New Varieties of Zinc–Chromium–Sulfate Lamellar Double Hydroxides

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The synthesis of zinc–chromium lamellar double hydroxides (LDHs) intercalated by sulfate anions is carried out with a one-step method that combines coprecipitation and anionic exchange. The materials obtained in a reactor containing a sodium sulfate solution are compared with those prepared from lithium, potassium, and ammonium sulfate solutions. The compounds are characterized by chemical analysis, powder X-ray diffraction, and infra-red spectroscopy. Depending on pH conditions, the washing process, and the nature of the monovalent cation, the sulfate intercalated compounds exhibit two 2H hexagonal varieties with different layer spacings $d \approx 8.9$ Å and $d \approx 11$ Å at room temperature; this last phase is related to the insertion of alkaline interlamellar cations. Under dry air, the loss of intercalated water leads to a 3R rhombohedral variety with $d \approx 8.2$ Å. A second rhombohedral variety with $d \approx 10.9$ Å is reversibly obtained from the "8.9 Å" phase under high relative humidity. These four [Zn–Cr–SO$_4$] LDHs differ by their stacking sequences and interlamellar distances and can be selectively obtained.   © 1997 Academic Press

INTRODUCTION

Lamellar double hydroxides (LDHs) of the general formula $[M_x^{II} M_{1-x}^{III}(OH)_2]^{x+}[X_{x/m}^{m-} \cdot nH_2O]^{x-}$ (M^{II}, M^{III} = metals, X = anion) are built up of cationic $M(OH_2)$ brucite-like layers intercalated by interlamellar anionic domains. According to this formula, it is possible to obtain a wide range of such compounds by changing the nature and proportions of metallic cations in the main hydroxylated sheets and by intercalation of a great number of solvated anions.

We use the short notation $_x^n[M^{II}-M^{III}-X]_{ss}^d$ (1) to describe them. d is the distance (Å) between two adjacent sheets and depends mainly on the nature of the interlamellar species and their electrostatic interaction with the main layers. SS represents the stacking sequence (1H, 2H, 3R, …) leading to hexagonal or rhombohedral symmetry of the structure (2, 3). The structure is described in an hexagonal cell where $a_0 \approx 3.1$ Å corresponds to the distance of neighboring

metallic cations in the main sheets and c to a multiple (related to stacking sequence) of the basal spacing.

The intercalation behavior of LDHs toward different anions has been extensively investigated. For example, [Mg–Fe–CO$_3$] LDHs are known to occur in two polytypes that differ only by their stacking sequence: rhombohedral pyroaurite and hexagonal sjögrenite (2, 4–6). The presence of sulfate anions displays very particular behavior with a wide range of basal spacings ($8.8 \leq d \leq 11$ Å) (3, 7–12). In a previous work (13) we reported structural results for the two compounds $_{0.33}[Zn-Cr-SO_4]_{2H}^{8.9}$ and $_{0.33}[Zn-Cr-SO_4]_{2H}^{11}$. A more systematic study of phases related to this system seemed nevertheless necessary for the sake of acquiring a better knowledge of interactions between sulfate anions and the LDH hydroxylated backbone.

The aim of this paper is to present an approach to selective synthesis of [Zn–Cr–SO$_4$] compounds obtained under various preparative methods and post-synthesis modifications. The main experimental parameters are the trivalent metal ratio x, the nature of precipitating agent, and the pH of coprecipitation. We examine the evolution, and the stability of the obtained compounds with hygrometry.

EXPERIMENTAL

Synthesis

All of the reagents were of analytical grade; deionized and CO$_2$-free water was used to prepare solutions and for the washing process to avoid carbonate intercalation in the prepared LDHs.

Several synthetic routes were used to prepare [Zn–Cr–SO$_4$] compounds.

Method 1: Some samples were prepared from the well-known [Zn–Cr–Cl] (14) precursor by anionic exchange with a large amount of molar sodium sulfate solution (15, 12).

Method 2: The direct intercalation of the sulfate anion during the synthesis of the sheets was also performed by coprecipitation of a zinc sulfate and chromium sulfate solution by sodium hydroxide at constant pH.

Method 3: We mainly used a one-step method that combines coprecipitation and anionic exchange. Two molar solutions of zinc chloride and chromium chloride are mixed to obtain a solution with the required trivalent metal ratio, $x_0 = n_{Cr}/(n_{Cr} + n_{Zn})$, and where n_{Cr} and n_{Zn} are the number of moles of Cr and Zn in the solution. This solution is slowly added (0.3 mL h^{-1}) into a reactor containing a 100 mL sodium sulfate solution of $C_0 = 0.10$ mol L^{-1} initial concentration under vigorous stirring. The pH is kept constant at a determined value via a regulator by addition of a 1.5 mol L^{-1} NaOH solution in the reactor. The precipitate is then aged for 72 h under gentle stirring and separated from the supernatant solution by filtration through a sintered-glass filtering crucible. This synthesis procedure is repeated with other precipitating reagents, LiOH, KOH, and NH$_4$OH with respectively Li$_2$SO$_4$, K$_2$SO$_4$, and (NH$_4$)$_2$SO$_4$ in the reactor.

