Variable Temperature PXRD Studies of LiAl$_2$(OH)$_6$X·H$_2$O ($X = \text{Cl, Br}$): Observation of Disorder → Order Transformation in the Interlayer

Grace S. Thomas,† P. Vishnu Kamath,* † and S. Kannan*,‡

Department of Chemistry, Central College, Bangalore University, Bangalore 560 001, India, and Discipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals Research Institute, G.B. Marg, Bhavnagar 364 002, India

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The layered double hydroxides of Li with Al containing intercalated chloride and bromide ions (Li−Al−X; $X = \text{Cl, Br}$) crystallize with turbostratic disorder. Turbostraticity in these compounds arises not only on account of disorder in the stacking of the metal hydroxide slabs but also due to positional disorder in the interlayer. On heating to 100–275 °C, as dehydration proceeds, a disorder → order transformation is observed in the interlayer. The emergence of structural order is due to the migration of the X$^-$ ion from a position of higher site degeneracy to one of lower site degeneracy. This is facilitated by the decrease in the number density of atoms in the interlayer due to dehydration. The stacking disorders are however retained as the thermal energy is inadequate to bring about a long-range reorganization of the structure.

Introduction

The double hydroxide of Al with Li, having the general formula LiAl$_2$(OH)$_6$X·H$_2$O ($X = \text{Cl, Br}$) has been widely used in preferential ion exchange intercalation studies.$^{1,2}$ It is also a useful precursor material for the synthesis of oxides such as LiAlO$_2$, γ-Al$_2$O$_3$, and other ternary oxides of the Li$^+$−Al$^{3+}$−O$^2-$ phase diagram,$^3$ many of which are lithium ion conductors.$^4$ There are a number of studies in the literature dealing with the structure and composition of this LDH in both its pristine and anhydrous forms and on the nature of the oxide residue obtained on thermal decomposition.$^{5-9}$ It has been shown that the Li−Al LDH decomposes in two steps; the first low temperature ($\sim 125$ °C) mass loss corresponds to dehydration involving the loss of some structural water and the second high-temperature ($\sim 400$ °C) mass loss corresponds to the simultaneous dehydroxylation and deamination of the metal hydroxide slabs.$^8$ Earlier work$^{10}$ from this laboratory has further shown that the oxide residue obtained by thermal decomposition is metastable and reconstructs the original hydroxide on standing in a solution of a suitable anion.

Given the importance of the Li−Al LDH for different applications and our own continuing interest in the evolution of order, disorder, and polytypism among the layered hydroxides,$^{11-12}$ we investigated the thermal behavior of the Li−Al−X ($X = \text{Cl, Br}$) LDHs by variable temperature powder X-ray diffraction (VTXRD), with a view to understand the structural changes that take place during heat treatment.

Experimental Section

LiAl$_2$(OH)$_6$Cl·γH$_2$O (Li−Al−Cl) was prepared by soaking a freshly prepared Al(OH)$_3$ gel in a decarbonated LiCl solution containing 10 times the stoichiometric requirement of Cl$^-$ ions.$^7$ This slurry was subjected to two consecutive hydrothermal treatments in a Teflon-lined autoclave under autogenous pressure (150 °C, 24 h, 50% filling). The supernatant was replenished.
before the second hydrothermal step. For the preparation of LiAl$_2$(OH)$_6$X$_2$H$_2$O (Li−Al−Br), freshly prepared Al(OH)$_3$ was soaked in a decarbonated solution of LiBr taken 10 times in excess. The slurry was digested at 90°C for 2 days. The LiBr solution was replenished, and the soaking was continued for a further 8 days at 90°C. In each case, the product was washed, dried, and characterized by powder X-ray diffraction (PXRD).

**TABLE 1: Available Sites for Cl$^-$ and O in the P6$_3$/m Space Group**

<table>
<thead>
<tr>
<th>site</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>6h</td>
<td>0.25</td>
<td>0.3333</td>
<td>0.6667</td>
</tr>
<tr>
<td>4f</td>
<td>0.0</td>
<td>0.0</td>
<td>0.25</td>
</tr>
<tr>
<td>4e</td>
<td>0.3333</td>
<td>0.0</td>
<td>0.25</td>
</tr>
<tr>
<td>2d</td>
<td>0.6667</td>
<td>0.3333</td>
<td>0.25</td>
</tr>
<tr>
<td>2c</td>
<td>0.3333</td>
<td>0.6666</td>
<td>0.25</td>
</tr>
<tr>
<td>2a</td>
<td>0.0</td>
<td>0.0</td>
<td>0.25</td>
</tr>
</tbody>
</table>

