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Article

# New Attempts to Synthesize Layered Double Hydroxides Intercalated with $SO_4^{2-}$/$Cs^+$ Using Co-Precipitation and Exchange Reactions

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Layered double hydroxides (LDHs) with the compositions $(Cs^+/NH_4^+)_{0.111}[M^{2+}_{0.667}Al_{0.333}(OH)_{2.0}(SO_4)_{0.222}]$ ($M^{2+}$ = Mn, Zn) and basal distance of ca. 11 Å were obtained by co-precipitating Mn/Al and Zn/Al sulfate salts with aqueous $NH_3$, using excess of $Cs_2SO_4$. $[Mn_{0.667}Al^{3+}_{0.333}(OH)_2]Cl_{0.333}{\cdot}nH_2O$ and $[M^{2+}_{0.667}Al^{3+}_{0.333}(OH)_2](NO_3)_{0.333}{\cdot}nH_2O$ ($M^{2+}$ = Mn, Zn) were also synthesized by co-precipitation, presenting respective basal distances of 8.92 and 7.92 Å. After applying exchange reactions with excess of $Cs_2SO_4$, materials with basal distances of ca. 11 Å were obtained, indicating the exchange of chloride and nitrate with sulfate, without incorporation of $Cs^+$. When $Na^+_{0.111}[M^{2+}_{0.667}Al_{0.333}(OH)_{2.0}(SO_4)_{0.222}]$($M^{2+}$ = Mn, Zn) obtained by co-precipitation and having basal distances of ca. 11 Å was exchanged with excess of $Cs_2SO_4$, the content of sulfate remained constant and $Na^+$ was partially replaced with $Cs^+$, but the amount was lower, indicating the probable composition $(Na^+/Cs^+)_y[M^{2+}_{0.667}Al_{0.333}(OH)_{2-y}(SO_4)_{y/2}(SO_4)_{0.222-(y/2)}]$($M^{2+}$ = Mn, Zn), where some of the hydroxide anions were replaced with grafted $SO_4^{2-}$.

**Keywords:** layered double hydroxide, intercalation, exchange reactions, sulfate, cesium

## Introduction

The removal of radioactive nuclides from contaminated waters is an important topic of research, especially after the Fukushima Daiichi nuclear power plant accident in 2011, which released large amounts of radioactive nuclides into the environment, especially the dangerous radioactive nuclide $^{137}Cs$. Several methods of cesium intercalation in layered materials have been reported in the literature, such in graphite,[1] 2H-$NbS_2$,[2] C-60,[3] 1T-$TaSe_2$,[4] manganese thiophosphate,[5] clay minerals,[6] 1T-$MoS_2$,[7] sulfate green rusts ($GR_{SO4}$) with the formula $NaFe^{II}_6Fe^{III}_3(SO_4)_2(OH)_{18}{\cdot}12H_2O$[8] clay minerals from the smectite group,[6] and other clay minerals,[9-11] but to the best of our knowledge, none of them have reported the intercalation of cations in layered double hydroxides (LDH), especially due to the fact that LDHs are typically anion exchangers.

Traditional LDH with the chemical composition $[M^{2+}_{1-x}M^{3+}_x(OH)_2](A^{n-})_{x/n}{\cdot}nH_2O$ are natural minerals and synthetic materials derived from the brucite-like structure ($Mg(OH)_2$), in which $M^{2+}$ octahedrally coordinated to six $OH^-$ anions share edges to form two-dimensional layers that are stacked in the basal direction. In the LDH structure, $M^{2+}$ cations in the brucite-like structure are partially replaced by $M^{3+}$ and the excess positive charges of the layers are compensated by the intercalation of normally hydrated $A^{n-}$ anions.[12-20]

Recently, it has also been reported that LDHs can be obtained with the chemical composition $(D(H_2O)_6)[M^{2+}_6Al_3(OH)_{18}(SO_4)_2]{\cdot}6H_2O$ ($D^+$ = Li, Na or K and $M^{2+}$ = Mn, Zn, Mg, Co, Ni, Cu). These compounds were intercalated with hydrated sulfate anions, alkali metal cations and ammonium.[21-24] Although the synthetic phases involved the intercalation of $Li^+$, $Na^+$, $K^+$ and $NH_4^+$, the minerals containing $M^{2+}/Al^{3+}$ in the molar ratio of 2:1 were reported only with the intercalation of $Na^+$ (natroglaucocerinite-$M^{2+}$ = Zn; shigaite-$M^{2+}$ = Mn and motukoreaite-$M^{2+}$ = Mg).[25-28] Other phases have also been reported with the compositions $Fe^{2+}/Fe^{3+}$, like nikischerite and sodium sulfate green rusts.[8,29,30] In fact, nikischerite and sulfate green rusts have the same composition $[NaFe^{2+}_6Fe^{3+}_3(SO_4)_2(OH)_{18}{\cdot}(H_2O)_{12}]$ and also similar lattice parameters (nikischerite: a = b = 9.347 Å, c = 33.00 Å and sulfate green rust: a = b = 9.258 Å, c = 10.968 Å), but they occur in different polytypes, which differ only in the number of stacked layers in the unit cell.[29-31]

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Only sulfate green rusts have $Cs^+$ and $Rb^+$ intercalated together with sulfate anions,[8] but washing of the materials with water indicated that $Na^+$ and $K^+$ were not affected, while $Rb^+$ and $Cs^+$ were leached out of the structure, with the corresponding reduction of the amount of intercalated sulfate and the basal distance. The reaction can be probably formulated as described in equation 1, when the cesium sulfate green rusts are converted into regular LDH.

$$(Cs^+)Fe_6^{2+}Fe_3^{3+}(SO_4)_2(OH)_{18} \rightarrow Fe_6^{2+}Fe_3^{3+}(SO_4)_{1.5}(OH)_{18} + \tfrac{1}{2}Cs_2SO_4 \quad (1)$$

Due to the possibility to extend the broad range of applications of LDH, especially related to the possibility to remove radioactive $Cs^+$ from contaminated solutions and the lack of data about the intercalation of $Cs^+$ in LDH/$SO_4$, the objective of the present work is to describe attempts to synthesize and characterize Zn/Al and Mn/Al LDH containing $SO_4^{2-}$/$Cs^+$, obtained by co-precipitation at increasing pH and exchange reactions.

