and “tilt-or-
ientation” models for nitrate anions (middle) in which the tri-
angles and circles represent nitrate groups and water molecules,
respectively. Right: brucite layer with possible distribution of Al
Octahedra (yellow) and resulting possible coordination environ-
ments for OH groups.
tion (ND) data aims to fill gaps in knowledge and provide a comprehensive description of the decomposition process. The results are discussed in relation to the vast information in the literature on Mg-Al LDH materials.

Results and Discussion

Phase Purity, Unit Cell and Raman Data

The unit cell dimensions at room temperature for the investigated phase-pure Mg$_{1-x}$Al$_x$(OH)$_2$(NO$_3$)$_x$·mH$_2$O samples are shown in Figure 2. Consistent with earlier reports,[16] the $a$-axis decreases linearly with increasing layer charge, that is, Al$^{III}$ substitution. On the other hand, the $c$-axis undergoes a major expansion in the compositional range around $x = 0.25$. To explain the sigmoid-like variations, two models for the re-orientation of the nitrate molecules have been proposed, namely the “tilt-orientation” and “stick-laying” models.[15–22] At lower and higher Al contents, $c(x)$ decreases approximately at the same rate. The diffraction patterns of the carbonate and nitrate $x = 0.25$ analogues are very similar, however, the $c$-axis is contracted for the carbonate relative to the nitrate variant; $c = 23.52$ and 25.28 Å, respectively (see Table S1 in the Supporting Information). The carbonate samples show no anomalous expansion as a function of Al substitution, $x$; the linear fit of the $c$-axis data taken from Mollan Jensen are included in Figure 2.[29]

![Figure 2. Unit cell dimensions $a$ and $c$ vs. composition $x$ for Mg$_{1-x}$Al$_x$(OH)$_2$(NO$_3$)$_x$·mH$_2$O at around 20 °C. (●) Present study, (−−) linear fit of data in present study, (Δ) data taken from Xu and Zeng,[16] (···) linear fit of the $c$-axis for Mg$_{1-x}$Al$_x$(OH)$_2$(CO$_3$)$_{1/2}$·mH$_2$O taken from Mollan Jensen.[29]](image)

Figure 2. Unit cell dimensions $a$ and $c$ vs. composition $x$ for Mg$_{1-x}$Al$_x$(OH)$_2$(NO$_3$)$_x$·mH$_2$O at around 20 °C. (●) Present study, (−−) linear fit of data in present study, (Δ) data taken from Xu and Zeng,[16] (···) linear fit of the $c$-axis for Mg$_{1-x}$Al$_x$(OH)$_2$(CO$_3$)$_{1/2}$·mH$_2$O taken from Mollan Jensen.[29]

The observed X-ray diffraction profiles are in general broad. However, as displayed in Figure 3, the peak widths of (003) and (006) are by far the largest for Mg$_{0.75}$Al$_{0.25}$·mH$_2$O. This has earlier been suggested to result from significant variations in particle sizes, based on calculations using the Scherrer formula.[16] However, stacking faults and stacking inhomogeneity will also contribute to peak broadening. As shown in the TEM images in Figure 3, the particle sizes are fairly equal for $x = 0.20$, 0.25 and 0.33. Hence features related to the interlayers and stacking of the brucite sheets are the likely cause for the peak broadening (see below).

![Figure 3. X-ray diffraction profiles of as-synthesized, freeze-dried Mg$_{1-x}$Al$_x$(OH)$_2$(NO$_3$)$_x$·mH$_2$O ($x = 0.20$, 0.25 and 0.33) showing the peaks (003) and (006) and the corresponding TEM images.](image)

Microwave plasma atomic emission spectroscopy (MP-AES) shows excellent correspondence between the chemical compositions that were aimed for and those that were achieved (see Table S1 in the Supporting Information). However, because MP-AES measures the average composition of the synthesized product, the XRD unit cell data are important to confirm that the changes in the interatomic distances ($ab$ plane) of the crystalline LDH phase are consistent with the proposed Mg-Al variation. Likewise the M–OH–M Raman modes confirm such a compositional variation on the local atomic scale. This excludes erroneous composition analysis for the LDH phase. For the M–OH–M modes, the symmetric $A_{1g}$ stretching and $E_g$ bending modes ($D_{3d}$ symmetry) are Raman-active and can be observed for $x = 0.25$ at around 473 and 550 cm$^{-1}$, respectively.[30] These frequencies are weakly affected by the type of anion, whereas the charge state of the cations and hence the Mg/Al ratio has a significant effect. As $x = 0.18$ is increased to $x = 0.38$, the $E_g$ mode shifts from 545 to 555 cm$^{-1}$ and the $A_{1g}$ band shifts from 466 to 480 cm$^{-1}$ (Figure 4). Hydroxy stretching bands are observed in the 3000–3800 cm$^{-1}$ region. The sharp peak at around 3690 cm$^{-1}$ has a low-frequency shoulder at 3610 cm$^{-1}$ for $x = 0.18$. The high-frequency peak decreases as $x$ approaches 0.38 to leave the band as a shoulder and the low frequency shoulder becomes dominant. These correspond to OH-stretching bands for aluminium and magnesium hydroxide local structures. The broad band observed at around 3400 cm$^{-1}$ is likely due to intercalated water and metal–hydroxy groups interacting through hydrogen bonds.
Ignoring the difference between Mg and Al, the vibrational modes of the $\text{M(OH)}_6$ unit are best described by $D_{3d}$ symmetry. This symmetry appears to be insensitive to changes in Al substitution ($x$) as the factor group splitting due to the vibrational couplings of neighbouring $\text{M(OH)}_6$ units is small for the $A_{1g}$ and $E_g$ modes. The more acidic $\text{Al}^{3+}$ ion will weaken the O–H bond leading to a lower stretching frequency, that is, a downshift compared with the pure brucite case. Such a trend is observed for $\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2(\text{NO}_3)_x\cdot m\text{H}_2\text{O}$ ($x = 0.25$ for carbonate and chloride LDHs and artefact spectrum in the regions 200–1600 and 3000–4000 cm$^{-1}$). Selected Raman modes are marked. See Table S2 in the Supporting Information for positions of bands (in cm$^{-1}$) in the Raman spectra.

