Reversible hydration of the perchlorate-intercalated layered double hydroxides of Li and Al: structure models for the dehydrated phases

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Abstract. Imbibition of lithium sulphate into aluminium hydroxide is known to result in a sulphate-intercalated layered double hydroxide (LDH) of Li and Al. The perchlorate ion has the same size and molecular symmetry as the sulphate ion, but only half its charge. Consequently, twice the number of ClO_4^- ions is needed to balance LDHs the charge on the metal hydroxide layer, compared to the SO_4^{2-} ions. In this work, the ClO_4^- -intercalated LDHs were obtained from both the bayerite and gibbsite precursors. Inclusion of the hydration sphere along with the ClO_4^- anion, induced turbostratic disorder in the stacking of the metal hydroxide layers. Temperature-induced dehydration ($T \sim 100\text{--}140^\circ\text{C}$) brought about a partial ordering in the interlayer region and the ClO_4^- ion oriented itself with one of its C_2 -axes parallel to the metal hydroxide layer. The close packing of ClO_4^- ions could be realized by the complete dehydration of LDH and the distribution of the ClO_4^- ions in all the available interlayer sites. In contrast, within the crystal of the sulphate analogue, the sulphate ions occupy only half the number of interlayer sites. The other half is occupied by the residual water molecules, as the sulphate analogue does not fully dehydrate even at elevated temperatures. This difference in the behaviour of the two LDHs has its origin in the large difference in the hydration enthalpies of the two anions.

Keywords. Layered double hydroxide; aluminium hydroxide; perchlorate; sulphate.

1. Introduction

$\text{Al}(\text{OH})_3$ has a layered structure, in which a third of the cationic sites are vacant [1–4]. The layer composition is $[\text{Al}_2\Box(\text{OH})_6]$ ($\Box$: cation vacancy). A positive charge can be generated in the metal hydroxide layer by inserting Li^+ ions in the cation vacancies. The two-cation (double)-hydroxide layer acquires the composition $[\text{Al}_2\text{Li}(\text{OH})_6]^+$. To compensate the positive charge, an interlayer of anions and water molecules of the composition $[(\text{A}^{n-})_{1/n} \cdot y\text{H}_2\text{O}]$ is incorporated simultaneously with the imbibition of Li^+ in the metal hydroxide layer [5,6]. The resulting phase has the composition $[\text{LiAl}_2(\text{OH})_6](\text{A}^{n-})_{1/n} \cdot y\text{H}_2\text{O}$.

A range of anions such as NO_3^- , Cl^- , Br^- , CO_3^{2-} and SO_4^{2-} have been successfully intercalated into the interlayer gallery of [Li–Al] layered double hydroxides (LDHs), and their structures are reported [7–13]. The size, charge, degree of hydration and molecular symmetry of the anion not only determine the basal spacing in the LDHs, but also the manner in which the metal hydroxide layers are stacked. Consequently, different anions select for different polytypes.

The CO_3^{2-} ions are planar and crystallize LDHs with prismatic interlayer sites, wherein there is a coincidence of the molecular symmetry of the anion with the local symmetry of the interlayer site. The CO_3^{2-} ion is intercalated with its molecular plane parallel to the metal hydroxide layer (local symmetry D_{3h}) with a basal spacing of 7.5 Å. The H-bonding between the OH groups of the layer and the ‘O’ atoms of the CO_3^{2-} ion is maximized in this mode of coordination, and there is a perfect registry between the carbonate ion sublattice and the metal hydroxide layer [14]. In the nitrate-intercalated LDHs, twice the number of nitrate ions as the number of carbonate ions is included within the same interlayer space. The tight packing of nitrate ions in the interlayer results in strong anisotropic repulsive forces, and generates incommensurate structures, wherein the unit mesh of nitrate ions in the interlayer is not in registry with the metal hydroxide layer. Simultaneously, the nitrate ions reorient themselves in such a way that their molecular plane is tilted at an angle to the metal hydroxide layer and the basal spacing increases to 8.8 Å [10,12].

Sulphate and perchlorate ions constitute another pair of isostructural ions with a similar size but different charge.

