



# Synthesis, structure refinement and chromate sorption characteristics of an Al-rich bayerite-based layered double hydroxide



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## ABSTRACT

"Imbibition" of  $\text{Zn}^{2+}$  ions into the cation vacancies of bayerite- $\text{Al}(\text{OH})_3$  and  $\text{NO}_3^-$  ions into the interlayer gallery yields an Al-rich layered double hydroxide with Al/Zn ratio  $\sim 3$ .  $\text{NO}_3^-$  ions are intercalated with their molecular planes inclined at an angle to the plane of the metal hydroxide slab and bonded to it by hydrogen bonds. Rietveld refinement of the structure shows that the monoclinic symmetry of the precursor bayerite is preserved in the product, showing that the imbibition is topochemical in nature. The nitrate ion is labile and is quantitatively replaced by  $\text{CrO}_4^{2-}$  ions from solution. The uptake of  $\text{CrO}_4^{2-}$  ions follows a Langmuir adsorption isotherm, thus showing that the hydroxide is a candidate material for green chemistry applications for the removal of  $\text{CrO}_4^{2-}$  ions from waste water. Rietveld refinement of the structure of the hydroxide after  $\text{CrO}_4^{2-}$  inclusion reveals that the  $\text{CrO}_4^{2-}$  ion is intercalated with one of its 2-fold axes parallel to the *b*-crystallographic axis of the crystal, also the principal 2 axis of the monoclinic cell.

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## 1. Introduction

$\text{Al}(\text{OH})_3$  is a layered hydroxide and comprises charge-neutral layers having the composition  $[\text{Al}_{2/3}\square_{1/3}(\text{OH})_2]$  ( $\square$ =cation vacancy). The packing of hydroxyl ions is similar to that in mineral brucite,  $\text{Mg}(\text{OH})_2$ . The cation vacancies within the metal hydroxide sheets are ordered yielding an 'a' parameter  $=\sqrt{3} \times a_0$  wherein  $a_0$  corresponds to the 'a' parameter in  $\text{Mg}(\text{OH})_2$ .

The intralayer bonding is strong ionocovalent and interlayer bonding is weak van der Waal's. As a consequence of the anisotropy in bonding, the layers can be stacked one above the other in different ways giving rise to a range of polytypes known as bayerite [1], gibbsite [2], nordstrandite [3] and doyleite [4]. The vacancies in the  $[\text{Al}_2\square(\text{OH})_6]$  layer can be filled with  $\text{Li}^+$  ions to yield positively charged layers of the composition  $[\text{Al}_2\text{Li}(\text{OH})_6]^+$ . Simultaneous incorporation of anions in the interlayer region restores charge neutrality, yielding a layered double hydroxide (LDH) of the composition  $[\text{LiAl}_2(\text{OH})_6][\text{A}^{n-}]_{1/n} \cdot y\text{H}_2\text{O}$  (A=anion) [5]. Given the diversity of polytypes in the precursor  $\text{Al}(\text{OH})_3$ , the Li-Al LDHs also crystallize in diverse structures. LDHs obtained from gibbsite crystallize in structures of hexagonal symmetry [6], while those obtained from bayerite, crystallize in structures of monoclinic symmetry [7].

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Another way of imparting a positive charge to the  $[\text{Al}_2\square(\text{OH})_6]$  layers is to insert divalent cations  $\text{M}^{2+}$  ( $\text{M}=\text{Ni}^{2+}, \text{Zn}^{2+}, \text{Co}^{2+}$ ) in half the number of available vacancies to generate layers with the composition  $[\text{M}_{0.5}\text{Al}_{2.5}\square_{0.5}(\text{OH})_6]^+$  [8]. Incorporation of anions in the interlayer region leads to layered double hydroxides having the composition  $[\text{MAl}_4\square(\text{OH})_{12}][\text{A}^{n-}]_{2/n} \cdot x\text{H}_2\text{O}$  (A=anion). For brevity, we refer to this formula with the symbol  $[\text{M}-\text{Al}_4-\text{A}]$ .