## Experimental

The synthesis of $Mn_2Al$:Cl, $Mn_2Al$:$NO_3$ and $Zn_2Al$:$NO_3$ phases was performed as recently reported.[21] Briefly, LDH containing $M^{2+}$:Al with molar ratios of 2:1 were synthesized by co-precipitation with increasing pH using an automatic glass titration reactor operating at 90 °C, under $N_2$ flow, to avoid contamination with carbonate, where the pH was controlled by an internal pHmeter. A 100 mL solution of $MnCl_2/AlCl_3$, $Mn(NO_3)_2/Al(NO_3)_3$ or $Zn(NO_3)_2/Al(NO_3)_3$ were prepared with Milli-Q water and slowly titrated with a solution of NaOH 1 mol $L^{-1}$, until attaining the desired pH. In the absence of CsOH to perform the co-precipitation, the $M^{2+}{}_2Al$:$SO_4$/Cs ($M^{2+}$ = Mn, Zn) samples were also synthesized by adding aqueous $NH_3$ 1 mol $L^{-1}$ solutions to 200 mL solutions of $M^{2+}SO_4$ ($M^{2+}$ = Mn, Zn), $Al_2(SO_4)_3$ and $Cs_2SO_4$ prepared with Milli-Q water, with $M^{2+}$:Al metal molar ratios of 2:1 using an excess of $Cs_2SO_4$ (Table 1).

All the chemicals were of analytical grade and used without any treatment: $Al_2(SO_4)_3.16H_2O$ 98-102%, NaOH 99%, $Al(NO_3)_3{\cdot}9H_2O$ 98.50%, $Mn(NO_3)_2{\cdot}4H_2O$ 98%, $Li_2SO_4{\cdot}H_2O$ 99%, $ZnSO_4{\cdot}7H_2O$ 99% and NaCl 99.85% were from Reatec (São Paulo, Brazil); $AlCl_3{\cdot}6H_2O$ 99.50%, $MnCl_2{\cdot}4H_2O$ 98-101%, $ZnCl_2$ Vetec 97% and $Zn(NO_3)_2{\cdot}6H_2O$ 99% were from Vetec (Rio de Janeiro, Brazil); $LiOH{\cdot}H_2O$ Biotec 98% (São Paulo, Brazil); $Na_2SO_4$ Neon 99.9% (São Paulo, Brazil); $NaNO_3$ F. Maia 99%; (São Paulo, Brazil); Aqueous $NH_3$ Quimex 28-30% (Minas Gerais, Brazil); $MnSO_4{\cdot}H_2O$ Alphatec 98-101% (Rio de Janeiro, Brazil); $Cs_2SO_4$ Merck 99.9% (Darmstadt, Germany).

After precipitation, the resulting slurries were ripened at 90 °C for 5 days in closed Erlenmeyer flasks, and separated by centrifugation at 4,000 rpm for 5 min (centrifugal force of 2,125 g), with the process being repeated after redispersing the slurry with an ultrasound bath for several seconds.[22] The samples were dried at room temperature. The $M^{2+}{}_2Al$:$SO_4$/Na, $M^{2+}{}_2Al$:$NO_3$ ($M^{2+}$ = Mn, Zn) and $Mn_2Al$:Cl samples were synthesized as previously reported.[21,22]

In the exchange reactions, the phases $Mn_2Al$:$SO_4$/Na, $Zn_2Al$:$SO_4$/Na, $Mn_2Al$:$NO_3$, $Zn_2Al$:$NO_3$ and $Mn_2Al$:Cl were dispersed in Milli-Q water containing excess of $Cs_2SO_4$ (three times the sulfate in relation of nitrate and chloride and three times in relation to sodium), and the mixtures were gently stirred for 7 days under $N_2$ flow at room temperature. The same procedure was used in the centrifugation washing and drying process of the other samples. In all exchanged samples, the pH was kept almost constant and close to neutral (in the range of 6.7 to 7.7).

The synthesized compounds were characterized by X-ray diffraction (XRD) using a Shimadzu XRD-6000 diffractometer (Kyoto, Japan). After aging and the last centrifugation step, drops of the slurry were deposited on glass sample holders and dried at room temperature. The analyses were performed using Cu Kα = 1.5418 Å

**Table 1.** Amount of chemicals used and pH control during the LDH syntheses

| Compound | $M^{2+}SO_4$ / mmol | $Al_2(SO_4)_3$ / mmol | $D_2SO_4$ / mmol | Initial pH | Final pH |
|---|---|---|---|---|---|
| $Zn_2Al$:$SO_4$/Cs | 14.700 | 3.675 | 3.650 | 3.54 | 9.48 |
| $Mn_2Al$:$SO_4$/Cs | 15.493 | 3.873 | 3.871 | 3.89 | 8.98 |
| $Mn_2Al$:$SO_4$/Na | 26.186 | 6.551 | 2.188 | 3.43 | 9.06 |
| $Zn_2Al$:$SO_4$/Na | 24.783 | 6.418 | 2.007 | 3.46 | 9.51 |
| Compound | $M^{2+}B_2$ / mmol | $AlB_3$ / mmol | NaB / mmol | Initial pH | Final pH |
| $Mn_2Al$:$NO_3$ | 24.922 | 12.448 | 4.168 | 3.07 | 9.06 |
| $Mn_2Al$:Cl | 27.372 | 13.714 | 4.560 | 3.15 | 9.11 |
| $Zn_2Al$:$NO_3$ | 31.071 | 15.509 | 5.179 | 2.88 | 9.31 |

$M^{2+}$ = Mn or Zn; D = $Na^+$ or $Cs^+$; B = $NO_3^-$ or $Cl^-$.

radiation, tension of 40 KV and current of 30 mA, with a dwell time of 2° $min^{-1}$.

The samples were also characterized by Fourier transform infrared (FTIR) spectroscopy using a Bruker Vertex 70 spectrophotometer (Karlsruhe, Germany). KBr pellets containing around 1% (m/m) of LDH were gently mixed and pressed at 10 tons and the spectra were collected in transmission mode by accumulating 32 scans in the region of 400-4000 $cm^{-1}$, using resolution of 2 $cm^{-1}$.

Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDS) data of some precursors were obtained with a Tescan Vega3LMU microscope (Brno-Kohoutovice, Czech Republic) with an AZ Tech software. The sample dispersions in water were dripped on copper tapes and after EDS measurements, the samples were sputtered with a thin gold layer to obtain the SEM images.

The quantitative analyses of the metals and sulfur (relative to $SO_4^{2-}$) used to formulate the samples' chemical composition were performed with a Thermo Scientific model iCAP 6500 inductively coupled plasma optical emission spectrometry (ICP-OES) (Waltham, United States) after dissolving the samples in 1.0% v/v of $HNO_3$ in Milli-Q water. The data were collected in triplicate, treated with the Thermo Scientific iTeVa software version 1.2.0.30 and average values were used to obtain the LDH compositions.

## Results and Discussion

In general, during exchange reactions, the layer lattice parameters remain almost constant while the basal parameter is normally dependent on the size of the intercalated cations and/or anions. During these reactions, it is also common for interpolytype transitions to occur due to the re-ordering of the layer stacking sequence. However, this seems not to be the case of exchange reactions of $(D_1^+)[M^{2+}_6Al_3(OH)_{18}(SO_4)_2]$ to $(D_2^+)[M^{2+}_6Al_3(OH)_{18}(SO_4)_2]$ ($D_1^+$ and $D_2^+$ = alkali metal cations), since the basal distance is obtained by the combination of different factors: the hydrated sulfate size in the form of a double layer; the size of the hydrated alkali metal cations with variable numbers of water molecules in the first hydration shell; and also to the interactions of sulfate with the alkali metal, water molecules and both with the layers having different compositions.