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The sulphate ion has been shown to intercalate in the interlayer region in an approximately D_{2d} local symmetry with one of the C_2 -axes of SO_4^{2-} being normal to the metal hydroxide layer [13], in the gibbsite-derived LDH. In the bayerite-derived LDH, the orientation of the sulphate ion is different, and the local symmetry is further reduced. These orientations are selected to maximize the H-bonding between the O atoms of the sulphate ions and the metal hydroxide layers. The perchlorate-intercalated [Li-Al] LDH was shown to undergo a reversible expansion of the basal spacing on humidity cycling [15], but no attempt was made in this early study to investigate the structure of the LDH or the orientation of the intercalated ions.

The main objective of this work was to obtain structure models to predict the manner in which twice the number of perchlorate ions is packed within the same interlayer space as occupied by the sulphate ions. A second objective was to examine if the perchlorate-LDH undergoes interpolytype transitions on variation of humidity and temperature.

2. Experimental

2.1 Synthesis

Gibbsite used in this study was a gift from Jawaharlal Nehru Aluminum Research Development and Design Centre (JNARDDC), Nagpur, India. Bayerite was synthesized in the laboratory by a procedure reported in the literature [16]. The [Li-Al- ClO_4] LDHs were synthesized by soaking ~2 g of gibbsite or bayerite in ~18 M $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ solution taken in a screw cap vial. The vial was immersed in an oil bath at 90°C for 7 days with constant stirring. The sample was then aged at 90°C for 30 h without stirring [17]. The precipitate obtained was centrifuged and washed with water. The solid sample was dried in a hot air oven maintained at 60°C. The LDHs prepared are denoted as g-[Li-Al- ClO_4] and b-[Li-Al- ClO_4] (g: gibbsite derived; b: bayerite derived), respectively.

2.2 Characterization

The LDHs were analysed for their Li^+ content by flame photometry, ClO_4^- content by ion chromatography (Metrohm Model 861 Compact Ion Chromatograph fitted with a Metrosep SUP150 column) and Al^{3+} content by gravimetry. The estimations yielded a Li/Al ratio of 0.39 for g-[Li-Al- ClO_4] and 0.37 for b-[Li-Al- ClO_4] LDHs, respectively. The ratio is less than the ideal value (0.5) expected. The ClO_4^- content was nevertheless equivalent to the Li^+ content within the limits of experimental error. The nominal composition ($[\text{Li}^+]/[\text{ClO}_4^-] = 1$) was assumed for the LDH phases. The Al in excess of the ideal Li/Al ratio was attributed to the unreacted precursor, gibbsite or bayerite. The composition of the product in the two cases was $\text{Li}_{0.44}\text{Al}(\text{OH})_3(\text{ClO}_4)_{0.44} + 0.12[\text{Al}(\text{OH})_3]$ and $\text{Li}_{0.5}\text{Al}(\text{OH})_3(\text{ClO}_4)_{0.5} + 0.34[\text{Al}(\text{OH})_3]$ for g-[Li-Al- ClO_4] and b-[Li-Al- ClO_4] LDHs, respectively.

The powder X-ray diffraction (PXRD) patterns of the samples were recorded using a Bruker D8 Advance diffractometer (Cu $K\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$) operating in reflection geometry. *In situ* measurements were carried out at different temperatures, and relative humidity (RH) values using an Anton Paar CHC plus Humidity Chamber as an attachment. The PXRD patterns were recorded over 5–100° 2θ range. A step size of 0.02° 2θ (counting time of 10 s per step) was used for data collection.

2.3 PXRD pattern simulations and structure refinement

The relationship between the successive layers in the LDH was established using the structural synthon approach described elsewhere in detail [14]. A Fortran-based computer code *DIFFaX* [18,19] was used to simulate the PXRD patterns of all the possible polytypes using different stacking vectors. A metal hydroxide layer obtained from the reported structure of g-[Li-Al-X] ($X = \text{Cl}^-$, Br^-) LDH [20] was identified as a structural synthon, and all its symmetry-related atoms were used as input. The Laue symmetry was declared UNKNOWN, and the *DIFFaX* code was allowed to compute the Laue symmetry. The *DIFFaX* code integrates the diffraction intensity layer by layer for an infinite stacking. A full-width at half-maximum value of 0.2° 2θ (Lorentzian profile function) was used to broaden the simulated Bragg reflections. A good match between the observed and the simulated PXRD patterns yielded a partial structure model based on the metal hydroxide layer and the stacking vector. The partial structure model was introduced in code FOX (Free Objects for Crystallography) [21] to obtain the positions of the ClO_4^- ions in the interlayer.