Fogg et al. [9] first synthesized the  $[\text{M}-\text{Al}_4-\text{nitrate}]$  ( $\text{M}=\text{Zn}, \text{Ni}, \text{Co}$ ) LDHs using activated gibbsite as a precursor. This novel compound had an interlayer spacing of 8.5 Å. Structure refinement of the as-prepared LDH was not attempted on account of the disorder in the intercalated nitrate ions and water molecules. Removal of intercalated water was found to introduce ordering of the nitrate ions in the interlayer. The LDH was dehydrated (175 °C, 6 h) to facilitate structure refinement. The results of preliminary structure refinement of the dehydrated LDH were provided although the powder pattern of the dehydrated LDH itself was not presented. Their work suggested the formation of metal hydroxide layers as indicated by the idealized formula. The  $\text{Zn}^{2+}$  ions and vacancies were reported to be arranged alternatively along the *c*-crystallographic axis. Subsequently we synthesized the  $[\text{Zn}-\text{Al}_4-\text{sulfate}]$  LDH starting from bayerite [10] and showed that the compound crystallized in the structure of the mineral nickelalumite [11]. In a recent paper [12], O'Hare's group have completed the refinement of the  $[\text{M}-\text{Al}_4-\text{nitrate}]$  structure whose preliminary results they had reported earlier [9]. In their later paper they present the PXRD pattern of the dehydrated LDH which reveals an interlayer spacing of 8.32 Å, showing that dehydration

does not result in any significant contraction of the interlayer spacing.

The reported structure has a few outstanding issues which have not been adequately addressed. (i) A plot of the structure using the reported atomic coordinates appears to contain face sharing as well as corner sharing octahedra which are chemically not expected. (ii) Prolonged heating at 175 °C could induce the migration of  $Zn^{2+}$  ions from octahedral to tetrahedral sites which vitiates the choice of the structure model. (iii) There appear systematic residual intensities in the difference profile after the final stage of the refinement, that indicates that not all the electron density is accounted for. (iv) The detailed interlayer structure namely, the mode of coordination and nature of ordering of the nitrate ions is also not fully described.

While the domain of possible polytypes that may result from a layer of a particular symmetry may be arrived at by the structural synthon approach [13], polytype selection under a given set of experimental conditions is governed by a number of other factors which include the molecular symmetry of the intercalated anion, its mode of coordination and its capacity to make hydrogen bonds with the metal hydroxide layer. It is therefore important to gain an understanding of the packing of atoms in the interlayer gallery. In this paper we refine the structure of the as-prepared [Zn–Al4–nitrate] LDH including that of the interlayer. We also exchange the nitrate ion for chromate ions from solution, refine the structure of the [Zn–Al4–chromate] LDH and carry out sorption studies.

## 2. Experimental

[Zn–Al4–nitrate] LDH was prepared by soaking 0.5 g of bayerite in ~6.5 M (40 mL)  $Zn(NO_3)_2$  solution and hydrothermally treating the suspension in a Teflon lined autoclave (50% filling) at 150 °C for 24 h. The products were washed 4–5 times with distilled water, once with isopropanol and then dried in an air oven at 65 °C.

Anion exchange of the intercalated nitrate for chromate ions from solution was carried out by suspending 0.2 g batches of the LDH in 30 mL of a solution containing 10 times the stoichiometric requirement of chromate, taken in the form of the  $K_2CrO_4$ . The reaction was carried out for 24 h with stirring after which the solid was separated by centrifugation and washed with deionized water.

### 2.1. Chromate uptake studies

Pre-weighed (0.20 g) batches of the LDH were suspended in 25 mL of 1 M  $KNO_3$  solution made up to 0.008–0.1 M (pH 8.5–9.0) in chromate ions taken in the form of  $K_2CrO_4$ . In this way, the ionic strength of the solution was kept nearly constant to maintain equilibrium conditions required for Langmuir adsorption. The slurry was stirred for 24 h at the ambient temperature (24–26 °C) after which it was centrifuged and the chromate concentration of the centrifugate was determined by means of potentiometric titration versus standard (0.025–0.1N) ferrous ammonium sulfate (FAS) solution. For lower chromate concentrations ( $\leq 0.025$  M), a larger volume (50–500 mL) of the  $K_2CrO_4$  solution was used to affect the chromate uptake. The chromate uptake by the LDH was calculated from the difference in the initial and final chromate concentrations and is reported in moles of chromate uptake per gram of LDH taken. The isotherm was used to obtain a Langmuir plot.