Washing of precipitates. The filtered precipitates need to be washed to remove adsorbed electrolytes; two different processes were used leading to different results. The first, called "fast washing," corresponds to the percolation of a few mL of water through the filtering crucible. The second, called as "complete washing," corresponds to a series of dispersions in water and centrifugations until the resistivity of supernatant becomes higher than 10^4 Ω cm. The washed compounds were finally dried at room temperature.

Hygrometry control. The so-obtained LDHs were stored in air at room temperature for 1 week over appropriate reagents to obtain atmospheres with well-known relative humidities (%RH). The uptake or the loss of water of the samples was characterized by their gravimetric evolution. Values between 20% RH and 90% RH were obtained with sulfuric acid solutions; by air (0% RH) was realized with phosphorus pentoxide.

Characterization

The samples were characterized by powder X-ray diffraction (PXRD), infrared spectroscopy (IR), chemical analysis, and gravimetric analysis. X-ray diffractograms were obtained on a Siemens D501 diffractometer with the Cu$K\alpha$ radiation filtered by a graphite back-monochromator. A step-scan from $2°$ to $74°$ (2θ) was used with an $0.08°$ step and with a 4 s/step integration time, IR spectra were recorded ($4000–400$ cm^{-1}) from 200 mg KBr pellets containing 2 mg of sample on a 16 PC Perkin–Elmer FTIR spectrometer. Elemental analysis was performed at the Service Central d'Analyse du CNRS (Vernaison France). The gravimetric data were obtained on a Mettler AE 163 analytical balance with a 10 µg resolution.

RESULTS

Preparative Methods

Three preparative methods were used to prepare [Zn–Cr–SO$_4$] LDHs. The PXRD diagrams of the corresponding compounds after complete washing and of the [Zn–Cr–Cl] precursor are reported in Fig. 1.

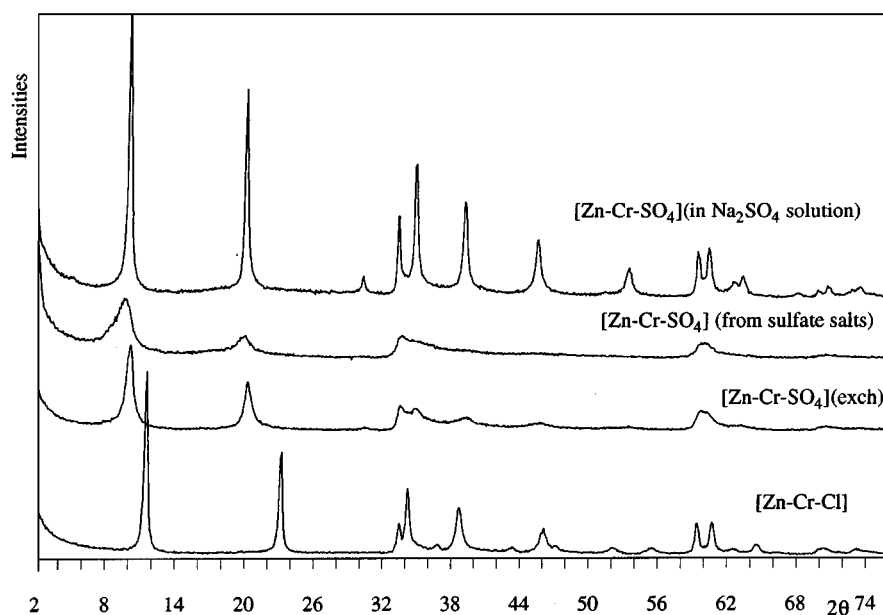**FIG. 1.** PXRD diagrams (Cu$K\alpha$) of [Zn–Cr–Cl] precursor and of [Zn–Cr–SO$_4$] samples prepared by anionic exchange of precursor (method 1), coprecipitation from sulfate salts (method 2), and coprecipitation from chloride salts with a sodium sulfate solution in the reactor (method 3). All samples were characterized after complete washing.

[Zn–Cr–SO$_4$] LDHs prepared by anionic exchange (method 1) display lower crystallinity than the [Zn–Cr–Cl] precursor. We attribute this effect to the stress of the anionic layers which are expanded by more than 3 Å during anionic exchange.