For $0.20 \leq x \leq 0.33$, the $\text{Mg}_2\text{Al}_2$-OH and $\text{Al}_3$-OH sites can only form in the case of compositional irregularities. However, for $x = 0.38$ (Figure 4), some $\text{MgAl}_2$-OH sites are necessarily present. The OH groups will furthermore occur at external edges of the nanoparticles, which have thicknesses of less than 10–20 nm and lateral dimensions of less than 50 nm.\textsuperscript{31} Assessment of their stretching frequencies is complicated. At such surfaces OH-bridging of two metal ions as well as non-bridging corner OH groups are expected. This may locally affect the Mg/Al ratio due to charge compensation. Configurations with less bridging are likely to favour the presence of aluminium. Coordination to water molecules rather than hydroxy groups is an alternative mechanism. Furthermore, the lower acidity of Mg would favour water over OH. The OH frequencies reported herein differ from those of the carbonate analogues. The stronger coulombic field of the carbonate ion causes its hydrogen bonds to be stronger than those of the nitrate ion, hence the associated hydrogen-bonded OH should have a weaker O–H bond and a larger reduced mass than a regular OH, leading to a lower stretching frequency. The frequencies of water molecules would follow the same trend.

### Intergallery Chemistry

#### Aspects of Crystal Water

The chemical and structural properties of the intergallery that separates the positively charged brucite-like hydroxide layers control delamination, ion exchange, decomposition pathways and thermal stability. In this respect, the LDH literature is hampered by conflicting data, partly due to the lack of single-anion systems and partly due to the lack of samples with well-defined water contents. We address this challenge by using phase-pure nitrate samples as a well-defined model system. Their high N/C molar ratios ($>10$, Raman analysis shows 2–4% carbonate) assure a very high degree of anion purity. Likewise, precautions have been taken to avoid that the highly susceptible LDH particles adsorb CO$_2$ on the outer surfaces of the platelet-like crystals.\textsuperscript{32} We are not aware of nitrate-based LDHs with even longer c-axes than those currently observed.\textsuperscript{16,23} This still gives no guarantee that the intergalleries are fully free from carbonate, however, the samples are at least state-of-the-art with respect to anion purity. In addition to the anion issue, the degree of hydration affects unit cell dimensions and intergallery properties. Figure 5 shows major variations in the c-axis for as-synthesized $\text{Mg}_{0.75}\text{Al}_{0.25}(\text{OH})_2(\text{NO}_3)_{0.25}\cdot m\text{H}_2\text{O}$ when exposed to ambient humidity over a period of 100 d after synthesis. There is a clear trend towards saturation of the c-axis length. The substantial spread is interpreted to be due to the variation in water content imposed by the temperature and relative humidity. Notably, the data refer to a sample freeze-dried before subjection to the described experiment.
In a careful study, samples of as-synthesized (freeze-dried) Mg\(_{1-x}\)Al\(_x\)(OH)\(_2\)(NO\(_3\))\(_x\)·\(m\)H\(_2\)O, \(x = 0.20, 0.25\) and 0.33, were exposed to a CO\(_2\)-free atmosphere saturated with water at 20 °C (100% relative humidity). CO\(_2\) was suppressed to avoid any cross-effects through anion exchange. The \(c\)-axis of all the samples expanded on exposure to the CO\(_2\)-free atmosphere (Figure 6, left). The degree of expansion is composition-dependent, being small for \(x = 0.20\) (<0.15%) and 0.33 (ca. 0.5%), but as much as 1.5% for \(x = 0.25\). This is a likely consequence of the anion arrangement. Indeed, a correlation between anion orientation and hydration has been indicated by systematic studies of water content as a function of relative humidity at ambient temperature.[18,23] To quantify the variation in water content, thermogravimetric analyses (TGAs) were conducted (see below).

For \(x = 0.20\), the height of the interlayer gallery (–OH HO– separations being about 3.8 Å) is limited and the diffraction data show that the nitrate (carbonate) anions and water molecules are randomly distributed in the centre of the gallery, that is, the nitrate anions are flat-lying.[7,15] This complies well with the modest expansion upon hydration and the low degree of additional water being incorporated. The more complex situation for \(x = 0.25\) and 0.33 in Mg\(_{1-x}\)Al\(_x\)(OH)\(_2\)(NO\(_3\))\(_x\)·\(m\)H\(_2\)O is discussed below. For these, the intergallery is wider, 3.9 and 4.2 Å, respectively, based on the unit cell data in Figure 2 (Table S1), thereby providing more space for the further incorporation of water. In general, the water content of the intergallery is tuneable, yet difficult to assess exactly.

TGA was used to correlate the amount of interlayer water with the expansion of the \(c\)-axis for samples treated in the CO\(_2\)-free atmosphere and saturated with water at 20 °C. The TGA data for the nitrate LDHs show a similar trend upon exposure to humidity. As presented for \(x = 0.25\) (nitrate) in Figure 6 (right), two major weight losses occur below 150 °C. Humidity treatment only affects these two regions and is associated with the loss of adsorbed and crystal water. For LDHs with flat-lying nitrate anions, illustrated by \(x = 0.20\), there is a correlation between the amount of nitrate and intercalated water, both randomly distributed in the centre of the intergallery.[13] By correlating the X-ray diffraction and TGA data for \(x = 0.25\) (nitrate) in Figure 6, it is evident that the intergallery contains additional crystal water when the LDHs have been exposed to humidity for prolonged periods of time. Unfortunately, a quantitative deconvolution of the TGA data to differentiate adsorbed and crystal water is not feasible; consequently, an accurate determination of the amount of crystal water in the LDHs reported herein is not reported.

The XRD data in Figure 7 show no significant changes in Bragg positions during the first water loss recorded by TGA at temperatures below 80 °C. Given a modest thermal expansion, \(d\)(003) should mainly depend on the amount of crystal water. This indicates that the corresponding water lost during the TGA must reside solely on the outer surfaces. The TGA data for samples exposed to 100% relative humidity for a few days show that water is adsorbed on the surfaces and edges corresponding to a change in relative weight of 10–20 (setting the fully calcined mixed oxide in the TGA calculations to a relative weight of 100; Figure 6, right). The substantial amount of surface-adsorbed water is consistent with the small particle sizes of these clays (Figure 3).

**Figure 6.** Left: variation of the \(c\)-axis of Mg\(_{1-x}\)Al\(_x\)(OH)\(_2\)(NO\(_3\))\(_x\)·\(m\)H\(_2\)O \((x = 0.20, 0.25\) and 0.33) as a function of exposure time \((0, 5, 20\) h, 3 d) to humidity under CO\(_2\)-free conditions at around 20 °C. The dotted lines are guidelines for the eye. Right: TGA data for the \(x = 0.25\) sample exposed to humidity under CO\(_2\)-free conditions at around 20 °C for 0 (i.e. as-synthesized), 5, 20 h and 3 d. Insert: low-temperature weight losses of surface-adsorbed water and of water in the intergallery. Heating rate: 5 °C/min in N\(_2\). Note: weight changes normalized to weight of calcined products at 875 °C in order to show that the dominant differences between these samples are the quantities of adsorbed and crystal water.
The dehydration of LDHs into their water-free modifications may follow various pathways. An interesting staging for $x = 0.33$ (nitrate LDH) as a function of relative humidity has been reported in the literature. Other possibilities include a first-order transformation with the coexistence of two phases, or a continuous dehydration with the water content steadily decreasing with temperature. For $x = 0.25$ (carbonate LDH; see Figure S1 in the Supporting Information), the diffraction data show the formation of a distinct water-free LDH phase, $\text{Mg}_{1-x}\text{Al}_x \text{OH}_2(\text{CO}_3)\cdot y \text{H}_2\text{O}$, that is, a one-step decomposition reaction without any intermediate situations.