**DIFFaX Simulations**

The stacking unit of an LDH comprises a hydroxide layer and an interlayer of intercalated anions and water molecules. The layer is described in terms of the atomic coordinates obtained from International Crystal Structure Database (hydrated Li−Al−Cl LDH: CC = 83512; anhydrous Li−Al−Cl LDH: CC = 83509; anhydrous Li−Al−Br LDH: CC = 83510). The coordinates of the symmetry related oxygen atoms of the layer are explicitly generated by the Diamond computer code and used as input data for the DIFFaX simulation. We declare the point group as unknown, and the DIFFaX code computes the point group. The details of the DIFFaX simulation$^{13,14}$ are given in our earlier work.$^{12}$

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**Figure 3.** TGA data of the pristine (a) Li−Al−Cl and (b) Li−Al−Br LDH.

**Figure 4.** PXRD pattern of the (a) pristine Li−Al−Cl LDH overlaid with its DIFFaX simulation compared with (b) the Li−Al−Cl LDH at 100°C overlaid with its DIFFaX simulation. The 002 reflection has not been included for purposes of clarity.

**Figure 5.** DIFFaX simulation of the PXRD pattern of (a) the model anhydrous Li−Al−Cl LDH and (b) the LDH at 125°C overlaid with the experimental pattern.

**Figure 6.** PXRD pattern of the Li−Al−Cl LDH at 275°C overlaid with its DIFFaX simulation.

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TABLE 2: Results of the DIFFaX Simulations of the PXRD Patterns of the Li–Al–Cl LDH

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>disorder</th>
<th>interlayer water (y)</th>
<th>layer thickness (Å)</th>
<th>Wyckoff position</th>
</tr>
</thead>
<tbody>
<tr>
<td>pristine</td>
<td>55% turbostractity + 10% 1H</td>
<td>1.0</td>
<td>∞</td>
<td>6h 6h</td>
</tr>
<tr>
<td>100 °C</td>
<td>40% turbostractity + 20% 1H</td>
<td>0.3</td>
<td>∞</td>
<td>2a,2c, 2a,2c, 2d, 2d</td>
</tr>
<tr>
<td>125 °C</td>
<td>10% turbostractive</td>
<td>0.0</td>
<td>∞</td>
<td>2a</td>
</tr>
<tr>
<td>200 °C</td>
<td>10% turbostractive</td>
<td>0.0</td>
<td>357</td>
<td>2a</td>
</tr>
<tr>
<td>275 °C</td>
<td>10% turbostractive</td>
<td>0.0</td>
<td>107</td>
<td>2a</td>
</tr>
</tbody>
</table>

O atom of the intercalated water molecule.

Results and Discussion

The structure of the Li–Al LDH is based on that of gibbsite–Al(OH)₃. The metal hydroxide slabs are stacked in the sequence AC, CA, AC, ... in gibbsite. The slab composition is [Al₆(OH)₁₈]₄⁻, where ⌒ represents an octahedral cation vacancy. The gibbsite structure is vacancy ordered. The Li–Al–X LDH is obtained by the “imbibition” of LiX by gibbsite, with Li taking the octahedral vacancy and the X⁻ ions entering the interlayer region along with water molecules. This reaction is expected to take place topochemically. In situ energy dispersive XRD (EDXRD) studies have indeed shown that the reversible liithiation of the gibbsite layer takes place by a topotactic mechanism. The mirror plane of reflection between the successive metal hydroxide slabs is retained in the LDH. In keeping with the vacancy ordered structure of gibbsite, the Li–Al–LDH is also cation ordered (space group: P6₃/m, a = 5.096 Å, c = 15.292 Å). Consequently, the oxygen atoms of the hydroxyl ions, referred to in this paper as O₁, are distributed in the (12i) sites. This disorder causes the rich polytypism observed among the more conventional Mg–Al LDHs to coalesce into a single 2H polytype. 2 stands for the number of layers in the unit cell, and H stands for the hexagonal symmetry. Corresponding to the disorder in O₁, the intercalated Cl⁻ ions and the oxygen atoms of the water molecules, referred to in this paper as O₂, are distributed in two separate sets of five different (6h) sites.

In Figure 1a is shown the PXRD pattern of the Li–Al–Cl LDH. Also shown (Figure 1b) is the DIFFaX simulated pattern expected for the reported structure of the Li–Al–Cl LDH.