The samples $Mn_2Al:SO_4/Cs$ (Figure 1Aa) and $Zn_2Al:SO_4/Cs$ (Figure 1Ab) obtained by co-precipitation presented, respectively, basal distances of 11.36 and 10.91 Å. $Zn_2Al:SO_4/Cs$ (Figure 1Ab) also was slightly contaminated with compounds having a basal distance of 8.9 Å, exactly the same impurity observed when $Zn_2Al:SO_4/NH_4$ was prepared,[24] attributed probably to the intercalation of dehydrated sulfate.[32,33]

The values of the prevalent compounds are slightly bigger than those obtained for the $Mn_2Al:SO_4$ phases intercalated with sodium (11.02-11.03 Å) and potassium (11.27-11.28 Å) and slightly smaller than those observed for $Zn_2Al:SO_4$ phases intercalated with sodium (11.22-11.14 Å) and potassium (11.40 Å). Both values are consistent with the intercalation of sulfate in double layer arrangement and a single layer of hydrated $Cs^+$ and $NH_4^+$, as observed for other alkali metal cations.[24]

An expansion of the XRD pattern of $Mn_2Al:SO_4/Cs$ (Figure 1Aa, insert) presents the (100; d = 4.80 Å) and (101; d = 4.42 Å) diffraction peaks, which correspond to an $a = a'\sqrt[3]{}$ superlattice, common for LDH with $2M^{2+}:M^{3+}$ molar ratios intercalated with different anions and also observed in LDH intercalated with sulfate and alkali metal cations,[21,22] attributed to the ordering of metal cations in the layers. The cell parameters were calculated and found to be a = b = 5.54 Å and c = 11.36 Å with average distance between the metals of a' = 3.20 Å, very close to a' = 3.171 Å observed in the sodium shigaite structure.[28] The same was not observed for $Zn_2Al:SO_4/Cs$ due to the overlapping of the second peak of the 8.9 Å phase, in the same region.

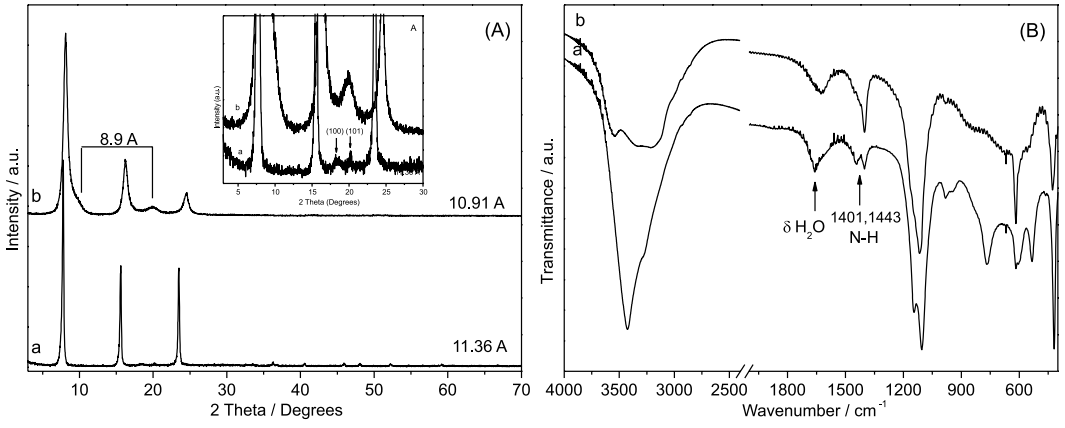


**Figure 1.** XRD patterns (A) and FTIR spectra (B) of $Mn_2Al:SO_4/Cs$ (a) and $Zn_2Al:SO_4/Cs$ (b) obtained by co-precipitation with increasing pH.

Although the a = a'$\sqrt[3]{}$ × a$\sqrt[3]{}$' superstructure is also observed in synthetic LDHs intercalated with sulfate and alkali metal cations,[21,22] natural LDHs intercalated with sulfate and alkali metal cations present the superstructure a = 3a' × 3a', which correspond to the ordering of the metal cations and/or sulfate anions between the layers.[28-32] These superstructure differences are probably associated with the sizes of the crystals and corresponding long and short-range order/disorder in synthetic and natural LDH. Since the basal distances are similar, the hydration shell of the intercalated alkali metal cations and ammonium should be different from those observed in solution, being respectively tetrahedral and octahedral for $Li^+$, octahedral for $Na^+$, square antiprismatic for $K^+$ and $Rb^+$, probably 12-coordinated for $Cs^+$ [34] and not well established for $NH_4^+$, for which the number of water molecules in the hydration shell ranges from 4 to 6.[35,36]

The average thicknesses of the particles along the basal axis and the respective number of stacked layers were calculated by the Scherrer equation using the first basal peak. The data correspond to 13.5 and 41 nm, respectively, for $Mn_2Al:SO_4/Cs$ and $Zn_2Al:SO_4/Cs$, which corresponds to 12 and 36 stacked layers, respectively.

The presence of ammonium was inferred since the precipitation was conducted with aqueous $NH_3$ instead of CsOH, so no other cations were available in the alkaline solution to explain the higher content of sulfate anions. Although hydrated $SO_4^{2-}$ and $NH_4^+$ were intercalated between the layers, the basal distance was only slightly affected in comparison to the other sulfate/alkali metal cations.

The FTIR spectra of $Mn_2Al:SO_4/Na$ (Figure 1Ba) and $Zn_2Al:SO_4/Na$ (Figure 1Bb) indicated the presence of typical stretching vibration bands of hydroxyl groups and water molecules in the region of 3430 $cm^{-1}$, sulfate bands and M–O and M–OH bands below 600 $cm^{-1}$ and a band in the region of 770-790 $cm^{-1}$. The absorption band in the region of 1620 $cm^{-1}$ is attributed to the bending vibration of water molecules.[21-24,37]

Due to different compositions and metals involved in the structure, the FTIR bands attributed to M–O and M–OH bonds were observed at 419, 534 and 767 $cm^{-1}$ for $Mn_2Al:SO_4/Cs$ (Figure 1Ba), while only two bands, at 427 and 617 $cm^{-1}$, were observed for $Zn_2Al:SO_4/Cs$ (Figure 1Bb). This absence can be attributed to the mixture of phases and low crystallinity of $Zn_2Al:SO_4/Cs$ in comparison with $Mn_2Al:SO_4/Cs$. The sulfate bands in distorted tetrahedral symmetry also changed positions, being observed as a broad band at 1116 and 617 $cm^{-1}$ for $Zn_2Al:SO_4/Cs$ (Figure 1Bb) and at 1145, 1105, 981, 617 and 606 $cm^{-1}$ for $Mn_2Al:SO_4/Cs$ (Figure 1Ba). The presence of typical N–H bending vibration bands with low-symmetry ammonium was detected by FTIR in both samples at 1401 and 1443 $cm^{-1}$, along with a low-intensity O–H overlapping band in the region of 3000-3700 $cm^{-1}$.[24,35,38] The band splitting in the region of 1400 $cm^{-1}$ is probably related to hydrogen bonding occurring between $NH_4^+$ ions and $H_2O$ molecules and interactions with the negatively charged layers $[M^{2+}_6Al_3(OH)_{18}(SO_4)_2]^-$. In solid $NH_4Cl$, the band in the region of 1400 $cm^{-1}$ is attributed to symmetric deformation mode $\nu_4$ of tetrahedral ammonium symmetry,[39,40] and this band was also observed at 1450 $cm^{-1}$ when $NH_4^+$ was in solution.