The situation is complex for nitrate LDHs, as revealed by the in situ synchrotron XRD data in Figure 7. For $x = 0.20$ (nitrate LDH), there is a continuous shift in the Bragg position for (003), which indicates a continuous loss of water from the fully hydrated to the completely dehydrated phase. The main shift in the corresponding $c$-axis occurs in the range 90–130 °C. A similar situation is encountered for $x = 0.33$ (nitrate LDH; see Figure 7, right). There is a notable difference in the relative intensities of (003) for the hydrated and dehydrated modifications of the $x = 0.20$ and 0.33 LDHs, which may indicate significant differences in the atomic arrangement in the interlayer region.

The 3D visualization of the variable-temperature powder diffraction patterns for $x = 0.25$ (nitrate LDH) in Figure 7 (middle) show at least one intermediate phase. Hence, the LDH thermal behaviour is composition-dependent. The $d$(003) for the intermediate phase corresponds to a $c$-axis in between those for the hydrated and dehydrated modifications. This two-step behaviour complies with reports on $x = 0.25$ during dehydration at low relative humidities. The lower quality of the diffraction patterns for $x = 0.20$ and 0.33 makes a detailed analysis difficult for the weaker reflections. Nevertheless, contrary to the situation for $x = 0.25$ (Figure 7), the lack of indication of staging in (003) is supported by analysis of the peak profiles of the weaker (006).

The differences in unit cell volumes between the hydrated and dehydrated modifications are of relevance for considering the expansion upon water uptake described above, as well as for helping to explain anion orientations based on crystal structure arguments. The $c$-axis contractions between 20 and 160 °C on dehydration are $\Delta c = 0.40$, 0.66 and 1.03 Å for $x = 0.20$, 0.25 and 0.33, respectively. It is worth noting that the $c$-axis increases with Al content for the dehydrated phase above 160 °C from 22.84 Å for $x = 0.20$, to 22.98 Å for $x = 0.25$, to 23.52 Å for $x = 0.33$. Wegrzyn et al. observed an unusual shift of (003) towards higher $d$ values during the in situ heating of $x = 0.303$. This is consistent with our findings for $x = 0.25$ (nitrate LDH) in Figure 7 (middle; see region with loss of intensity for (003) marked as “staged decomposition?”). However, the underlying structural aspects remain poorly understood and may possibly involve nucleation of the denser high-temperature structures.

The described structural variations are based on dynamic studies as a function of time, relative humidity or temperature. In this work, approaches were taken towards synthesizing (isolating) LDH samples with water contents intermediate between $m = 0$ and 0.5. Two approaches were followed (see the Exp. Sect.). Attempts to dehydrate as-synthesized LDH with $x = 0.25$ (nitrate) by using $\text{P}_2\text{O}_5$ inside closed capillaries (at ca. 20 °C for 24 h) were unsuccessful. However, the hydration of water-free $\text{Mg}_{0.75}\text{Al}_{0.25}(\text{OH})_2(\text{NO}_3)_0.25$ at 70 °C was possible. As shown in Figure S2
the Supporting Information, the c-axes of the products take intermediate values between those of the dehydrated and hydrated modifications. Similar results were obtained for Mg_{0.67}Al_{0.33}(OH)_{2}(NO_{3})_{0.33}. The calculated c-axes (see Figure S2) correspond quite well to those obtained for as-synthesized, freeze-dried samples (see Table S1). This adds proof to the concept of achieving partly hydrated LDHs by water titration during the post-treatment of water-free polymorphs.

**Nitrate Group Orientation – Raman Spectroscopy and Crystal Structure Considerations**

The expansion of the c-axis with increased Al content (x; Figure 2) reflects a change in orientation of the nitrate anions.[15–22] For the corresponding carbonate LDHs no such expansion occurs due to a higher anion charge (–II) and hence lower anion concentration.[20] Because LDHs are hampered by the poor quality of their powder XRD patterns (stacking faults, thin platelets, non-even water/anion distributions in the intergallery), structural details can barely be received from the Rietveld analysis. Therefore diffraction data must be supplemented by local structure information from spectroscopic techniques such as Raman (and IR) and NMR (see below).

The LDH Raman spectra are dominated by the anion vibrational features [ν1, (ν2), ν3 and ν4] of the nitrate (carbonate) groups, as well as showing plentiful modes arising from H_{2}O, OH– and intralayer LDH vibrations (Figure 4). A feature at around 1650 cm\(^{-1}\) has contributions from the overtone band 2ν3 of nitrate and the ν3 bending mode of water. The weak yet evident very narrow symmetric stretching band of molecular oxygen (νO=O; Figure 4) serves as an internal frequency reference to increase the precision. The ν1, (ν2), ν3 and ν4 bands carry information on the type and structure of the anions in the gallery, and help identify nitrate groups with different orientations/local structures and bonding patterns, as well as discriminating between carbonate and nitrate. The low content of carbonate (as an impurity anion in the current LDHs), along with its weaker Raman scattering amplitude due to a higher charge density cross-section, makes the ν1 (and ν3 and ν4) carbonate bands much weaker than the corresponding nitrate signals, by around a factor six for the pure LDHs.[34] The detection limit for carbonate is estimated to be around 1%. The x = 0.25 sample is here used as a reference, being in the middle of the investigated range of x for Mg_{x−1}Al_{x}(OH)_{2}−(NO_{3})_{0.25}mH_{2}O.

Owing to its non-degenerate nature, the ν1 symmetric stretching mode at around 1050 cm\(^{-1}\) does not split by distortion of the nitrate group. However, factor group splitting may theoretically occur due to the vibrational coupling of several nitrate groups. This effect is expected to be so weak that splitting of this type will be completely embedded in the observed band width. Hence any occurrence of more than one fairly intense peak in this region is a token of more than one type of species, that is, more than one type of nitrate anion or an admixture with carbonate species. The control data for x = 0.25 (chloride LDH) proves that there are no interfering modes from hydroxide. For the samples studied in this work, the ν1 position shifts by about 20 cm\(^{-1}\) between x = 0.33 and 0.20 (both nitrate LDHs; see Figure 9). This shift is likely caused by differences in local coulombic fields and in hydrogen bonding.