3. Results

The PXRD pattern of the g-[Li-Al- ClO_4]-ASP (ASP: as-prepared) phase exhibited strong basal reflections with spacings of 9.17 Å (9.6° 2θ) and 4.59 Å (19.3° 2θ), respectively (figure 1a). Upon heating to 140°C, the LDH labelled as g-[Li-Al- ClO_4]-T140, showed a PXRD pattern with strong basal reflections at 8.74 Å (10.1° 2θ) and 4.37 Å (20.3° 2θ), respectively (figure 1b). Both the patterns also included a number of weak *hkl* reflections in mid- 2θ region (25–55° 2θ), which could be indexed to two-layer hexagonal cells (table 1). On cooling and rehydration (RH ~80%), a new phase was observed (g-[Li-Al- ClO_4]-RH80, figure 1c). The ingress of massive amounts of water resulted in the expansion of the basal spacing by ~3 to 11.82 Å and strong *00l* ($l = 1, 2, 3, 4, 5$) reflections are obtained. The complete absence of any *hkl* reflections is indicative of a high degree of orientation.

The b-[Li-Al- ClO_4]-ASP phase comprised two structural motifs with different degrees of hydration corresponding to basal spacings of 11.63 Å (7.6° 2θ) and 9.21 Å (9.6° 2θ), respectively (figure 2a). The difference in basal spacing of the two motifs (~2.5 Å) matches the van der Waals diameter

Figure 1. PXRD patterns of (a) g-[Li-Al-ClO₄]-ASP, (b) g-[Li-Al-ClO₄]-T140 and (c) g-[Li-Al-ClO₄]-RH80 LDH phases. In the inset, the mid-2θ region (30–65° 2θ) is expanded to show the weak reflections.

of a water molecule. The simultaneous presence of two structural motifs is indicative of the sensitivity of this phase to changes in the ambient temperature and humidity. On heating to 50°C, the 9.14 Å (9.7° 2θ) phase (b-[Li-Al-ClO₄]-T50) was

Table 1. Observed 2θ values and the corresponding indices of g-[Li-Al-ClO₄]-ASP and g-[Li-Al-ClO₄]-T140 LDHs.

g-[Li-Al-ClO ₄]-ASP		g-[Li-Al-ClO ₄]-T140	
$a = b = 5.1021 \text{ Å}$, $c = 18.3459 \text{ Å}$, $\beta = 90^\circ$, FM value = 14.14		$a = b = 5.1154 \text{ Å}$, $c = 17.4854 \text{ Å}$, $\beta = 90^\circ$, FM value = 26.5	
2θ°	hkl	2θ°	hkl
9.6	002	10.1	002
19.3	004	20.3	004
38.2	113	22.5	102
39.3	008	30.7	006
40.4	114	35.5	111
43.2	115	36.9	106
46.4	116	38.5	113
53.8	118	40.9	114
63.1	300	41.3	008
64.0	302	43.9	115
		47.3	116
		55.3	118
		62.9	300
		64.2	216

Figure 2. PXRD patterns of (a) b-[Li-Al-ClO₄]-ASP, (b) b-[Li-Al-ClO₄]-T50, (c) b-[Li-Al-ClO₄]-T100 and (d) b-[Li-Al-ClO₄]-RH80 LDH phases. The reflection marked by asterisk in each trace corresponds to unreacted bayerite.

obtained (figure 2b) and all the reflections could be indexed to a one-layer cell of monoclinic symmetry (table 2) with a non-orthogonal stacking angle, $\beta = 100.6^\circ$. Two features of the PXRD profile stand out: (i) the second basal reflection (19.4° 2θ) is followed by a broad hump, and (ii) the profile in the mid-2θ region of the PXRD pattern is similar to that of the as-prepared precursor, suggesting that the phase obtained at 50°C is structurally similar to the precursor. Heating has merely eliminated the hydrated motifs. On further heating to 100°C, a new phase (b-[Li-Al-ClO₄]-T100) was obtained with basal spacings 8.71 Å (10.2° 2θ) and 4.36 Å (20.4° 2θ) (figure 2c), respectively. A strong reflection is observed at 22.6° 2θ in the close vicinity of the second basal reflection.