The composition of the synthesized sample (Table 2) indicated that the observed values for the $M^{2+}$ and $M^{3+}$ metals in $Zn_2Al:NO_3$, $Mn_2Al:NO_3$ and $Mn_2Al:Cl$ were almost identical to the expected ideal formulas $[M^{2+}_{0.667}Al^{3+}_{0.333}(OH)_2](A^-)_{0.333}\cdot nH_2O$, according to the proportions used during the synthesis procedures (Table 1), with the exception of $Zn_2Al:SO_4/Cs$, which indicated a slightly higher content of $Al^{3+}$, due to the presence of impurities (Figure 1Ab) (0.372 instead of 0.333).

The same observation occurred after the exchange reaction of $Zn_2Al:SO_4/Na$ with $Cs_2SO_4$ (0.367 instead of 0.333). The chemical composition of the phases $Zn_2Al:SO_4/Cs$ and $Mn_2Al:SO_4/Cs$ obtained by direct synthesis also indicated the correct proportions of $M^{2+}$ and $M^{3+}$ and sulfur from sulfate for the ideal composition $Cs^+_{0.111}[M^{2+}_{0.667}Al_{0.333}(OH)_2](SO_4)_{0.222}$, but the content of cesium was lower than predicted.

Although not quantified, this difference can be attributed to $NH_4^+$, as indicated by FTIR (Figure 1Ba,b), since the precipitation was conducted in the presence of aqueous $NH_3$ and $NH_4^+/SO_4^{2-}$. Intercalated LDH have already been reported in the literature, having similar basal distances.[24] These compositions are proposed to be $(Cs_{0.111-x}NH_4^+{}_x)[M^{2+}_{0.667}Al_{0.333}(OH)_2](SO_4)_{0.222}$.

The reduced content of intercalated $Cs^+$ and $Rb^+$ have already been reported for sulfate green rusts ($GR_{SO4}$), having chemical composition close to $D^+Fe^{II}_6Fe^{III}_3(SO_4)_2(OH)_{18}\cdot 12H_2O$ ($D^+$ = Na, K, Rb, Cs),[8] while rinsed samples of intercalated cesium were observed to have smaller basal distance (10.85 Å) than sodium (10.96 Å) and potassium (11.20 Å), in spite of the bigger ionic radius of the first. A single washing step was sufficient to remove all intercalated $Cs^+$ from $GR_{SO4}$, and only a double layer of sulfate was retained.[8] This behavior was not observed in our samples, in which cesium was still observed despite being washed twice, indicating a stronger interaction with the LDH layers.

In the attempt to exchange $Na^+$ from $Mn_2Al:SO_4/Na$ and $Zn_2Al:SO_4/Na$ with $Cs^+$, again the content of $Cs^+$ plus

**Table 2.** Composition of the samples obtained by ICP-OES analyses

| Sample | $M^{2+}$ 0.667[a] | $Al^{3+}$ 0.333[a] | $B^-$ 0.333[a] | $Na^+$ 0.00[a] |
|---|---|---|---|---|
| $Zn_2Al:NO_3$ | 0.665 | 0.335 | n.e. | 0.00 |
| $Mn_2Al:NO_3$ | 0.670 | 0.330 | n.e. | 0.00 |
| $Mn_2Al:Cl$ | 0.662 | 0.338 | n.e. | 0.00 |
| Sample | $M^{2+}$ 0.667[b] | $Al^{3+}$ 0.333[b] | $SO_4^{2-}$ 0.222[b] | D = $Na^+$, $Cs^+$ or $NH_4^+$ 0.111[b] |
| $Zn_2Al:SO_4/Cs$ | 0.628 | 0.372 | 0.246 | 0.023 (0.088[c]) |
| $Mn_2Al:SO_4/Cs$ | 0.646 | 0.354 | 0.242 | 0.014(0.097[c]) |
| $Mn_2Al:SO_4/Na$ | 0.661 | 0.339 | 0.223 | 0.121 |
| $Zn_2Al:SO_4/Na$ | 0.645 | 0.355 | 0.217 | 0.099 |
| $Mn_2Al:SO_4/Na$-Cs | 0.660 | 0.340 | 0.220 | Na = 0.015; Cs = 0.036 |
| $Zn_2Al:SO_4/Na$-Cs | 0.633 | 0.367 | 0.239 | Na = 0.067; Cs = 0 |
| Sample | $M^{2+}$ 0.667[d] | $Al^{3+}$ 0.333[d] | $SO_4^{2-}$ 0.167[d] | D = $Na^+$, $Cs^+$ or $NH_4^+$ 0.00[d] |
| $Mn_2Al:NO_3/Cs$ | 0.659 | 0.341 | 0.167 | 0.027 |
| $Zn_2Al:NO_3/Cs$ | 0.663 | 0.337 | 0.146 | 0.000 |
| $Mn_2Al:Cl/Cs$ | 0.667 | 0.333 | 0.150 | 0.025 |

[a]Expected value of $[M^{2+}_{0.667}Al^{3+}_{0.333}(OH)_2](B^-)_{0.333}\cdot nH_2O$ ($B^- = NO_3^-$ or $Cl^-$). [b]Expected values of $D_{0.111}[M^{2+}_{0.667}Al_{0.333}(OH)_2](SO_4)_{0.222}$. [c]Predicted content of $NH_4^+$; D = $Na^+$, $Cs^+$ or $NH_4^+$. [d]Expected values of $[M^{2+}_{0.667}Al_{0.333}(OH)_2](SO_4)_{0.167}$. n.e.: not evaluated.

$Na^+$ did not have the expected value, and the content of sulfate was again higher, suggesting the maintenance of the original composition $D^+_{0.111}[M^{2+}_{0.667}Al_{0.333}(OH)_2](SO_4)_{0.222}$. $HSO_4^-$ is not expected at neutral and slightly alkaline pH,[41] since this would increase the amount of sulfur in the samples and the absence of other cations in solution, an alternative is to consider that part of the alkali metal cations was replaced with hydrated protons. However, this hypothesis is unlikely since the pH of the exchange solution was neutral or slightly alkaline.