The following observations are made:

1. The basal reflections, 00l( l = 2, 4) are reasonably sharp in the observed pattern and uniformly broadened (fwhm = 0.3 °2θ). They appear at the Bragg angles expected of the reported structure showing that the LDH has a periodic stacking of the metal hydroxide slabs.

2. The 100 and 300 reflections in the observed pattern appear at 20.1 and 63.2° 2θ, respectively, as expected of the reported structure and have the same fwhm (0.3 ± 0.1 °2θ) as that of the basal reflections. These reflections are characteristic of the ordering within the metal hydroxide slabs.

3. There are however significant differences between the observed and the expected patterns. The calculated pattern has a family of 11l( l = 1, 3, 4, 5, 6, 8) reflections appearing in the region 55–60° 2θ. In this region, the experimental pattern shows three nonuniformly broadened features, whose positions do not match with any of the calculated Bragg reflections. This kind of nonuniform broadening as shown in earlier papers is on account of structural disorder. Turbostratic disorder arising from loss of orientation of the metal hydroxide slabs about the stacking direction is chiefly responsible for the loss of 3-D periodicity leading to excessive broadening of the hk/0 reflections. Stacking faults can also be envisaged, the simplest being the one that destroys the plane of reflection between the successive metal hydroxide slabs. We refer to this faulted motif as 1H, as such a faulted stacking would conserve the hexagonal symmetry. Incorporation of 10% 1H stacking motifs and 55% of turbostratic disorder yields a pattern that best matches with the experimental pattern (Figure 1a).

In Figure 2 are shown the in situ VTPXRD data recorded for the Li–Al–Cl LDH over the temperature range 100–325 °C.

On equilibrating at 100 °C, the basal reflections shift to higher angles showing a decrease in the basal spacing from 7.67 Å in the pristine LDH to 7.26 Å. Such changes in the II–III LDHs are attributed to the loss of intercalated water. The loss of electron density in the interlayer region due to dehydration is also responsible for the enhancement of the intensity of the 002 reflection relative to 004, I₀₀₂/I₀₀₄, from 2.38 in the pristine LDH to 3.6. Such changes in intensity have been reported earlier among the II–III LDHs. In addition, there are significant changes in the diffraction profile in the mid-2θ region indicating considerable increase in disorder.

TGA data (see Figure 3) show a mass loss of 10% on equilibration at 100 °C. Such a high mass loss accounts for the loss of intercalated water in addition to adsorbed water.

There are two primary causes for the increase in disorder in the LDHs:

1. Additional stacking disorders induced by the displacement of metal hydroxide slabs relative to one another. Such a displacement can be induced by forces of friction and drag generated during the diffusion of intercalated species from deep within the interlayer region to the edges of the lamellae.

2. Due to the disorder in the residual intercalated species. It has already been observed that X⁻ ions and O atoms of the intercalated water occupy ten sets of (6h) sites. These provide 15 different sites in the interlayer region for the X⁻ ions, of which only one is occupied. There is another set of 15 different sites for the O atoms, of which again only one is occupied. As explained elsewhere, this high site degeneracy is on account of the mutual repulsion between the anions, combined by the needs of optimizing H-bonding interactions between the intercalated species and the metal hydroxide slabs. Quite often as in the case of the II–III LDHs, the site most favored by H-bonding considerations is not adequate to accommodate all of the intercalated atoms. In such a case, a site with a higher degeneracy is preferred. In principle therefore when the number of intercalated species is reduced, by for instance thermal dehydration, the anions can potentially migrate to new positions, better suited for H-bonding with the metal hydroxide slabs.

At 100 °C, the thermal energy is inadequate to alter significantly the stacking of the metal hydroxide slabs. Consequently, we favor the latter possibility. Within the P6₃/m space group, there are other sites (see Table 1) with a lower site degeneracy, which can potentially accommodate the X⁻ ions.

In Figure 4 is given the simulation of the PXRD pattern seen in Figure 2a obtained at 100 °C. This simulation is obtained by decreasing the water content from 1 H₂O per formula unit in the pristine LDH to 0.3 H₂O and placing this in 2a, 2c, and 2d sites. Simultaneously the Cl⁻ ion is also distributed in the 2a, 2c, and 2d sites. The stacking disorders are maintained at approximately the same incidence (40% turbostratic disorder, 20% 1H stacking fault motifs) as in the pristine LDH. The simulated and experimental patterns match satisfactorily. Also
shown is the simulation of the PXRD pattern of the pristine LDH within the same range of $2\theta$ for comparison.