![Figure 9. Raman shift of the symmetric ν1 stretching mode of ZO_{3}− anions (Z = N, C) in Mg_{x−1}Al_{x}(OH)_{2}(ZO_{3})_{0.25}mH_{2}O.](image-url)

The ν1 mode of the sample with x = 0.25 (nitrate LDH; Figure 9) indicates the presence of two types of nitrate anions. Detailed curve-fitting reveals, however, that the spectrum for x = 0.25 cannot be fully described by using only two envelopes derived from the x = 0.20 and 0.33 spectra. Attempts to add a carbonate sub-band at its observed frequency did not solve this issue. The ν1 mode at 1044 cm\(^{-1}\) for x = 0.20 is ascribed to planar nitrate groups (D_{3h} symmetry) flat-lying between the AB (BC, CA) and stacked brucite-like layers consistent with a short c-axis (24.08 Å).

It has been debated by various experimental and theoretical means whether the highly elongated c-axis (26.85 Å) for x = 0.33 (nitrate LDH) is caused by “stick-lying” or “tilt-orientation” of the nitrate anions.[15–22] Both these models for an expanded interlayer gallery will expectedly lower the symmetry of the nitrate anions as a result of modified hydrogen-bonding interactions. If the distortions are small and towards C_{2v} or C_{s} symmetry, they will appear as bandwidthening for ν3 and ν4 in addition to positional changes of all the Raman and IR bands. Hence it is difficult to decide on the correct model from spectroscopic data alone. We therefore performed computational simulations (see the Exp. Sect.) of the atomic arrangement of the interlayer galleries as a function of anion and water content. On the basis of the optimized structures, the corresponding Raman and IR spectra were calculated for direct comparison between observations and predictions from the modelling. Although Rietveld fitting of diffraction patterns might appear feasible, the number of well-resolved peaks does not allow a detailed analysis. As mentioned previously, the poor patterns are caused by small particle size, stacking disorder or structural disorder in the galleries, possibly interstratified. PDF analysis has so far been limited to describing the basic backbones of the layered structures.[15,27]
The optimized low-energy configurations determined for Al concentrations of $x = 0.125$ and 0.33 are displayed in Figure 10. When the Al concentration is low, especially for the extreme composition $x = 0.125$, NO$_3^-$ and H$_2$O are closely packed midway between the brucite-like sheets. A similar situation was observed for Ni-Al-based LDHs by Li et al.[19] When the Al concentration is above 18.75%, the NO$_3^-$ and H$_2$O molecules become rotated and randomly distributed (MRRD) in between the brucite-like sheets. For the theoretical simulations, many of the initially assumed different packing models relaxed towards the MRRD model, which clearly indicates the packing model to be highly favourable. At an even higher Al concentration, the molecular tilting increases more and more (see Figure 11), that is, the molecules initially oriented within the $ab$ plane become tilted along [001]. This is directly mirrored in the major expansion of the $c$-axis for Al concentrations above 20–25%.

Figure 10. Crystal structure of LDH without any interlayer anions within the A-B-C-A stacking (a). Intercalated NO$_3^-$ and H$_2$O molecules in Mg$_{1-x}$Al$_x$(OH)$_2$(NO$_3$)$_x$$·$mH$_2$O for $x = 0.125$ (b) and 0.33 (c). For ease of visualization, the NO$_3^-$ and H$_2$O species within the interlayers are displayed only between the A-B stacking layers. The structure fragment shown is cleaved from the optimized Mg-Al-based LDH.

As mentioned above, the experimental characterization of the interlayers, surface regions, and even detailed structures of the layers is very difficult. To verify our theoretical models we simulated the Raman (not shown) and IR spectra for the compositions $x = 0.125, 0.1875, 0.20, 0.25$ and 0.33, and compared these with the experimental observations (0.20, 0.25 and 0.33) presented in Figure 12. It is evident that the simulated IR spectra comply well with the recorded spectra, which shows that the proposed structure models are reliable. The IR spectrum for NO$_3^-$ in the range between 800 and 1400 cm$^{-1}$ is characterized by two symmetry-allowed modes, $\nu_2$ (non-degenerate N out-of-plane bending mode, 810–850 cm$^{-1}$) and $\nu_3$ (double-degenerate N–O asymmetric stretching mode, 1350–1410 cm$^{-1}$), and one forbidden mode, $\nu_1$ (non-degenerate N–O symmetric stretching mode, 1051 cm$^{-1}$). The latter mode becomes partially IR-allowed on distortion of the $D_{3h}$ symmetry. The present experimental and simulated spectra for the LDHs indeed show the presence of such a mode in the IR spectra.

Figure 11. Calculated minimum (min.) and maximum (max.) tilting angles ($\theta$) for NO$_3^-$ and H$_2$O in Mg$_{1-x}$Al$_x$(OH)$_2$(NO$_3$)$_x$$·$mH$_2$O ($x = 0.125, 0.1875, 0.25$ and 0.33).

Figure 12. Recorded (left) and theoretically simulated (right) IR spectra for Mg$_{1-x}$Al$_x$(OH)$_2$(NO$_3$)$_x$$·$mH$_2$O (experimental: $x = 0.20, 0.25, 0.33$; theory: $x = 0.20, 0.25, 0.33$) as well for gas-phase NO$_3^-$ under ambient conditions (from theory). The origin for each mode is graphically represented in an insert.
of two types of nitrate species; both planar and tilted NO₃

To guarantee that higher Al content leads to the co-existence of brucite sheet serve as three-metal bridging ligands. In line with the local surroundings of the cations in the brucite layers.

The distinct kinks in some of the TGA weight-loss curves (Figure 8) at around 350 °C are signatures of the onset of anion decomposition along with progressing dehydroxylation, as supported by combined TGA–MS investigations.[35] Note that the dehydroxylation occurs at lower temperatures for increasing x, whereas the final decomposition appears to be completed at higher temperatures for high x, consistent with greater coulombic interactions. Our XRD data shows that this coincides with an increased disordering in terms of ill-defined Bragg reflections and diffuse scattering. A ND-based PDF study[27] showed interestingly that the backbone of the 2D structure remains intact during these major stages of decomposition. In this respect, insight from Raman and NMR data as local probes becomes essential. The Raman data presented in Figure S3 in the Supporting Information shows that the sharp 1 mode observed for the dehydrated LDH with x = 0.25 (nitrate LDH) at 150 °C with flat-lying nitrate anions becomes broad with an asymmetric shape at higher temperatures. This is consistent with a change in the local structure upon loss of OH groups with the consequent formation of O atoms bound to Mg/Al cations and tetrahedrally coordinated Al species, which enhances the perturbation of nitrate anions even more. At 480 °C no significant remaining nitrate is observed (Figure S3), consistent with the observed rock salt like phase observed by X-ray diffraction. The results of the aforementioned PDF study showed carbonate still to be present in this metastable oxide. Although it is feasible that carbonate may exchange for cations at octahedral interstices (cf. perovskite-related carbonate oxides),[36] the amount ought to be minute and probably beyond detection limits according to the weight losses indicated by high-temperature TGA. Therefore we believe that any remaining carbonate (and nitrate) at temperatures above 450 °C is due to minute amounts of undecomposed LDH, newly formed carbonate or surface-bound species rather than carbonate incorporated into the metastable oxides.