The compounds obtained by coreciptation of a mixed zinc–chromium sulfate solution (method 2) are ill-organized materials. This is probably related to the presence in the metallic salts solution of sulfate groups coordinated to Cr^{III} leading to less favorable conditions for the formation of $M(OH)_6$ octahedra than from hexa-aqua complexes.

The best results were obtained by coprecipitation of a solution of zinc and chromium chlorides in a reactor containing the sulfate anions (method 3). During the reaction, the concentration of chloride ions increase in the reactive medium and the sulfate concentration decreased. For a SO$_4$/Cl molar ratio lower than 29%, a critical threshold point was reached and both [Zn–Cr–SO$_4$] and [Zn–Cr–Cl] phases were simultaneously obtained. We never observed phases with intermediary basal spacings; chloride and sulfate anions seem thus to exclude each other in the interlamellar domains of [Zn–Cr] LDHs. This behavior is consistent with results on [Ni–Fe] LDHs with the same interlamellar anions (16). Further study was therefore performed with this last preparative method and SO$_4$/Cl molar ratios higher than 40%.

Effect of Coprecipitation pH

By using a trivalent molar ratio of $x_0 = 0.33$ in the starting solution, [Zn–Cr–SO$_4$] compounds are obtained for all experiments from pH 5 to 10. The PXRD diffractograms corresponding to fast washed samples are reported in Fig. 2. The best crystallinity was obtained at pH 5, leading to a grey–pink compound with $d \approx 11$ Å basal spacing. We were not able to prepare samples at lower pH owing to the increasing solubility of LDHs in such acidic media. At neutral pH, this "11 Å" phase coexists with a "8.9 Å" phase, which is the major phase at basic pH with poor crystallinity. At acidic pH, the diffraction lines of the "8.9 Å" phase become progressively weaker.

Effect of Trivalent Metal Ratio

Samples are prepared for different molar ratios $0.25 \leq x_0 \leq 0.50$ at various preparation pH. The best results are
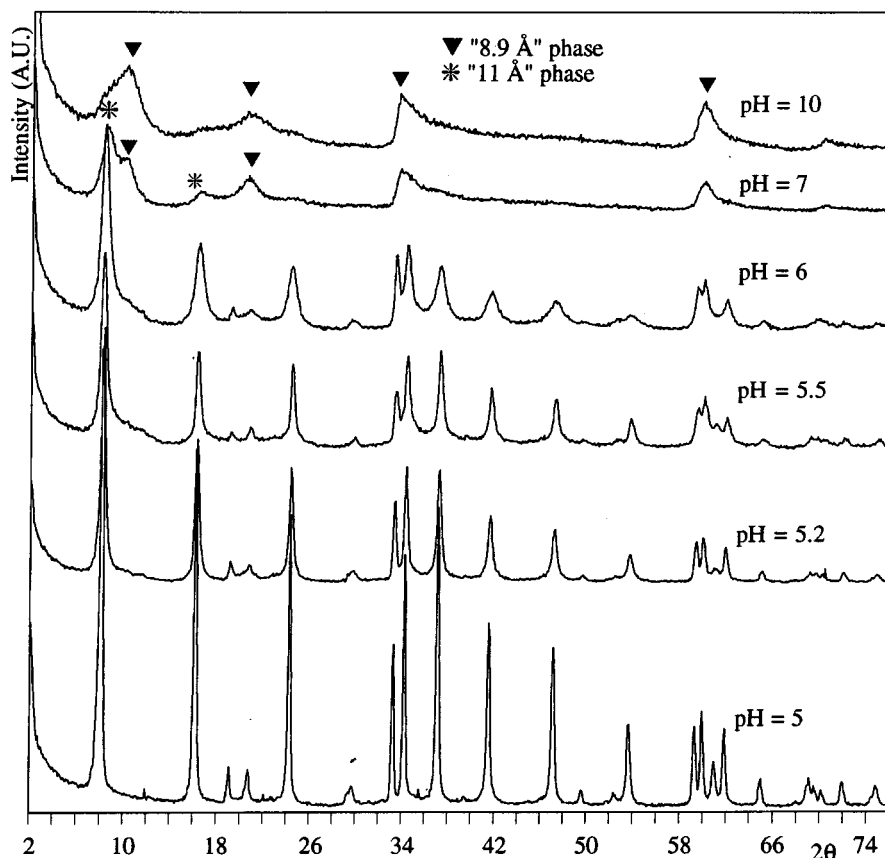