The second possibility is the adsorption of sulfate on the protonated hydroxide anions of the particles' surface through $-OH_2^+(SO_4^{2-})_{0.5}$.[41] However, it is highly unlikely that the exact amount proposed in the ideal formula $D^+_{0.111}[M^{2+}_{0.667}Al_{0.333}(OH)_2](SO_4)_{0.222}$ would be obtained.

A third and more feasible hypothesis is the grafting of sulfate, as observed in layered hydroxide salts like sodium gordaite ($NaZn_4(OH)_6(SO_4)Cl.6H_2O$),[42,43] where part of the structural hydroxide anions is replaced and grafted with chloride and sulfate, generating negatively charged layers $[Zn_4(OH)_6(SO_4)Cl]^-$, whose charges are compensated by the intercalation of $Na^+$ cations. Although bereft of alkali metal cations, layered double hydroxides with the proposed grafting mechanism have similar structures to spangolite ($Cu_6Al(OH)_{12}(SO_4)Cl\cdot 3H_2O$)[44] and jamborite ($Ni^{2+}_{1-x}Co^{3+}_x(OH)_{2-x}(SO_4)_x\cdot nH_2O$),[45] where the $SO_4^{2-}$ tetrahedra are grafted to the layer, partially replacing surface $OH^-$. Using the structures of jamborite (where sulfate is grafted to the layers) and zincowoodwardite ($[Zn_{1-x}Al_x(OH)_2][(SO_4)_{x/2}\cdot nH_2O$)[46] (where sulfate is only intercalated) as examples, and with x = 0.333, the formulas would be $Ni^{2+}_{0.667}Co^{3+}_{0.333}(OH)_{1.667}(SO_4)_{0.333}\cdot nH_2O$ and $Zn_{0.667}Al^{3+}_{0.333}(OH)_2(SO_4)_{0.167}\cdot nH_2O$.

In jamborite, the content of sulfate would double in relation to zincowoodwardite while the $M^{2+}$:$M^{3+}$ ratio would be the same (2:1). Grafting of sulfate and carbonate has even been observed in single hydroxides, as is in the case of paraotwayite ($Ni(OH)_{2-x}(SO_4,CO_3)_{x/2}$)[47] and was also in LDH intercalated with dehydrated sulfate.[32,33] Hence, it would not be surprising to find this pattern in LDH intercalated with hydrated sulfate.

Using x = 0.333 and y = 0.50 in the formula $D^+_y[M^{2+}_{1-x}Al_x(OH)_{2-y}(SO_4)_{y/2}(SO_4)_{0.222-(y/2)}]$ as an example (reduction of the content of alkali metal cations of 50%) in relation to the shigaite-like formula $Cs[M^{2+}_6Al_3(OH)_{18}(SO_4)_{2.0}]$ and keeping the metal molar ratio of 2:1, LDHs with the composition $(Cs)_{0.50}[M^{2+}_6Al_3(OH)_{17.5}(SO_4)_{0.25*}(SO_4)_{1.75}]$ would be obtained, which in a reduced way would be formulated as $(Cs)_{0.056}[M^{2+}_{0.667}Al_{0.333}(OH)_{1.944}(SO_4)_{0.028*}(SO_4)_{0.194}]$ (total $SO_4^{2-}$ = 0.222 and *= grafted $SO_4^{2-}$) or even $(Cs)_{0.056}[M^{2+}_{0.667}Al_{0.333}(OH)_{1.944}(SO_4)_{0.222}]$.

These propositions where some of hydroxide anions from the layers are replaced and grafted with $SO_4^{2-}$ are in relatively good agreement with the formulas suggested by the ICP-OES analyses (Table 2).

The XRD patterns and FTIR spectra before and after exchange reactions are shown in Figure 2. When the samples $Mn_2Al:SO_4/Na$ (Figure 2Aa) and $Zn_2Al:SO_4/Na$ (Figure 2Ac) were exchanged with $Cs_2SO_4$, the basal distances remained almost constant in both cases (11.04 to 11.15 Å for $Zn_2Al:SO_4/Na$ (Figure 2Aa,c) and 11.15 to 11.14 Å for $Mn_2Al:SO_4/Na$ (Figure 2Ab,d). This indicates that the exchange reaction was unsuccessful, since the basal distances observed for the samples of $Mn_2Al:SO_4/Cs$ (Figure 1Aa) and $Zn_2Al:SO_4/Cs$ (Figure 1Ab) obtained by co-precipitation were also in the same range (11.36 Å for $Mn_2Al:SO_4/Cs$ and 10.91 Å for $Zn_2Al:SO_4/Cs$).

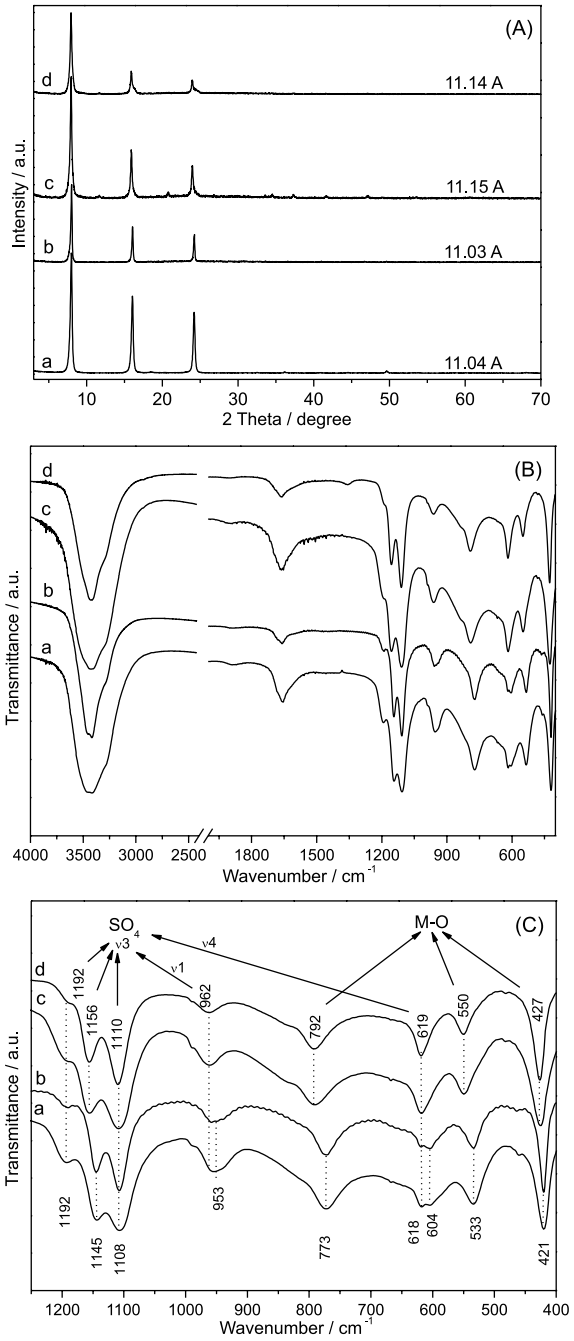


**Figure 2.** XRD patterns (A) and FTIR spectra (B, C) of $Mn_2Al:SO_4/Na$ (a) and $Zn_2Al:SO_4/Na$ (c) and after respective exchange reactions with $Cs_2SO_4$: $Mn_2Al:SO_4/Na$-Cs (b) and $Zn_2Al:SO_4/Na$-Cs (d).