### 2.2. Characterization

All samples were characterized by powder X-ray diffraction (Bruker D8 Advance Diffractometer, Cu  $K\alpha$  radiation,  $\lambda = 1.5418$  Å, reflection geometry). Data were collected at a continuous scan rate of

$1^\circ 2\theta \text{ min}^{-1}$  and a step size of  $0.02^\circ 2\theta$ . For Rietveld refinement, data were collected over  $5\text{--}100^\circ 2\theta$  (step size  $0.02^\circ 2\theta$ , 10 s  $\text{step}^{-1}$ ).

Rietveld refinement was carried out using the GSAS software package [14] using the structure of nickelalumite as the model to describe the metal hydroxide layer. The atomic coordinates of interlayer atoms were found using the program FOX [15]. For refinement, a TCH-pseudo-Voigt line shape function (Profile Function 2) with eight variables was used to fit the experimental profile. A cosine Fourier series function with eight terms was used to refine the background. Bond distance restraints were imposed on Al–O ( $1.940 \pm 0.05$  Å) and Zn–O ( $2.050 \pm 0.05$  Å) bonds to enable stable refinement. The relative weights of these restraints were reduced as the refinement progressed.

IR spectra were recorded using a Bruker Alpha-P FTIR spectrometer (ATR mode,  $400\text{--}4000 \text{ cm}^{-1}$ ,  $4 \text{ cm}^{-1}$  resolution). The LDH composition was determined by a combination of chemical and instrumental methods.  $Al^{3+}$  content was estimated gravimetrically as  $Al_2O_3$ . The divalent metal ion content was estimated by Atomic Absorption Spectroscopy (Varian Model AA240 atomic absorption spectrometer). The nitrate content of the LDH was determined by ion chromatography (Metrohm Model 861 Advanced Compact Ion Chromatograph fitted with a Metrosep A SUPP5 anion column and conductivity detector). The chromatograph was calibrated using standard solutions prepared from AR grade  $NaNO_3/K_2CrO_4$  reagents (Aldrich Chemical Co., USA). The layer charge estimated on the basis of the  $[Al]/[Zn]$  ratio is found to match with the nitrate content estimated by ion chromatography. The unaccounted mass after accounting for the metal, nitrate and hydroxyl contents is attributed to intercalated water (see Table 1). The total mass loss expected for this composition is verified by thermogravimetry analysis (Mettler Toledo TG/SDTA Model 851<sup>e</sup> system,  $30\text{--}800$  °C, heating rate  $5^\circ \text{ min}^{-1}$ , flowing air).

Diffused reflectance UV–vis absorption spectra were obtained using a Shimadzu ISR-3100 UV–vis–NIR scanning spectrophotometer. The spectra were recorded from 200–800 nm.

## 3. Results and discussion

### 3.1. Structure of the [Zn–Al4–nitrate]LDH

Layered hydroxides, on account of anisotropy in bonding, often exhibit poor crystallinity and crystallize with varying proportions of stacking faults, which lead to extensive broadening of the reflections in the PXRD patterns of these materials. Single crystals of these materials are rare and obtainable only from mineral sources. Laboratory synthesized materials crystallize as polycrystalline powders. Refinement of the structures of the layered double hydroxides therefore poses a considerable challenge. The PXRD pattern of [Zn–Al4–nitrate] (Supporting information, SI. 1 and 2), however, exhibits sharp reflections and can be indexed on the basis of a monoclinic cell belonging to the  $P12_1/n1$  space group ( $a = 10.2917(3)$  Å,  $b = 8.9211(6)$  Å,  $c = 17.1612(6)$  Å,  $\beta = 95.2^\circ$ ).

A successful structure refinement is contingent upon the selection of a suitable structure model. An LDH comprises two

**Table 1**  
Results of wet chemical analysis and TGA data.

Sample	Al/Zn ratio	$A^{n-}/Zn$ ratio	% mass loss from TGA	Approx. composition of sample
Zn–Al– $NO_3$ LDH	2.96	1.2	48.3	$[Zn_{0.207}Al_{0.0612}(OH)_2][NO_3]_{0.25} \cdot 0.74H_2O$
Zn–Al– $CrO_4$ LDH	2.96	0.59	43.7	$[Zn_{0.207}Al_{0.0612}(OH)_2][CrO_4]_{0.122} \cdot 1.29H_2O$

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