FIG. 2. PXRD diagrams (Cu$K\alpha$) of $_{0.33}$[Zn–Cr–SO$_4$] LDHs prepared by method 3 for different values of coprecipitation pH and after fast washing. The best results were obtained at the lowest pH; at high pH an ill-organized material with lower basal spacing is obtained.
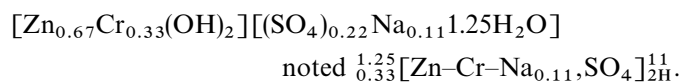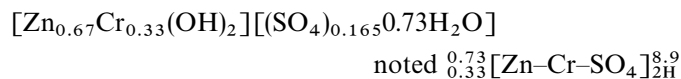
obtained at pH 5.5 except for $x_0 = 0.33$ (pH 5). They show almost the same PXRD patterns with a slightly different crystallization quality of the "11 Å" phase except for a quasi-amorphous green precipitate obtained with $x_0 = 0.50$, which contains an important amount of chromium hydroxide. No evolution of lattice parameters of crystallized phases is observed; moreover the chemical analysis of these samples confirms an $x \approx 0.33$ molar ratio common to all of the precipitates. The deviation of composition in comparison with the original solution indicates that the excess of metallic cation (zinc or chromium) remains in the supernatant solution. At pH > 6.5 and $x_0 < 0.33$, the LDH phase is obtained with zinc hydroxide. These results point out that the well-organized [Zn–Cr–SO$_4$] compounds correspond to the unique molar ratio $x \approx 0.33$. This agrees with previous results for [Zn–Cr–CO$_3$] and [Zn–Cr–Cl] (14, 15, 17).

Washing Process

Depending on the washing process, two varieties are observed as reported in our previous structural study (13). The "11 Å" phase is obtained from fast washing, which evolves after complete washing to give a well-organized "8.9 Å" phase. PXRD diagrams of both phases are reported in Fig. 3 and agree with a hexagonal 2H stacking sequence. The PXRD diagrams performed during the sucessive steps of complete washing display a decrease in the "11 Å" phase diffraction line intensities and a correlative increase in those

of the "8.9 Å" phase without any evolution of their respective basal spacings.

Chemical analysis shows that for both phases the trivalent metal ratio remains the same; on the other hand the "11 Å" phase contains sodium and a corresponding excess of sulfate whereas the "8.9 Å" phase is sodium-free. The chemical analysis and PXRD data agree with the following formulas:

$$[Zn_{0.67}Cr_{0.33}(OH)_2][(SO_4)_{0.165}0.73H_2O]$$

$$\text{noted } {}^{0.73}_{0.33}[Zn\text{–}Cr\text{–}SO_4]^{8.9}_{2H}$$

$$[Zn_{0.67}Cr_{0.33}(OH)_2][(SO_4)_{0.22}Na_{0.11}1.25H_2O]$$

$$\text{noted } {}^{1.25}_{0.33}[Zn\text{–}Cr\text{–}Na_{0.11},SO_4]^{11}_{2H}.$$

The IR spectra of these two phases are given in Fig. 4. The broad band around 3400 cm^{-1} is representative of the stretching vibration of hydroxyl groups and water molecules. The absorption at 1620 cm^{-1} is assigned to the bending vibration of water. IR spectroscopy is very sensitive to the presence of carbonate anions in LDHs (v_3 at 1370 cm^{-1}). The band here is very weak; we can therefore assume that these samples are carbonate-free. The sharp bands at low wavenumbers (400–600 cm^{-1}) arise from the lattice vibrations, which can be assigned to translational motions of oxygen in the layers (18). They are similar for both phases (as well as for the [Zn–Cr–Cl] precursor); this reflects that the hydroxylated layer structure is not affected by the washing process or anionic exchange.
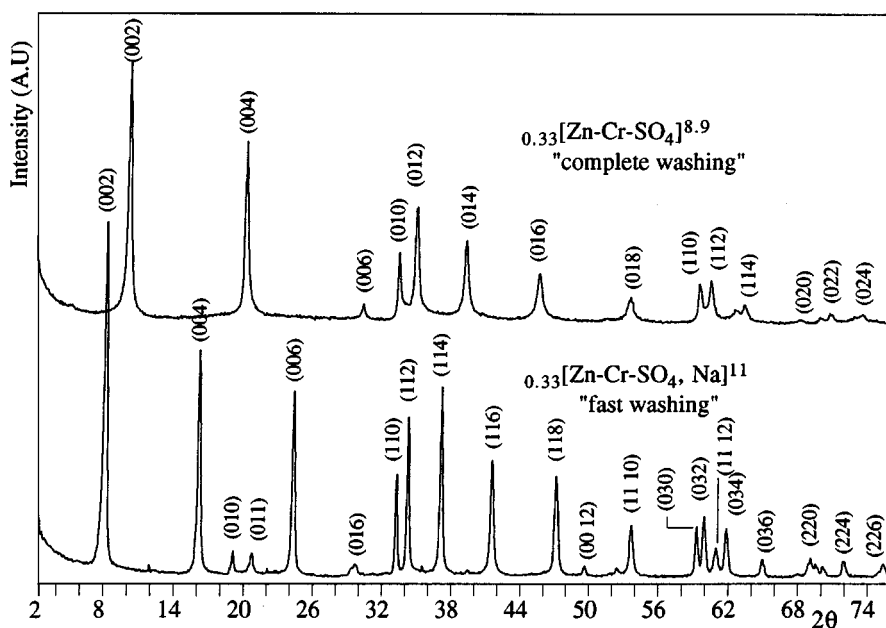