On equilibration at 125°C, there is dramatic sharpening of the lines in the mid-$2\theta$ region with the emergence of prominent peaks at 24.9 and 43.5°$2\theta$ (see Figure 2b). At the same time, the 100 reflection is extinguished, although the 300 reflection retains its position and intensity. The $I_{002}/I_{004}$ is further enhanced to 4.29. The diffraction profile in general is representative of a phase with a greater amount of order. Once again, it is reasonable to assume that the thermal energies involved are inadequate to dramatically alter the stacking of the metal hydroxide slabs, and the emergence of greater structural order, if any, is due entirely to changes taking place within the interlayer. In the light of the mass loss observed at 125°C, we used the structure model of the anhydrous phase LiAl$_2$(OH)$_6$Cl (P6/mcm, $a = 5.10$ Å, $c = 14.299$ Å) for the simulation. In this structure, the Cl$^-$ ions order themselves in the 2$a$ site in the interlayer [see Figure 5a for the pattern expected of this structure]. This structure is characterized by strong reflections at 23.7 and 43.2°$2\theta$ due to the 102 and 114, respectively. These signature reflections are observed in the experimental pattern (see Figure 2b) obtained at 125°C. The pattern at Figure 2b is simulated in Figure 5b. A nominal 10% turbostratic disorder was introduced to generate the nonuniform broadening of lines in the observed pattern.

There are no further changes in the PXRD patterns up to 200°C (see Figure 2c). At 275°C (see Figure 2d), while all of the essential features simulated in Figure 5b are conserved, a slight broadening of all the peaks is observed. The observed mass loss (15.4%) at this temperature indicates the beginning of the breakdown of the layered structure. We ascribe the line broadening to a fall in the crystallite size due to mass loss taking place on the onset of decomposition. The PXRD pattern in Figure 2d is simulated by incorporating a crystallite thickness of 10.8 nm (see Figure 6).

At 325°C (see Figure 2e), the basal reflections are completely extinguished signaling the completion of the decomposition reaction (mass loss = 17.2%) and the emergence of an X-ray amorphous oxide residue from which the oxide products emerge after prolonged sintering. In Table 2 are summarized the results of all of the simulations in the Li−Al−Cl system.

The VTPXRD of the Li−Al−Br LDH in the temperature range 50–275°C is given in Figure 7. The pristine LDH is poorly ordered as compared to its chloride counterpart, as is evident from the fact that the high angle reflection 300 is completely extinguished and the 302 reflection is considerably broadened.

The PXRD pattern at 50°C was simulated by introducing 60% turbostratic disorder into the 2H polytype with the Br$^-$ present exactly above the Li atoms in the 2$a$ sites and the O atoms of water in the 6$h$ site [Figure 8a]. This is in contrast to the as-prepared Li−Al−Cl LDH where both the Cl$^-$ and O atoms of water occupy five different 6$h$ sites. The PXRD at 75°C could also be fitted to a turbostratically disordered model, but the O atoms of H$_2$O are now shifted to the 2$c$ and 2$d$ positions, while the position of the Br$^-$ ion remains unchanged (Figure 8b).

The PXRD patterns from 225 to 275°C were all found to be single layered and turbostratically disordered with particle size effects coming into play beyond 225°C. Figure 8c shows the simulation at 225°C. A summary of the DIFFaX simulations for this system is shown in Table 3.

### Conclusions

The nature of disorder in the Li−Al LDHs is rather complex. In an earlier paper, Thiel and co-workers described the structure of the Li−Al−OH LDH. The PXRD patterns reported by them were devoid of excessive and nonuniform broadening of lines and were in good representative of more ordered phases. Nevertheless, their analysis showed the incidence of extensive stacking disorders within the hexagonal structure. The fact that this disorder did not result in any diffuse scattering, enabled them to define a monoclinic cell devoid of any disorder with cell parameters related to that of the hexagonal cell.

The LDHs reported in this work, however have extensive broadening of the lines in the PXRD patterns. A new disorder model, that within the interlayer is invoked to account for the observed PXRD patterns. Cation ordering in the metal hydroxide slabs opens up the possibility of a very large number of symmetrically related sites that can potentially accommodate the interlayer atoms. The large site degeneracy is reflective of disorder in the interlayer. As the LDH is heated, the onset of dehydration causes a decrease in the number density of atoms...
in the interlayer. The consequent decrease in the repulsion between the interlayer atoms facilitates a greater degree of structural order. The ordering of atoms in the interlayer is indicated by the migration of the atoms to sites with a lower site degeneracy. The observation of a disorder → order transformation on heating is rather unexpected. We attribute this unusual behavior to the cation ordering observed in this class of compounds.

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**References and Notes**