All the observed reflections were indexed to a one-layer hexagonal cell with orthogonal stacking (table 2). Together with this, the broad hump seen at 50°C is eliminated. These changes were reversed on cooling to 50°C showing that features in the PXRD profile of figure 2b are structural in origin. Cooling and rehydration (RH ~ 80%) of the b-[Li-Al-ClO₄]-T100 phase resulted in a 11.7 Å phase (b-[Li-Al-ClO₄]-RH80) (table 2, figure 2d) of hexagonal symmetry. The expansion in the basal spacing by 3 Å is due to the massive ingress of water into the interlayer. This is accompanied by turbostratic disorder as shown by the weak, broad and ill-defined *hkl* reflections.

3.1 Polytype identification in g-[Li-Al-ClO₄] and b-[Li-Al-ClO₄] LDHs

The [Li-Al] LDHs comprise covalently bonded metal hydroxide layers of the composition [LiAl₂(OH)₆]⁺ (denoted by the symbol P), which are stacked one above another and bound by weak forces. The structure and symmetry of the metal hydroxide layers (layer group $p\bar{3}12/m$; $a = b = 5.12$ Å) remain invariant in the cohort of compounds with different anions. The stacking sequence of the layers varies with the molecular symmetry, size, charge and orientation of the anions in the interlayer region giving rise to the phenomenon of polytypism. A series of *DIFFaX* [18,19] simulations of the PXRD patterns were carried out to identify the stacking sequences of the metal hydroxide layers in the various phases obtained by *in situ* humidity and temperature variations. The PXRD patterns of g-[Li-Al-ClO₄]-ASP and g-[Li-Al-ClO₄]-T140 LDHs matched with the PXRD patterns simulated with a (0, 0, 1) stacking vector for a ... P P P ... stacking sequence (P: mirror image of P), compatible with a two-layer cell of hexagonal symmetry (polytype 2H) (supplementary figure S1).

Figure 3. Full-profile fits of the PXRD patterns of (a) g-[Li-Al-ClO₄]-T140 and (b) b-[Li-Al-ClO₄]-T100 obtained using code FOX. The asterisk in trace (b) corresponds to an unidentified impurity.

Table 2. Observed 2θ values and the corresponding indices of b-[Li-Al-ClO₄] LDH obtained at different temperatures and humidity.

b-[Li-Al-ClO ₄]-T50		b-[Li-Al-ClO ₄]-T100		b-[Li-Al-ClO ₄]-RH80	
$a = 5.0974$ Å, $b = 8.8258$ Å, $c = 9.2929$ Å, $\beta = 100.6^\circ$, FM value = 7.4		$a = b = 5.11$ Å, $c = 8.7041$ Å, $\gamma = 120^\circ$, FM value = 12.9		$a = b = 5.0919$ Å, $c = 11.6994$ Å, $\gamma = 120^\circ$, FM value = 10.4	
$2\theta^\circ$	<i>hkl</i>	$2\theta^\circ$	<i>hkl</i>	$2\theta^\circ$	<i>hkl</i>
9.7	001	10.2	001	7.6	001
19.4	002	20.4	002	15.1	002
20.3	−110	22.6	101	20.3	100
35.8	−131	36.7	111	21.6	101
37.6	−123	41.0	112	22.8	003
39.0	201	47.4	113	36.1	111
44.3	202	52.0	203	38.5	112
51.3	203	55.5	114	42.4	113
63.2	−331	63.0	300	47.4	203
64.1	−332	64.0	301	63.3	300
		66.9	302	63.8	301

Figure 4. Structure models of (a) g-[Li-Al-ClO₄]-T140 and (b) b-[Li-Al-ClO₄]-T100.