FIG. 3. PXRD diagrams (CuKα) of the "11 Å" phase obtained by method 3 at pH 5 after fast washing and of the "8.9 Å" phase obtained by complete washing of the preceding compound. An indexation of diffraction lines is given for a 2H stacking sequence.
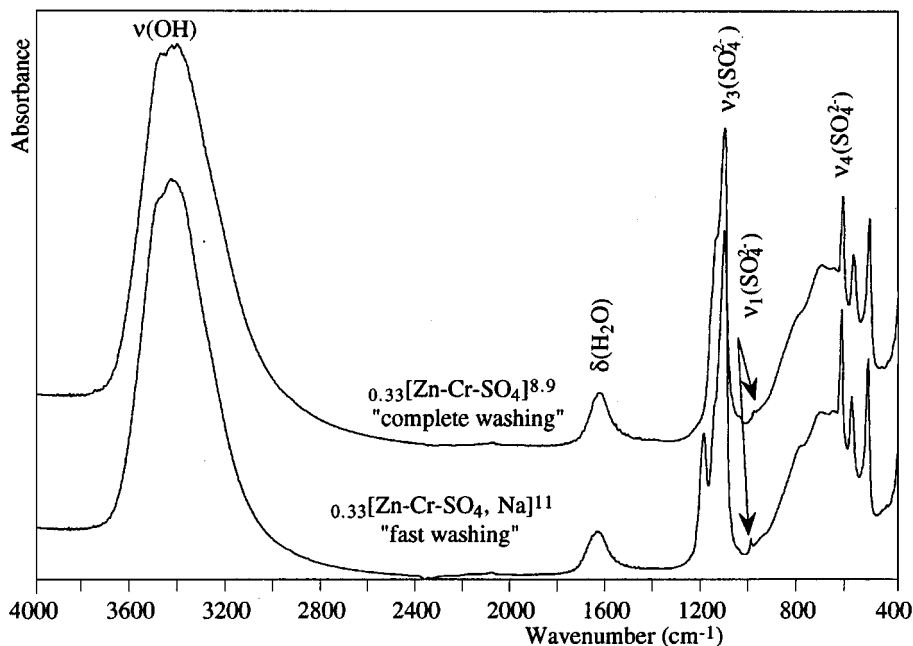
FIG. 4. FTIR spectra of the "11 Å" phase obtained by method 3 at pH 5 after fast washing and of the "8.9 Å" phase obtained by complete washing of the preceding compound.

Both phases display similar vibrational modes of sulfate groups; v_4 at 620 cm^{-1} and v_3 at 1110 cm^{-1} with a shoulder at 1154 cm^{-1}. The weak v_1 band at 993 cm^{-1} and the small splitting of v_3 are consistent with a weak C_{3v} distortion of the SO$_4$ tetrahedra (19). The main difference between the two samples is the v_3 band at 1190 cm^{-1} which is only observed for the "11 Å" phase. This effect must be connected with the presence of interlayer Na cations and additional water and sulfate anions.

Monovalent Cation Effect

The preceding results show that alkaline cations can be involved in the interlamellar organization of LDHs. The synthesis procedure optimized with sodium was therefore repeated in the same way with monovalent cations of different sizes: K$^+$, Li$^+$, and (NH$_4$)$^+$. In every case it was possible to prepare the "8.9 Å" phase. A phase similar to the "11 Å" phase could only be obtained with potassium ions. For lithium and ammonium, this compound could not be prepared despite attempts with higher concentrations of corresponding salts in the reactor. The lattice parameters of the obtained compounds were refined from their PXRD patterns. The results after fast washing and complete washing of the samples are reported in Table 1.

The PXRD patterns of fast washed samples prepared in sodium or potassium media are quite similar except for the increase of basal spacing with potassium. This correlation between the cation size and the interlamellar spacing

confirms the presence of Na$^+$ or K$^+$ within the structure. Both phases display the same superstructure $a = a_0\sqrt{3}$ and $c = 2d$.