When the FTIR spectra were evaluated, the same band positions were observed in the samples before and after exchange reactions, with $Cs_2SO_4$, at 1192, 1145, 1108, 953, 773, 618, 604, 533 and 421 $cm^{-1}$ for $Mn_2Al:SO_4/Cs$ (Figure 2Ca,b) and at 1192, 1156, 1110, 962, 792, 619, 550, 427 $cm^{-1}$ for $Zn_2Al:SO_4/Cs$ (Figure 2Cc,d). This observation is different than that of washed samples of green rusts intercalated with cesium and rubidium, when the removal of the cations was attributed to shifting of the $\nu_3$ bands of sulfate at about 15 $cm^{-1}$ to lower wavenumbers.[8]

The presence of the split band in the region of 1100 $cm^{-1}$ in all samples suggests that the sulfate environment is highly distorted,[37] since in the absence of sulfate/alkali metal/layer interaction, sulfate's undistorted tetrahedral symmetry would be characterized by a single band in the region of 1100 $cm^{-1}$.[48] Grafting of $SO_4^{2-}$ would only contribute to very low intensity bands in the same region,[32] which were overlapped by the other sulfate bands. More details of the band attributions can be found in the literature.[48] Figure 3A shows the results of our attempt to produce the phases intercalated with sulfate and cesium, using the precursor $Mn_2Al:NO_3$ (Figure 3Aa), $Zn_2Al:NO_3$ (Figure 3Ac) and $Mn_2Al:Cl$ (Figure 3Ae).

As expected, in all cases after the attempts to exchange the pristine anions with $SO_4^{2-}/Cs^+$, we found that the basal distances increased from 8.92 Å in $Mn_2Al:NO_3$ (Figure 3Aa) and $Zn_2Al:NO_3$ (Figure 3Ac) to around 11 Å, and from 7.82 Å in $Mn_2Al:Cl$ (Figure 3Ae)[32,49] also to around 11 Å (Figure 3Ab,d,f), indicating that the former's intercalated anions were replaced with $SO_4^{2-}$ [21,37] but not with $SO_4^{2-}/Cs^+$, as already indicated by the ICP-OES analyses (Table 2).

This is evidence that $Cs^+/SO_4^{2-}$ are not stable phases that can be obtained by exchange reactions, as already reported for sulfate green rusts,[8] but this is not true in the case of exchanging the same LDH with $Li^+$, $Na^+$ and $K^+$, where the exchange reactions were successful.[21] More studies are still necessary to explain this instability also for LDHs intercalated with $Rb^+/SO_4^{2-}$.

It has also been reported in the literature that sulfate contains several degrees of hydration and those with 11 Å correspond to double hydration. Lower basal distances and interpolytypic transitions can be obtained by heating or submitting the samples to dry air or vacuum.[33,50-52] However, our samples were dried at room temperature and no changes of the basal distances were observed (they remained close to 11 Å). The obtainment of exchanged compounds having the basal distance of 10.94 Å for $Mn_2Al:NO_3/Cs$ (Figure 3Ab), 11.00 Å for $Zn_2Al:NO_3/Cs$ (Figure 3Ad) and

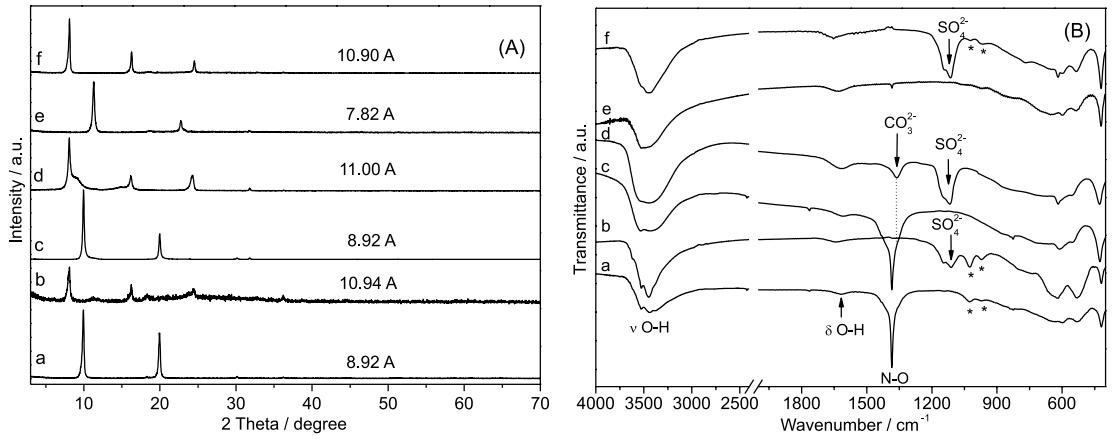


**Figure 3.** XRD patterns (A) and FTIR spectra (B) of $Mn_2Al:NO_3$ (a), $Zn_2Al:NO_3$ (c) and $Mn_2Al:Cl$ (e) and after respective exchange with $Cs_2SO_4$:$Mn_2Al:NO_3$/Cs (b), $Zn_2Al:NO_3$/Cs (d) and $Mn_2Al:Cl$/Cs (f).

10.90 Å for $Mn_2Al:Cl$/Cs (Figure 3Af) is an indication that the compounds are similar to those obtained with the direct synthesis (11.36 Å for $Mn_2Al:SO_4$/Cs and 10.91 Å for the $Zn_2Al:SO_4$/Cs). Nevertheless, as indicated by the ICP-OES analyses (Table 2), although traces of cesium were found, the content of sulfate was lower, indicating that the formulas are attributed to regular LDHs ($[M^{2+}_{0.667}Al^{3+}_{0.333}(OH)_2](SO_4)_{0.167}$).[37,52]

The confirmation of the exchange reactions $NO_3^-/SO_4^{2-}$ can also be clearly seen by the replacement of the sharp bands at 1384 $cm^{-1}$ (Figure 3Ba,c), attributed to nitrate, and appearance of bands in the region of 1100 $cm^{-1}$, attributed to sulfate (Figure 3Bb,d). This band split also indicated distorted sulfate symmetry. After the exchange reaction of $Mn_2Al:NO_3$ with $Cs_2SO_4$, (Figure 3Ba,b), extra bands were also observed at 968 and 1026 $cm^{-1}$, which could be attributed to O–H bending modes, similar to those observed in gibbsite.[53] The same bands (although that at 968 $cm^{-1}$ can be attributed to sulfate) were also observed for $Mn_2Al:NO_3$ and $Mn_2Al:Cl$/Cs (indicated by *). The origin of these bands was not clearly understood. A small contamination of carbonate (band at 1362 $cm^{-1}$) was also observed in the sample $Zn_2Al:NO_3$/Cs (Figure 3Bd),[28] already present as a shoulder in the sample $Zn_2Al:NO_3$before the exchange reactions (Figure 3Bc). The presence of carbonate can explain the slightly lower content of sulfate (0.146 instead of 0.167) (Table 2).