Table 3. Results of structure refinement in direct space obtained from code FOX.

	g-[Li-Al-ClO ₄]-T140	b-[Li-Al-ClO ₄]-T100
Molecular formula	[Li ₂ Al ₄ (OH) ₁₂](ClO ₄) ₂	[LiAl ₂ (OH) ₆](ClO ₄)
Crystal symmetry	Hexagonal	Hexagonal
Space group	<i>P</i> 6 ₃ / <i>m</i>	<i>P</i> $\bar{3}$ 1 <i>m</i>
<i>Cell parameters</i>		
<i>a</i> (Å)	5.1122	5.1156
<i>b</i> (Å)	5.1122	5.1156
<i>c</i> (Å)	17.4820	8.7656
β (deg)	90	90
<i>R</i> _{wp}	0.1465	0.1653
<i>R</i> _p	0.0460	0.1533
GoF	11.5029	3.7675

Figure 5. A schematic comparison of the packing of atoms in (a) g-[Li-Al-SO₄] LDH [13] with that in (b) g-[Li-Al-ClO₄] LDH.

Figure 6. A schematic comparison of the packing of atoms in (a) b-[Li-Al-SO₄] LDH [13] with that in (b) b-[Li-Al-ClO₄] LDH.

The PXRD patterns of all the b-[Li-Al-ClO₄] phases were simulated with $\cdots PPP \cdots$ stacking of the metal hydroxide layers. The $(2/3, 0, z)$ stacking vector yielded the PXRD pattern of b-[Li-Al-ClO₄]-T50 (supplementary figure S2). The fractional relative translation of successive layers along the a -crystallographic axis yielded a stacking angle 100.5° , which matches the $\beta = 100.6^\circ$ (table 2) of the monoclinic cell. The PXRD patterns of both b-[Li-Al-ClO₄]-T100 and RH80 phases (supplementary figure S2) could be simulated using a $(0, 0, 1)$ stacking vector. The orthogonal stacking generates a one-layer cell of hexagonal symmetry (polytype 1H) for both b-[Li-Al-ClO₄]-T100 (table 2, $c = 8.70 \text{ \AA}$) and b-[Li-Al-ClO₄]-RH80 (table 2, $c = 11.70 \text{ \AA}$) phases.

3.2 Packing of ClO₄[−] ions in the interlayer of *g*-[Li-Al-ClO₄]-T140 and *b*-[Li-Al-ClO₄]-T100 phases

Earlier work on the closely related sulphate-intercalated LDHs [13] and the reflection conditions in table 1 suggested the space group $P6_3/m$ for the two-layered *g*-[Li-Al-ClO₄]-T140 and $P\bar{3}1m$ for the one-layered *b*-[Li-Al-ClO₄]-T100 phase, respectively. LeBail fits of the PXRD patterns of the two phases were found to be satisfactory. Partial structure models were extracted for the two phases from the refined structures of *g*-[Li-Al-Cl] [20] and *b*-[Li-Al-Br] [11], respectively, and were introduced into code FOX [21]. The ClO₄[−] ion was introduced as a molecule in the interlayer region. Code FOX refines the structure in the direct space. The ClO₄[−] ion was allowed to randomly translate and rotate within the interlayer space. The structure was optimized by a Monte Carlo approach using the R -values as cost functions to secure a good fit of the observed and calculated PXRD patterns (figure 3).

In the case of *g*-[Li-Al-ClO₄]-T140, the nominal molecular formula corresponds to $[\text{Li}_2\text{Al}_4(\text{OH})_{12}](\text{ClO}_4)_2$. Of the two ClO₄[−] ions, one occupies the upper interlayer region and the other occupies the lower interlayer region in a two-layer unit cell (figure 4a). The Cl atom of the ClO₄[−] ion occupies a general position of multiplicity $12i$, which is in close proximity to the Li ions. The C_3 axis of the ClO₄[−] ion is observed to be tilted away from the stacking direction and the C_2 axis is parallel to the metal hydroxide layer. The R -values at this stage

($R_{\text{wp}} = 14.9\%$, $R_p = 4.7\%$) were found to be satisfactory (table 3). Structure refinement of *g*-[Li-Al-ClO₄]-T140 phase in the reciprocal lattice by the conventional Rietveld method was not attempted on account of the massive orientation of the crystallites. In the structure of *b*-[Li-Al-ClO₄]-T100 (nominal molecular formula $[\text{LiAl}_2(\text{OH})_6](\text{ClO}_4)$) predicted by code FOX, the ClO₄[−] ion adopts a position and orientation similar to that of the gibbsite-derived analogue (figure 4b). The R -values obtained from FOX at this stage are $R_{\text{wp}} = 16.5\%$, $R_p = 15.3\%$ (table 3).