The cell parameters of completely washed samples are not influenced, within experimental error, by the nature of the monovalent cation. With lithium or ammonium cations, the "8.9 Å" phase is also directly obtained from fast washed samples (corresponding lattice parameters are therefore not reported in Table 1).

Hygrometry Effect

The $^{0.73}_{0.33}$[Zn–Cr–SO$_4$]$^{8.9}_{2H}$ and $^{1.25}_{0.33}$[Zn–Cr–Na$_{0.11}$, SO$_4$]$^{11}_{2H}$ phases were stored for 1 week in air with well-known relative humidities: 0, 20, 40, 50, 60, 70, 80, and

TABLE 1
Cell Parameters of [Zn–Cr–SO$_4$] Phases Obtained with Different Monovalent Cations in the Reactive Media and for Different Washing Processes

Washing process	Fast washing		Complete washing	
Reactive media	$a = a_0\sqrt{3}$	$d = c/2$	$a = a_0\sqrt{3}$	$d = c/2$
KOH/K$_2$SO$_4$	5.413 (4)	11.30 (5)	3.118 (6)	8.91 (2)
NaOH/Na$_2$SO$_4$	5.411 (1)	11.058 (4)	3.120 (1)	8.916 (3)
LiOH/Li$_2$SO$_4$	—	—	3.117 (2)	8.911 (5)
(NH$_4$)OH/(NH$_4$)$_2$SO$_4$	—	—	3.116 (4)	8.93 (1)

100% RH. Their evolution was followed by PXRD and gravimetry. The mass evolution is assumed to correspond exclusively to changes in hydration state of the samples. The PXRD data give prominence to large variations of basal spacing with the relative humidity of air; the results are reported in Fig. 5.

The sodium-containing sample shows a weak basal-spacing evolution in the range 20–100% RH. The gravimetric evolution is low except at high % RH values where the powder has a moist aspect corresponding to the surface adsorption of a large amount of water. At 0% RH the basal spacing decreases dramatically ($d \approx 8.25$ Å) with the loss of hydration water.

The sodium-free sample displays more complex behavior. The 2H "8.9 Å" phase remains stable in the range 20–50% RH, but at higher relative humidities the basal spacing increases to $d \approx 10.9$ Å. While this basal spacing is close to that of the "11 Å" phase, this compound is quite different: the interlamellar domains contain no alkaline cation and a different 3R rhombohedral symmetry is observed. The formula $^{1.15}_{0.33}$[Zn–Cr–SO$_4$]$^{10.9}_{3R}$ is in agreement with experimental data. The PXRD diagrams of these two phases are reported in Fig. 6.

In dry air (0% RH), a low basal spacing is also observed for the alkaline-free sample ($d \approx 8.2$ Å). The PXRD diagram, also shown in Fig. 6, is very similar, to that of the sodium-containing sample. The hydration water is also removed.

DISCUSSION

The selected method of coprecipitation permits preparation of well-organized [Zn–Cr–SO$_4$] LDHs under specific experimental conditions.

The reactive medium needs to be as acidic as possible. This medium corresponds to an increase in the solubility of the prepared LDH, which gives more mild growing conditions for the microcrystallites during the addition of reagents. Moreover, this low pH decreases the condensation of chromium oligomers, which have to be broken to build the [Zn–Cr] brucite-like main layers.

The [Zn–Cr–SO$_4$] LDHs can be prepared for a unique $x = 1/3$ trivalent metal ratio. All attempts to obtain different values give secondary products or ill-organized materials. It is worthwhile to notice that at low pH the precipitate displays this preferred composition even if the metallic salt solution has a different composition.

These two experimental parameters (low pH of coprecipitation and particular trivalent metal ratio) seem to be favorable to the preparation of all [M^{II}–Cr–X] LDHs. An ordered disposition of the two metallic cations in the $M(OH)_2$ layers would lead to a superstructure with $a = a_0\sqrt{3}$ which is generally not observed by diffraction experiments. The only remaining hypothesis is that a short-range ordering of metallic cations occurs, corresponding to a particular arrangement of Cr(OH)$_6$ octahedra in the layers.