Intermediate Phases and Temperature-Induced Transformations

The water loss on dehydration (heating, dynamic vacuum, low relative humidity) and nitrate re-orientation as a function of layer charge (Al³⁺ and nitrate concentration) and water content are normally not related to further structural changes according to published [25]Mg, 27Al and 1H NMR spectroscopic data. However, the TGA data presented in Figure 8 shows that the dehydrated phase for the more Al-rich compositions (x = 0.33 and 0.38) does not exhibit a well-defined plateau, which suggests that simultaneous dehydroxylation occurs. This will necessarily modify the local surroundings of the cations in the brucite layers.

The 27Al NMR spectra of the as-synthesized nitrate-based LDH with x = 0.25 and its dehydrated variant calcined at 150 °C show just one main peak at around 10 ppm consistent with octahedrally coordinated Al (Figure 13, left). The peak at around 120 ppm is a spinning sideband. The dehydrated variant also shows a very weak signal at 70–80 ppm, likely due to tetrahedrally coordinated Al atoms (see below). Hence the brucite-like layers are close to being fully intact after dehydration at 150 °C.

The TGA data in Figure 8 show the onset of dehydroxylation at 200–250 °C, and the final weight loss related to dehydroxylation and nitrate decomposition is completed at around 550–600 °C. The hydroxy groups within a single brucite sheet serve as three-metal bridging ligands. In line with the lower thermal stability of Al(OH)₃ compared with Mg(OH)₂, the onset temperature for dehydroxylation is least for the composition with highest Al content (i.e., x = 0.38; Figure 8). Hence, Mg₂Al-OH sites tend to dehydroxylate prior to Mg₃-OH sites, whereas the MgAl₂-OH sites are the least stable and will only occur in samples very rich in Al. The TGA curve for x = 0.38 indicates that dehydroxylation runs in parallel with ongoing dehydration.

The 27Al NMR spectra of Mg₀.₇₅₅Al₀.₂₅(OH)₂(NO₃)₀.₂₅·mH₂O as-synthesized and annealed at 150 (left) and 275 °C (right) for 24 h. See the Supporting Information for spectra of all calcined and reconstructed samples.

![27Al NMR spectra of Mg₀.₇₅₅Al₀.₂₅(OH)₂(NO₃)₀.₂₅·mH₂O](image)
which according to dynamic TGA studies starts at around 290 °C for $x = 0.20$ and 0.25, 275 °C for $x = 0.33$, and 230 °C for $x = 0.38$ (Figure 8). The appearance of tetrahedral Al atoms reflects major structural changes, either in the brucite sheets at the local level or alternatively by the precipitation of nanoparticles of an Al-rich phase. However, because the metastable oxide obtained after enhanced heating (see below) can be fully reconstructed (the so-called memory effect, see, e.g., ref.[33]) to an LDH for which $^{27}$Al NMR spectroscopy shows solely octahedrally coordinated aluminium (see Figure S4 in the Supporting Information), phase separation with the formation of an Al-rich impurity phase is unlikely. This is further supported by noting that the LDH $a$-axis (3.062 Å) is unchanged and the $c$-axis corresponds to fully carbonated $x = 0.25$ (23.52 Å; see Table S1). Note also that the reconstructed LDH will accommodate carbonate in the interlayer gallery if no precautions are taken.

A detailed insight into the surroundings of Al was obtained from $^{27}$Al 3QMAS and $^{1}$H–$^{27}$Al CP experiments. The 3QMAS study shows correlations between a triple quantum transition and the single quantum central transition in the $^{27}$Al nuclei, and after Fourier and shearing transformations an isotropic spectrum is shown on the vertical axis and a MAS spectrum on the horizontal axis (Figure 14, left). The vertical spectrum indicates three non-equivalent Al positions for a sample heated at 275 °C. The octahedral region shows two different Al sites (denoted A and B, Figure 14, left), but only one type for the as-synthesized LDH. The diagonal shapes of the peaks A and B indicate a distribution of chemical shifts for the Al atoms involved, and that the quadrupolar couplings are rather small. A true octahedral environment would not cause any such broadening because the electric field gradient would be zero. However, the octahedral sites in the brucite-like layers contain Al and Mg in various (statistical) ratios and have a neighbourhood that is partly dehydroxylated at 275 °C. The horizontal shape of peak C indicates that these Al atoms have a significant quadrupolar coupling, larger than for atoms A and B, and with more regular surroundings.

The CP signal is caused by through-space dipole–dipole couplings and discriminates Al atoms that are close neighbours to protons and those that are not. An Al nucleus with no protons within a radius of a few Å will give a weak or no signal at all. Figure 14 (right) shows the CP (right, lower curve, 40000 scans) and the single pulse (right, upper curve, 400 scans) data. Two CP signals are seen in the 0–20 ppm region with octahedrally coordinated Al atoms. Hence these Al atoms have hydrogen as close neighbours, and some of the surrounding O atoms are probably hydroxy groups. In contrast there is a very weak signal at $\delta = 82$ ppm in the tetrahedral Al region. All the other signals are spinning sidebands. The signal at $\delta = -25$ ppm in Figure 14 (right) is a spinning sideband because it appears at exactly 14 kHz (the MAS spinning rate) from regular peaks and it originates from tetrahedral Al atoms at $\delta = 82$ ppm. However, the main tetrahedral Al peak is at a slightly lower ppm value. One can therefore conclude that there exist at least two types of tetrahedral Al atoms. Most of these do not have any close protons, but there are also a tiny number of tetrahedral Al atoms with nearby protons that give rise to the signal at 82 ppm in the CP spectrum. The corresponding data for samples heated at 340 and 480 °C do not contribute any additional features, however, the leftmost part of the octahedral Al signals become more dominant for samples treated at more elevated temperatures (see Figure S5 in the Supporting Information).