After the exchange of chloride (Figure 3Be), the expected band appeared in the region of 1100 $cm^{-1}$, attributed to sulfate (Figure 3Bf). All the other bands remained constant, indicating the maintenance of the LDH lattice and suggesting exchange reactions of chloride with sulfate but without the incorporation of $Cs^+$ (Table 2). SEM images of some key synthesized samples (Figure 4) indicated the expected morphology of LDH, with platelet-like particles, in which the diameter varied according to the compositions, being smaller than 1 mm in $Mn_2Al:SO_4$/Na (Figure 4a) and $Zn_2Al:SO_4$/Na (Figure 4b).

In the case of $Mn_2Al:NO_3$ (Figure 4c) and $Mn_2Al:Cl$ (Figure 4d), bigger particles were observed, reaching several micrometers with some powdered particles at the top of the crystals. These powdered particles are not attributed to crystalline impurities, since the XRD patterns indicated only basal peaks from the LDH, and chemical analysis also indicated the predicted composition (Table 2). The EDS spectra (Figures 4e-4h) also indicated qualitatively the presence of the expected elements according to the chemical compounds used during the synthesis.

As copper tapes were used to hold the samples, a small contamination with this element was observed in some of the spectra (indicated with asterisks).

All the compounds intercalated with hydrated sulfate in the presence of alkali metal cations, hydrated sulfate or even with grafted hydrated sulfate presented basal distances close to 11 Å (Figure 5), making them difficult to distinguish through XRD, but quantitative analysis by ICP-OES helped us to give some information about these complex systems.

## Conclusions

LDH intercalated with $Cs^+$ and $NH_4^+$ together with $SO_4^{2-}$ obtained by co-precipitation of sulfate salts with aqueous $NH_3$ in the presence of excess $Cs_2SO_4$, presented the composition $(Cs/NH_4)_{0.111}[M^{2+}_{0.667}Al_{0.333}(OH)_{2.0}(SO_4)_{0.222}]$ ($M^{2+}$ = Mn or Zn) (equation 2), attested by ICP-OES analyses, basal distances close to 11 Å in the XRD patterns and typical bands of $SO_4^{2-}$ and $NH_4^+$ in the FTIR spectra.

$$0.667\ M^{2+}SO_4 + 0.167\ Al_2(SO_4)_3 + Cs_2SO_4\ (\text{excess}) + NH_4OH \rightarrow (Cs^+/NH_4^+)_{0.111}[M^{2+}_{0.667}Al_{0.333}(OH)_{2.0}(SO_4)_{0.222}]\ (M^{2+} = \text{Mn, Zn}) \quad (2)$$

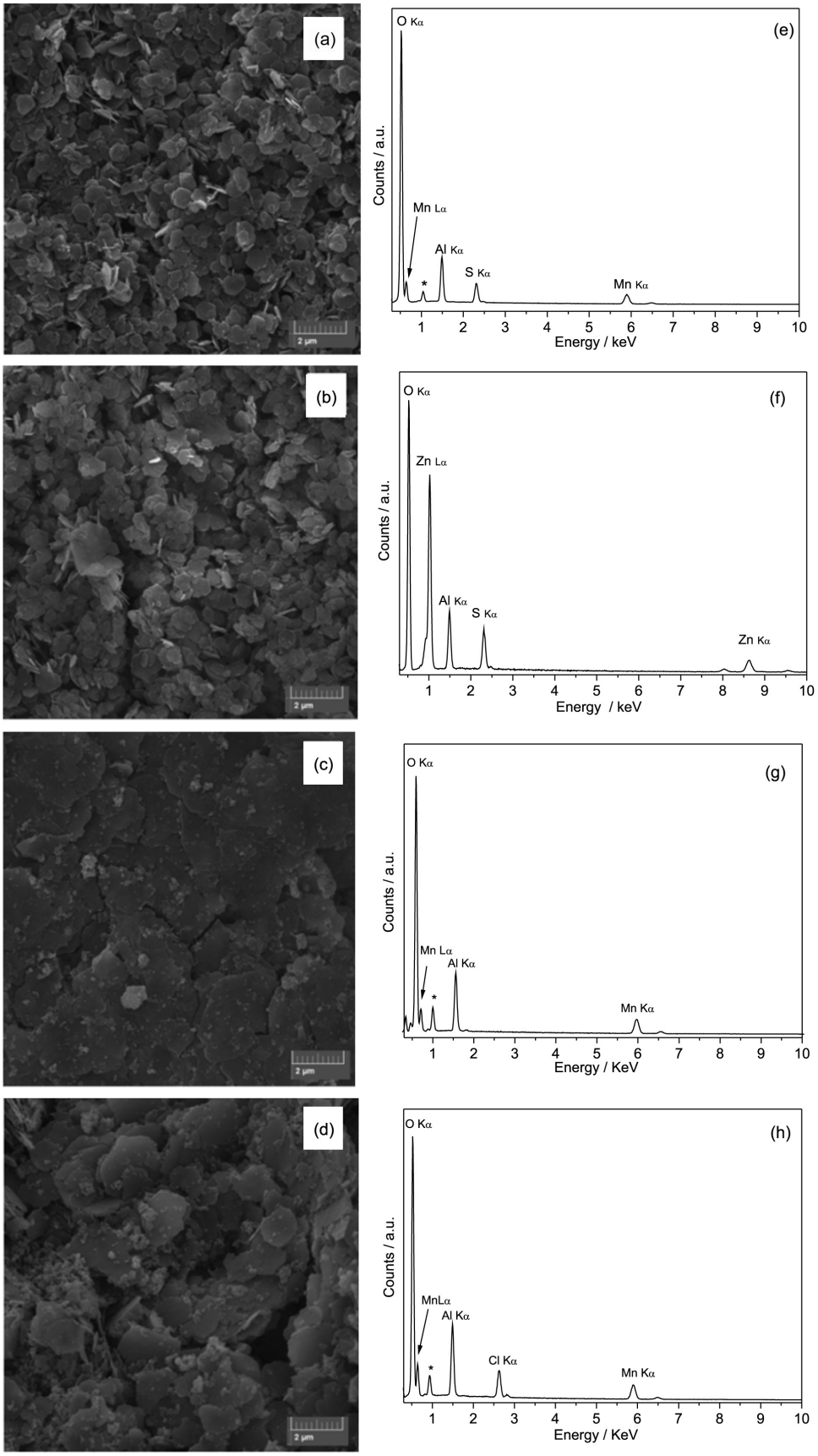


**Figure 4.** SEM images of $Mn_2Al:SO_4/Na$ (a), $Zn_2Al:SO_4/Na$ (b), $Mn_2Al:NO_3$ (c), $Mn_2Al:Cl$ (d) and the corresponding EDS spectra (e-h) (*Cu from the sample holder).