Standard LDH compounds contain only anionic species and water molecules in their interlamellar domains. The experimental results show that during the coprecipitation process from a reactive medium containing sulfate and sodium or potassium alkaline cations, these last species are also intercalated in the formed LDHs. A corresponding amount of sulfate anions is intercalated to ensure electroneutrality; the sulfate quantity in comparison with alkaline cation-free phase is increased by about 17%. Similar phases with lower crystallinity can also be obtained by anionic
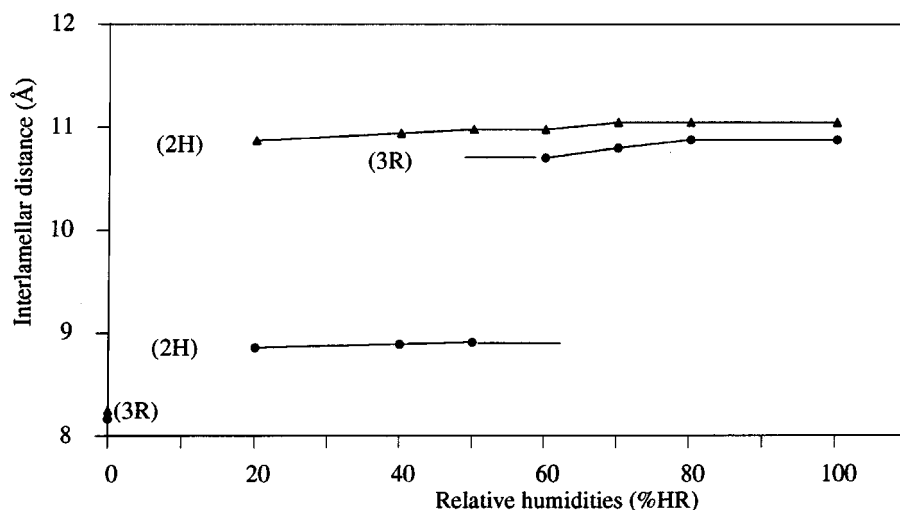

FIG. 5. Evolution of interlamellar spacing for the varieties of [Zn–Cr–SO$_4$] LDHs in relation to ambient hygrometry. Depending on their hydration state, three phases are obtained for the alkaline-free sample (solid circles) and two phases for the sodium-containing sample (solid triangles).
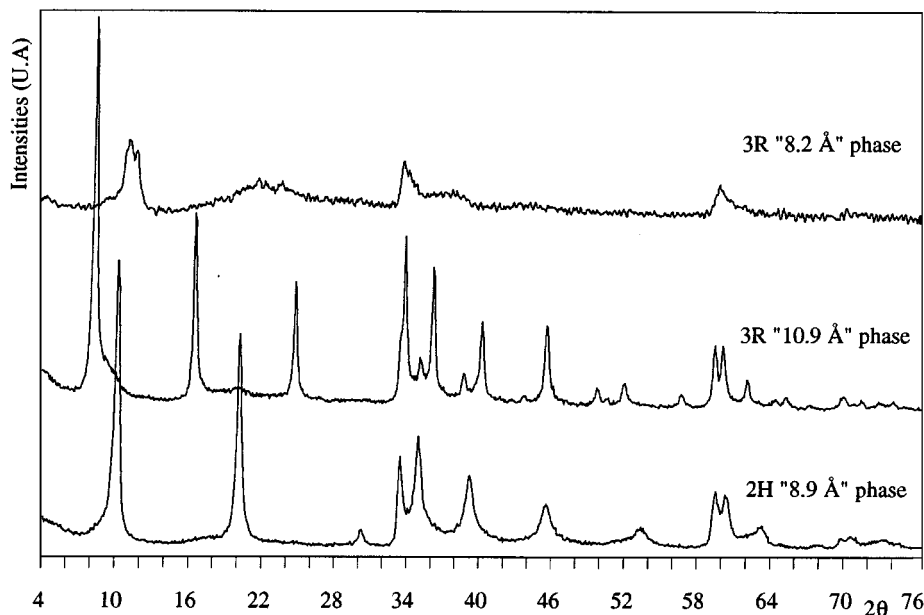
FIG. 6. PXRD diagrams (Cu$K\alpha$) of the three alkaline-free [Zn–Cr–SO$_4$] LDHs obtained: "8.2 Å" phase at 0% RH, "8.9 Å" phase in the range 20–50% RH, and "10.9 Å" phase in the range 60–100% RH.

exchange on other LDH precursors. These compounds are characterized by a $d \approx 11$ Å basal spacing. From previous structural results (13), the disposition of interlamellar species is schematically illustrated in Fig. 7a. Each sodium cation in the middle of interlamellar domains is surrounded by a distorted octahedra of water molecules. The sulfate groups are alternatively close to one of the two main layers,

FIG. 7. Schematic representation of the structures of the four structural varieties of [Zn–Cr–SO$_4$] LDHs phases selectively obtained in this work.

with water molecules on the opposite side. The higher value of basal spacing with the potassium cation ($d \approx 11.3$ Å) confirms this interlamellar localization.