According to XRD and mass analysis by TGA, the $x = 0.33$ sample heated at 480 °C corresponds well to a rock salt like oxide. The CP NMR spectroscopic data (see Figure S5) show that the octahedral Al atoms still have nearby hydrogen atoms, which indicates that the mixed oxide still contains hydroxy groups. This is in line with the well-known situation for $\text{Al}_2\text{O}_3$ made, for example, from bohemite.[17] The Rietveld refinement of powder neutron diffraction data (see fitted diffraction profiles in Figure 15) benefits from good scattering contrast between Al and Mg atoms (amplitudes 0.35 and 0.52 × 10$^{-12}$ cm, respectively) compared with the X-ray diffraction data. However, the small particle size (and/or strain) gives broad Bragg reflections (Figure 15). The nominal composition of the $x = 0.33$ rock salt like oxide is ($\text{Mg}_{0.67}\text{Al}_{0.33}\text{O}_{1.86}$). The refinements give an average description within the framework of a cubic unit cell [$a = 4.182(1)$ Å] based on ccp stacking of the oxygen sub-lattice.

The structure is not just of the regular rock salt type with cation vacancies (as indicated by the nominal formula), but has a substantial amount of filled tetrahedral interstices. Based on the $^{27}$Al NMR spectra it is reasonable to assume that the tetrahedral sites predominantly contain Al atoms. According to refined occupation numbers the data are consistent with a model in which all the Mg atoms reside in octahedral sites and 2/3 of the Al atoms lie in tetrahedral sites. Note that this is still an average description, and that major local deviations may exist. Anyhow, this metastable oxide is not of a regular rock salt type. Possibly the situation rather mimics that of wüstite ($\text{Fe}_{1-x}\text{O}$).[18] For wüstite, the incorporation of $\text{Fe}^{III}$ involves the formation of defect clusters (4:1, 13:4 clusters, etc., see, Figure S6) with $\text{Fe}^{III}$ in tetrahedral interstices surrounded locally by vacancies at the octahedral sites. We envisage a similar situation for the current material. This situation is significantly different from that encountered in crystalline spinel ($\text{MgAl}_2\text{O}_4$), in which Mg resides in tetrahedral and Al in octahedral sites.
To the best of our knowledge, $^{25}$Mg NMR spectroscopic data are not yet at hand for the metastable Mg-Al oxide, which would be required to claim that solely Al atoms reside in tetrahedral interstices. In conclusion, this metastable oxide mimics a disordered spinel rather than a regular rock salt type oxide. DIFFaX analysis was adopted by Johnsen and Norby\cite{39} to explain the peak in the powder X-ray diffraction pattern additional to (111), assuming disorder in layers stacked along [111] due to mixtures of rock salt like and spinel-like layers. The neutron diffraction data determined here fit reasonably well the (111) peak whereas additional features are weak or absent. The latter supports the suggested disorder in cation locations because these atoms are poorer scatterers of neutrons than oxygen.

At high Al$^{III}$ contents, the nitrate concentrations in the interlayers for charge compensation are too large to allow planar anion configurations. We have shown that the expansion in the interlayer separation as seen by XRD (Figure 2) corresponds to at least two nitrate orientations, as revealed by Raman and IR data (Figure 9 and Figure 12). Importantly, this spectroscopic evidence is fully consistent with spectra obtained from computational modelling, which shows that water and nitrate anions progressively become more and more tilted upon increasing nitrate content (Figure 11 and Figure 12). The so-called “tilt-orientation” model for the nitrate orientation is hence fully proven, whereas the “stick-laying” model is not supported. This combination of experimental and theoretical tools is indeed a strong means of understanding interlayer chemistry, and can easily be extended to fully dehydrated systems, more complex anions, and magnetic LDHs among other systems.

The span in reported unit cell dimensions of otherwise anticipated identical LDHs clearly stem from differences in anion concentrations in the interlayers, which is challenging to determine at a level better than 5%. This may easily give rise to variations in the $c$-axis for compositions close to the limit at which major anion re-orientation sets in (Figure 2). However, our studies of LDHs subjected to ambient moisture (accelerated on heating) show that the crystal water content is dependent on humidity and the treatment of the samples during drying and subsequent storage. Post-synthesis absorption of a significant amount of water into the gallery is feasible, being most enhanced for compositions that have a wide interlayer spacing owing to the orientation of the anions. In the extreme case, $\Delta c/e$ can be as large as 1.5% (Figure 6). This hydration capacity, which results in absorbed crystal water, can barely be well determined from TGA because significant water adsorption occurs simultaneously on the outer surfaces of the nanoparticles.

The as-synthesized Mg-Al LDHs can apparently exist for different contents of crystal water. The fully dehydrated variant is in most cases quite well defined, however, at extreme Al contents, at which a few less stable MgAl$_2$-OH coordinating situations exist, dehydroxylation appears to initiate simultaneously with progressing dehydration. In situ diffraction studies showed that (003) of samples with $x = 0.20$ and 0.33 continuously shifts on dehydration, which indicates that partial loss of crystal water is feasible while retaining the structure. However, for $x = 0.25$, an intermediate phase is observed (Figure 7). This corroborates literature reports of partial dehydration and staging upon heating under a dynamic vacuum. Note that in the $x = 0.25$ carbonate analogue the dehydration appears to involve two distinct phases with different $c$-axis dimensions. To achieve samples with well-defined intermediate water content, we have proven the applicability of water titration by using water-bearing copper sulfate in a closed capillary. This may lead to systematic studies of LDHs with intermediate water contents, probably of most interest with respect to certain physical properties (e.g., magnetism).

The onset and progress of dehydroxylation in the range 200–250 °C depends on the Al content and thereby on the
relative amounts of Mg\(_{2-}\), Mg\(_2\)Al- and MgAl\(_2\)-coordinated OH groups, with the stability decreasing in the said order (Figure 8). The stability towards further decomposition of the ill-defined, yet nitrate-containing layered material is opposite, being largest for samples with high layer charges (high Al contents), probably as a result of coulombic interactions. During these decomposition reactions it appears that nitrate adopts a planar orientation, although the Raman data shows broadened signals in line with highly perturbed chemical environments (loss of water, hydroxy groups, see Figure S3 in the Supporting Information). The in situ synchrotron XRD data for \(x = 0.25\) shows a low-angle shoulder emerging from (003) upon the final LDH decomposition and prior to the formation of the metastable oxide phase (Figure 7). This may possibly indicate staging, that is, that layered nitrate anion correlations prevail up to higher temperatures.