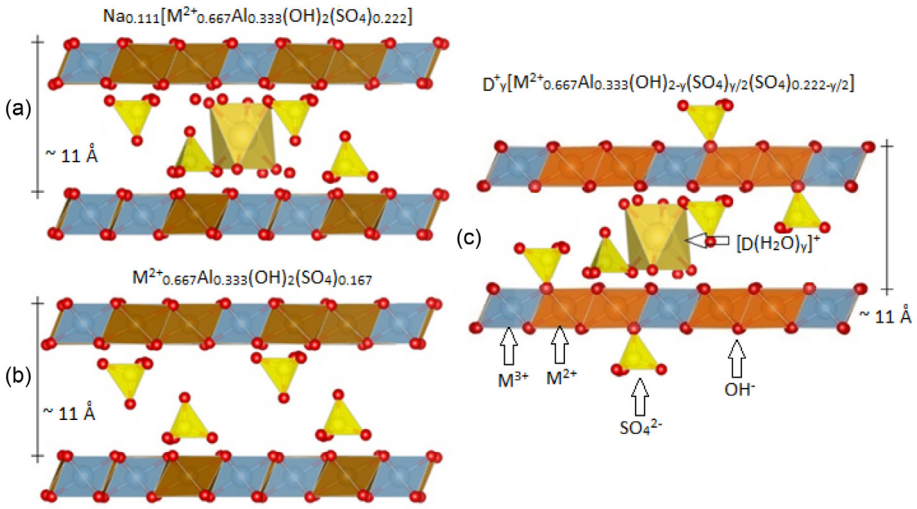


**Figure 5.** Schematic representation of the $2M^{2+}$:$M^{3+}$LDH structures intercalated with hydrated $Na^+/SO_4^{2-}$, such as in shigaite (a),[28] hydrated $SO_4^{2-}$ as in $[Zn_2Cr(OH)_6](SO_4)_{0.5}{\cdot}4H_2O$ (b)[54] and intercalated/grafted with $SO_4^{2-}$, as proposed in the present work (c). Water molecules were removed to facilitate visualization.

LDH synthesized by co-precipitation with increasing pH of sulfate salts with NaOH and excess of $Na_2SO_4$ presented the composition $Na_{0.111}[M^{2+}_{0.667}Al_{0.333}(OH)_{2.0}(SO_4)_{0.222}]$ ($M^{2+}$ = Mn, Zn) (equation 3), basal distances close to 11 Å and typical bands of $SO_4^{2-}$.

$$0.667\ M^{2+}SO_4 + 0.167\ Al_2(SO_4)_3 + Na_2SO_4\ (\text{excess}) + NaOH \rightarrow Na^+_{0.111}[M^{2+}_{0.667}Al_{0.333}(OH)_{2.0}(SO_4)_{0.222}]\ (M^{2+} = Mn, Zn) \quad (3)$$

After putting $Na_{0.111}[M^{2+}_{0.667}Al_{0.333}(OH)_{2.0}(SO_4)_{0.222}]$ in contact with excess $Cs_2SO_4$ in an attempt to exchange $Na^+$ with $Cs^+$, the LDH containing $SO_4^{2-}$/$Cs^+$ obtained were compared to those obtained by direct co-precipitation with increasing pH. In these samples, the basal distance was also close to 11 Å, but $Na^+$ were partially exchanged with $Cs^+$, while the amount of sulfate was constant, as attested by ICP-OES analyses and typical bands in the FTIR spectra, suggesting the formulas $D^+_y[M^{2+}_{0.667}Al_{0.333}(OH)_{2-y}(SO_4)_{y/2}(SO_4)_{0.222-(y/2)}]$ (equation 4) ($D^+$= $Na^+$ or $Cs^+$), where $(SO_4)_{y/2}$ represents grafted $SO_4^{2-}$, partially replacing the $OH^-$ in the layers: $((OH)_{2-y})$.

$$D^+_{0.111}[M^{2+}_{0.667}Al_{0.333}(OH)_{2.0}(SO_4)_{0.222}] + Cs_2SO_4\ (\text{excess}) \rightarrow D^+_y[M^{2+}_{0.667}Al_{0.333}(OH)_{2-y}(SO_4)_{y/2}(SO_4)_{0.222-(y/2)}]\ (M^{2+} = Mn, Zn) \quad (4)$$

Co-precipitating nitrate or chloride salts with NaOH, compounds with the composition $[M^{2+}_{0.667}Al^{3+}_{0.333}(OH)_2](NO_3)_{0.333}{\cdot}nH_2O$ ($M^{2+}$ = Mn, Zn) were obtained (equations 5,6), having respective basal distances of 8.92 and 7.92 Å and presenting typical bands in the FTIR spectra.

$$0.667\ M^{2+}(NO_3)_2 + 0.333\ Al(NO)_3 + NaOH \rightarrow [M^{2+}_{0.667}Al^{3+}_{0.333}(OH)_2](NO_3)_{0.333}{\cdot}nH_2O\ (M^{2+} = Mn, Zn) \quad (5)$$

$$0.667\ MnCl_2 + 0.333\ AlCl_3 + NaOH \rightarrow [Mn^{2+}_{0.667}Al^{3+}_{0.333}(OH)_2](Cl)_{0.333}{\cdot}nH_2O \quad (6)$$

After exchanging the samples intercalated with nitrate and chloride with $Cs_2SO_4$ in excess, the basal distance changed to around 11 Å and typical FTIR bands of $SO_4^{2-}$ were observed, indicating the intercalation of $SO_4^{2-}$. But the content of cesium was very low, suggesting the maintenance of the formula $[M^{2+}_{0.667}Al^{3+}_{0.333}(OH)_2](SO_4)_{0.167}{\cdot}nH_2O$ (equation 7), as also proposed by equation 1.

$$[M^{2+}_{0.667}Al^{3+}_{0.333}(OH)_2](A^-)_{0.333}{\cdot}nH_2O + Cs_2SO_4\ (\text{excess}) \rightarrow [M^{2+}_{0.667}Al^{3+}_{0.333}(OH)_2](SO_4)_{0.167}{\cdot}nH_2O\ (A = NO_3^-, Cl^-;\ M^{2+} = Zn, Mn) \quad (7)$$

This is the first report in the literature of synthesis and characterization of LDHs intercalated with $SO_4^{2-}$/$Cs^+$/$Na^+$ or $SO_4^{2-}$/$Cs^+$/$NH_4^+$, opening new alternatives to remove radioactive nuclides from contaminated waters using LDHs obtained by co-precipitation syntheses with increasing pH.

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