When such phases are washed with water, the alkaline anions can be removed and the alkaline cation-free compound is obtained. This last compound is also directly prepared from reactive media containing lithium or ammonium sulfate. Assuming that the results obtained for wet samples (stored under 100% RH air) can be extended to suspensions of LDH precipitates in water or reactive media, the basal spacing is then $d \approx 10.9$ Å with a 3R stacking sequence. This value, very close to the previous 11 Å value, leads to the hypothesis of a similar disposition of interlamellar sulfate groups and water molecules (Fig. 7b). For these compounds with high basal spacings, an additional layer of water molecules is intercalated between the sulfate groups and the hydroxyl layer. There is no evidence of a progressive transition between the "11 Å" and "10.9 Å" phases; all the alkaline cations seem to be removed in one step during the washing process with correlative hexagonal–rhombohedral symmetry change.

The lack of lithium-ion intercalation is probably related to its small size, which does not fit with an octahedral environment of water molecules as for sodium or potassium cations. In the case of ammonium cations, despite the fact that the preparation is performed in acid conditions, the interlamellar domains of LDHs are certainly too basic and deprotonation of the ammonium cation should occur. This basic behavior is confirmed by the fact that all LDHs easily
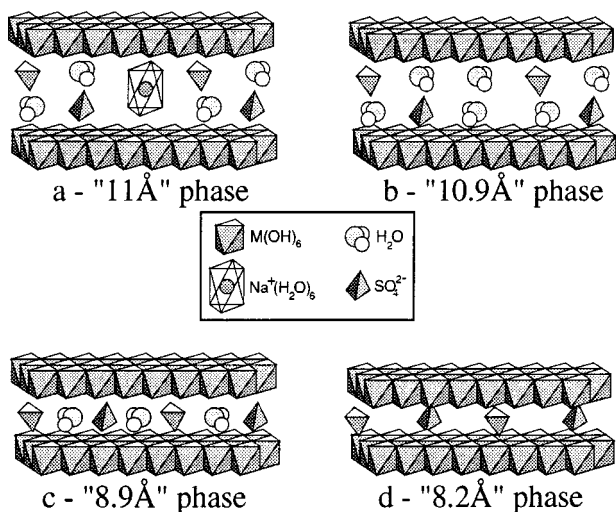
intercalate carbonate anions, but not hydrogeno-carbonate ones.

When [Zn–Cr–SO_4] LDHs are dried in air, interlamellar dehydration can occur. At room temperature, the "10.9 Å" phase (without alkaline cation) is stable at relative humidities of at least 60% RH. At lower values (20–50% RH) the "8.9 Å" phase results from the partial removal of interlamellar water. This 8.9 Å basal spacing corresponds to the size of the sulfate groups without any extra layer of water molecules (Fig. 7c). In contrast, the presence of sodium, octahedrally surrounded with water molecules, stabilizes the "11 Å" LDH at relative humidities as low as 20% RH.

In dry air (0% RH), whether or not the samples contain alkaline cations, low basal spacings ($d \approx 8.2$ Å) are observed. This distance is too low for a free interlamellar sulfate group, but too high for a grafted tetrahedral oxoanion as previously reported (12) for [Cu–Cr–CrO_4] with $d = 7.13$ Å. We assume that when the interlamellar water molecules are removed, the electrostatic interaction induces a deformation of some $M(OH)_6$ octahedra with an apical oxygen of the sulfate group coming closer to the main layers (Fig. 7d). We point out this behavior as a pregrafting process in contrast to the irreversible grafting reaction obtained by heating the material. The pregrafting is in fact reversible, as are all the other previous transformations related to hygrometry. Both "11 Å" and "8.9 Å" phases lead to the same contracted phase; the sodium is probably removed from interlamellar domains under dry air, the resulting sodium sulfate taking place as an amorphous phase at the surface of micro-crystallites.

CONCLUSIONS

This novel synthesis strategy offers important advantages, like accurate control of main experimental parameters. By optimization of the experimental conditions, samples with high crystallinity can be obtained. Depending on the nature of reactants, the washing process, and hygrometry control, four varieties of [Zn–Cr–SO_4] LDHs, which differ by their stacking sequences and interlamellar distances, are selectively obtained. Materials without interlamellar monovalent cations display two varieties with, respectively, 10.9 and 8.9 Å basal spacings. The presence of interlamellar sodium or potassium cations stabilizes a third variety with an 11 Å (resp., 11.3 Å) basal spacing. The dehydration of these compounds leads to a contracted phase with an 8.2 Å basal spacing.

Further studies on this [Zn–Cr–SO_4] system are in progress. The structure of the $^{1.15}_{0.33}$[Zn–Cr–SO_4]$^{10.9}_{3R}$ phase is being studied from PXRD data by the Rietveld method. The thermal evolution of these compounds and the grafting process of sulfate on [Zn–Cr] layers will soon be published.

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