A very intriguing aspect of the decomposition of LDH is the mobility of some aluminium cations from octahedral to tetrahedral sites, and furthermore, the reconstruction of an LDH upon the soaking in water of the oxide obtained upon calcination at around 480 °C. In this and in numerous other works, various pieces of evidence have been brought together to explain this puzzle. The sensitivity of the Raman M–OH–M modes to the charge state of the M cations provides some insight into the dehydroxylation, whereas NMR spectroscopy provides insight into the local Al environment. As shown here, the water-soaked and reconstructed LDH, after calcination under conditions in which the material is dehydrated, dehydroxylated, partly decomposed or fully converted into a metastable rock salt like oxide, contain solely octahedrally coordinated Al (see Figure S4 in the Supporting Information). Hence the departure from the original LDH atomic arrangement in all these cases is likely to be rather minute, otherwise tetrahedral Al and multiphase samples would be expected. This is consistent with PDF data that indicates that the layered backbone of the LDH prevails even for the metastable oxide.

The \(^1\)H–\(^{27}\)Al CP NMR spectroscopic data presented in Figure 14 show that already early during the decomposition at least two types of octahedral Al are present, both of which have nearby hydrogen atoms (i.e., hydroxy groups) as neighbours. One type of tetrahedral Al becomes quite dominant, however, this apparently has no near hydrogen neighbours. This situation is also the case for the metastable oxide. This is supported by the TGA data, which shows a small, yet measurable, weight loss on turning to higher temperatures, whereas the Raman data show no more indications of nitrate, which could be a second source of the weight loss. The resulting rock salt like oxide, obtained upon heating to 480 °C, has, according to neutron diffraction data, 2/3 of its Al atoms in tetrahedral interstices, thereby resembling more a disordered spinel-like material than a regular rock salt material. The ND data provides no clue with respect to hydrogen atoms, which certainly exist in low concentrations and are expectedly distributed at random and connected to the anionic sub-lattice. The average structure provided by the ND data is consistent with PDF data that suggests a certain layered character. The key point is the distribution of the tetrahedral atoms between the ccp-stacked layers of oxygen anions. We tentatively indicate massive local ordering, possibly mimicking wüstite, however, layer-like schemes are also equally likely.

**Experimental Section**

**Synthesis of Mg\(_{x}\)Al\(_2\)(OH)\(_2\)(A\(^{n+}\))\(_{x}\)\(_{0.5}\)mH\(_2\)O Samples**: LDH samples were prepared by co-precipitation at 60 °C and pH 10.0 (nitrate and chloride LDHs) or 11.5 (carbonate LDHs) using procedures described by Karthikeyan et al. and references cited therein[31] (see Table S1 in the Supporting Information for nominal compositions). The samples are denoted according to the full formula Mg\(_{x}\)Al\(_2\)(OH)\(_2\)(A\(^{n+}\))\(_{x}\)\(_{0.5}\)mH\(_2\)O or the degree of cation substitution (\(x\)). Nitrate and chloride LDHs were synthesized under CO\(_2\)-free conditions. The incorporation of CO\(_2\)\(_2\)\(^-\) was minimized by using 1) freshly boiled deionized water and He bubbling and 2) pure KOH stored inert in Schlenk flasks. All the chemicals were handled in an inert tent and the co-precipitation reaction was performed under an inert blanket of argon. A batch of LDH was typically produced by adding a 1.0 M cationic solution (100 mL) at a constant rate into a reaction vessel with water (100 mL). Nitrate-based magnesium and aluminium salts were used for nitrate- and carbonate-based LDHs whereas chloride salts were used for chloride LDHs. Simultaneously, a solution (ca. 300 mL) containing 0.85 M KOH and 0.15 M of a potassium salt (NO\(_3\)-, Cl\(^-\), CO\(_2\)\(_2\)\(^-\)) was added to the reaction vessel by using a peristaltic pump that maintained constant the pH by means of a feedback loop using a pH titrator (Mettler Toledo pH2100e with InPro 3100/120 Pt1000 electrode). The suspensions obtained were aged for around 90 min prior to four washing and centrifugation (3000 rpm for 10 min) cycles. Nitrate and chloride samples were freeze-dried and stored under inert and dry conditions, whereas carbonate LDHs were dried in an oven and stored without any further precautions.

**Chemical Composition, Phase Analysis, and Structural Analysis**: Phase purity and unit cell dimensions were derived from powder X-ray diffraction (XRD) data collected with a Siemens D5000 instrument (Cu-K\(_\alpha\) radiation \(\lambda = 1.540598\) Å) in transmission (0.5 mm diameter borosilicate capillaries) or reflection mode. Si (\(\alpha = 5.4306\) Å) was used as the internal standard. Owing to the poor crystallinity of the as-synthesized LDHs, the unit cell dimensions (\(a, c\)) were obtained from the \(d\) values of (003), (006) and (110), see, for example, Karthikeyan et al.[31] High-temperature powder synchrotron XRD data were collected at the Swiss Norwegian Beam Lines, ESRF in transmission mode by using a 2D detector (\(\lambda = 0.5056\) Å). Temperature calibration was based on collected thermal expansion data for metallic silver. Powder neutron diffraction data were collected at room temperature between 29 = 10 and 130° rebinned into steps of \(\Delta(2\theta) = 0.05°\) by using the two-axis PUS diffractometer at the JEEP-II reactor at Kjeller, Norway (\(\lambda = 1.5554\) Å). Rietveld refinements were performed by using the Fullprof suite of programs[40].

The aluminium contents, \(x\), of the phase-pure as-synthesized samples, were determined by using microwave plasma atomic emission spectroscopy (Agilent 4100 MP-AES). The targeted compositions were confirmed within an estimated uncertainty of \(x =\) nominal composition ± 0.01 units. Changes in the shapes and shifts in peak frequencies in the M–OH–M region of the Raman spectrum were used as evidence for changes in \(x\). A supplementary CN analysis was performed at the Ilse Beetz Microanalytisches Laboratorium, Kronach, Germany. All the nitrate LDH samples were found to...
have molar ratios of NO₃⁻/CO₃²⁻ > 10. Carbonate contaminations in the as-synthesized LDHs were also evaluated from Raman spectra using the vibrational modes at 1062 and 1032 cm⁻¹ attributed to carbonate and hydrogen carbonate, respectively. Raman analyses indicated carbonate impurity levels of 2–4% (see Table S2 in the Supporting Information).

Thermal Stability and Water Content: Thermogravimetric (TG) data were collected by using an STA 449 F1 Jupiter combined TGA-DSC system from Netzsch during heating to 900 °C in N₂ at a rate of 5 °C/min. Isothermal studies were conducted at selected temperatures. In situ powder diffraction data were collected at ESRF (see above) during heating of the as-synthesized samples at a rate of 4 °C/min in rotating 0.7 mm borosilicate capillaries open to the air. Full and partial dehydration of the as-synthesized LDHs was attempted by adding weighed amounts of P₂O₅ to the LDH within the XRD capillaries, which were subsequently closed, heated to 80 °C and examined by powder X-ray diffraction in transmission mode. These experiments were considered unsuccessful because no changes in unit cell dimensions were observed.