4. Discussion

The interlayer chemistry of the ClO₄[−] ions in LDHs is of special interest due to its chemical nature. Perchlorate is a monovalent polyatomic oxoanion with Cl in its highest oxidation state (+7). Among the various oxoanions, free ClO₄[−], like SO₄^{2−}, is a spherical top molecule with T_d molecular symmetry. Both anions have a similar ionic radius ($\sim 2.4 \text{ \AA}$) [22]. The ClO₄[−] ion has small charge to size ratio and a low hydration enthalpy ($-\Delta H^\circ = 229 \text{ kJ mol}^{-1}$) compared to that of the SO₄^{2−} ion ($-\Delta H^\circ = 1059 \text{ kJ mol}^{-1}$) [23]. The hydration of monoatomic anions is well studied due to the localization of the electron density. The non-uniform distribution of charge in polyatomic anions makes their hydration more complex, where the interaction with the surrounding water differs at different sites of the anions. Computations and experiments have shown that the hydration shell of both SO₄^{2−} and ClO₄[−] ions has a spherical symmetry regardless of the orientation of the ions and the exchange dynamics. The primary difference between the two anions arises from the weaker hydrogen bonds formed by the ClO₄[−] ions with the water molecules, resulting in their higher mobility and greater exchange kinetics when compared to the SO₄^{2−} ions. In the case of the SO₄^{2−} ions, the water molecules in the first hydration shell are bonded strongly in comparison with the water molecules in the outer shells. As a result, the hydration shell and bulk water are clearly distinguished in SO₄^{2−} [24]. Given such similarities and differences in the hydration behaviour of the ClO₄[−]

anions with that of SO_4^{2-} , the g-[Li-Al- ClO_4]-T140 and b-[Li-Al- ClO_4]-T100 structure models were compared with the refined structures of the g-[Li-Al- SO_4] ($T = 100^\circ\text{C}$) [13] and b-[Li-Al- SO_4] ($T = 120^\circ\text{C}$) [13], respectively (figures 5 and 6). The comparison provides an insight into the packing of the ClO_4^- ions in the interlayer region with a volume same as that in SO_4^{2-} intercalated LDHs.

The g-[Li-Al- SO_4] ($T = 100^\circ\text{C}$) LDH phase [13] has a molecular formula $[\text{Li}_2\text{Al}_4(\text{OH})_{12}]\text{SO}_4 \cdot 3\text{H}_2\text{O}$, and the SO_4^{2-} ion is not fully deprived of its hydration sphere. The three water molecules (Ow1, Ow2 and Ow3) together fill one interlayer site of the two-layer unit cell (figure 5a). The water molecules in the interlayer region form strong H-bonds with both the layer and SO_4^{2-} ions, thereby, stabilizing the LDH structure. The g-[Li-Al- ClO_4]-T140 phase, on the other hand, is completely dehydrated due to the low hydration enthalpy of the ClO_4^- ions. The second perchlorate ion occupies the region of interlayer space occupied by the water molecules in the sulphate-LDH (figure 5b). When the sulphate LDH is completely dehydrated, the layered structure itself collapses. A similar phenomenon is observed in the interlayer of b-[Li-Al- SO_4] and b-[Li-Al- ClO_4]-T100 LDHs (figure 6).

5. Conclusions

Lithium perchlorate imbibition into both bayerite and gibbsite led to the formation of perchlorate-intercalated LDHs of Li and Al. Both the LDHs reversibly take up water molecules from the ambient humidity and exhibit basal spacing dynamics. The gibbsite-derived LDH did not undergo any polytype changes during reversible hydration. The bayerite-derived LDH underwent a 1M $\leftrightarrow$ 1H interpolytype transition during reversible hydration. In contrast with the sulphate-intercalated LDH, the perchlorate-LDH dehydrates completely at $T > 100\text{--}140^\circ\text{C}$ and the perchlorate ions occupy all the available interlayer sites.

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