Water absorption was attempted by treating dehydrated LDH (treated at 150 °C) with a water-releasing salt. Weighed mixtures of dehydrated MgₓAlₓ(OH)₂(NO₃)₃ (x = 0.25 and 0.33) and CuSO₄·5H₂O were introduced into the reaction tube (using a Braun glove box) with a ceramic porous pellet to separate the reactants. The evacuated reaction tube (carefully closed to minimize water loss from the sulfate) was heated at 70 °C for 5 h. Under these conditions reaction (1) took place:

\[
\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2(\text{NO}_3)_3 + y\text{CuSO}_4\cdot5\text{H}_2\text{O} \xrightarrow{70^\circ\text{C}/5h} y\text{CuSO}_4\cdot3\text{H}_2\text{O} + \text{Mg}_{1-x}\text{Al}_x(\text{OH})_2(\text{NO}_3)_3 \cdot 2y\text{H}_2\text{O}
\]

After completion of the reaction, the LDH sample was transferred under inert conditions into a capillary that was immediately sealed and studied by powder XRD.

Raman and Fourier-Transform Infrared (FTIR) Studies: Two series of experiments were carried out. In series 1, the as-synthesized LDH samples (see Table S1 in the Supporting Information) were compared. A confocal microscope was employed to suppress most of the fluorescent stems pointing from outside the laser spot of interest. The samples were illuminated with light from a Spectra-Physics Millenna Pro 12aJS Nd:YVO₄ solid-state laser operating at 200 mW at 532 nm obtained through a neutral density optical filter (90%) and an Olympus 100× objective, resulting in a laser effect at the sample of around 2.4 mW. The Raman light was collected in back-scattering mode, guided through a confocal pinhole of 100 μm and a 532 nm Kaiser Optical holographic Super-Notch filter into a Jobyn–Yvon Horiba T64000 instrument working as a single spectrograph. The entrance slits were set to 100 μm and the height reduced to 25% to minimize stray-light and fluorescence. A grating with 1800 lines/mm was chosen for dispersion, which ensured a spectral width of 2.2 cm⁻¹. Six scans of 600 s were averaged for each Raman spectral section. Four pieces of overlapping spectra covered the ranges of 200–1800 and 3000–4000 cm⁻¹, respectively. Background fluorescence was subtracted by fits with polynomial methods, in particular DMOL3 [44] (molecular calculations of H₂O and NO₃⁻) together with non-principal modes from the laser generated artefact time of 7 h. The strong Rayleigh scattering from the samples together with non-principal modes from the laser generated artefact Raman signals. Therefore 180° Raman spectra of simple metal mirrors were used to correct artefacts.

FTIR spectroscopy (Perkin–Elmer S-2000) was used to analyse the interlayer anions in various as-synthesized LDHs (see Table S1) by using the KBr pellet technique. Oven-dried KBr (ca. 200 mg) was mixed with LDH (1–2 mg), ground moderately and prepared as pellets. Measurements were taken between 400 and 4000 cm⁻¹ with a resolution of 2 cm⁻¹ and 64 scans per spectrum. Dry KBr was used to record a background spectrum.

NMR Experiments: The corresponding nitrate-based x = 0.25 samples (as-synthesized, calcined at 150, 275, 340 or 480 °C) as used for the Raman analysis (series 2, see above) were packed under inert conditions (glove box) into suitable sample holders for NMR spectroscopy. In addition, reconstructed LDHs from intermediates calcined at 150, 275, 340 and 480 °C were investigated. Control experiments were conducted on selected samples stored inertly for periods of up to 3 months. No deviations in the spectral details were found. The ²⁷Al NMR experiments were performed at 11.7 T (500 MHz) with a Bruker Avance III spectrometer at a frequency of 130.318 MHz. The spectra were obtained by using a 4.0 mm MAS probe spinning at a rate of 14 kHz. The chemical shifts of ²⁷Al were referenced to aq. 1 M Al(NO₃)₃ by sample substitution at the same magnetic fields as used in the method recommended by IUPAC [41]. The ²⁷Al single pulse spectra were obtained by using π/12 pulses at a 38.5 kHz rf field, 5000 transients, and with a recycle delay of 0.5 s. The ²⁷Al 3QMAS experiments were carried out with a three-pulse z-filtering sequence [42]. These spectra were acquired with 4800 scans for each of the 60 experiments in the indirect dimension. The recycle delay was 0.8 s. The ¹H–²⁷Al cross-polarization (CP) experiment was carried out by using a 3.2 mm MAS probe. The MAS rate was 14 kHz and the chemical shifts of ²⁷Al were referenced as above. 40000 scans and a recycle delay of 5 s were applied for a total experimental time of 2 d and 8 h.

Computational Details: The experimental description of LDHs and their interlayers is complex. This makes it difficult to construct the initial structure models for theoretical simulations. A step-by-step construction method was therefore adopted [43]. DFT-based methods, in particular DMOL³ [44] (molecular calculations of H₂O and NO₃⁻) and CASTEP [45] (for LDH materials) as implemented in MATERIALS STUDIO 6.0, were used to optimize the atomic positions of all the structure models currently considered. For structural optimisation, Vanderbilt pseudo-potentials were utilized for all atoms together with a fine mesh of k points with an energy conversion threshold of 0.01 eV/atom, maximum displacement of 0.001 Å and maximum force of 0.03 eV/Å, yielding highly accurate energy values and atomic displacements. A plane-wave cut-off energy of 600 eV was employed. The Perdew–Burke–Ernzerhof and
the generalized gradient form (GGA-PBE) of the exchange-correlation functional were applied. The initial molecular structures of \( H_2O \) and \( NO_3^- \) were computed by applying the hybrid B3LYP to the structures optimized at the PBE level. Density functional perturbation theory (DFPT) as implemented in CASTEP was used for vibrational calculations. For the Raman and IR calculations we used norm-conserving pseudo-potentials with an energy cut-off of 850 eV for all atoms together with an \( 8 \times 8 \times 1 \) mesh of \( k \) points with an energy conversion threshold of 0.01 meV/atom. The reference configurations of the valence electrons for the elements were \( 2s^2, 2p^6, 3s^2 \) for Mg, \( 3s^2, 3p^1 \) for Al, \( 2s^2, 2p^3 \) for N, \( 2s^2, 2p^4 \) for O and \( 1s^1 \) for H. The initial structural model was based on the structure of Mg hydrotalcite\[7\] with \( R\bar{3}m \) symmetry for the primary layers of LDH \( Mg_2 Al(OH)_2(NO_3)_x \cdot mH_2O \) with \( x = 0.125, 0.1875, 0.250 \) and 0.334. The starting unit cell dimensions were taken from Table S1 in the Supporting Information.

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