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Abdelaliennadi [a], Mohamed Khaldi [a], Andre de Roy [a] & Jean-Pierre Besse [a]

[a] Laboratoire de Physico-Chimie des Matériaux, U.R.A. C.N.R.S. 444, University Blaise Pascal, F63177, AUBIERE Cedex

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STRUCTURAL RESULTS ABOUT LOCALISATION OF TETRAHEDRAL OXO-ANIONS INTERCALATED IN LAMELLAR DOUBLE HYDROXIDES

ABDELALI ENNADI, MOHAMED KHALDI,
ANDRE DE ROY AND JEAN-PIERRE BESSE
Laboratoire de Physico-Chimie des Matériaux, U.R.A. C.N.R.S. 444,
Université Blaise Pascal, F63177 AUBIERE Cedex

Abstract The structure of two synthetic Lamellar Double Hydroxides belonging to the [Zn-Cr-SO_4] system with basal spacings of 8.9Å and 11Å, is processed by the Rietveld method on PXRD data. The localization of interlamellar species is studied and the presence of co-intercalated alkaline cations is discussed.

INTRODUCTION

Lamellar Double Hydroxides (LDH) are a wide family of minerals and synthetic compounds (1,2). The main frame of their structure consists of brucite-like sheets described as a coplanar association of $M(OH)_6$ octahedra (M=metal). The presence of trivalent cations implies that the sheets are positively charged. The global electrical neutrality is obtained by anionic species distributed with water molecules in the interlamellar domains. These interlamellar species are generally exchangeable in mild conditions, this implies that no strong bonding is established with the host structure. For the same reason the number of water molecules present in the interlamellar domains depends on ambient temperature and hygrometry.

The general formula of a LDH: $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}\ [X^{m-}_{x/m}.nH_2O]^{x-}$ (X=anion) brings to the fore the cationic sheets and the anionic interlamellar domains. Two other important structural properties are the basal spacing of the sheets d(Å) and their stacking sequence ss (1H, 2H, 3R,...) (2-5). An abbreviated notation is used: ${}^{n}_{x}[M^{II}\text{-}M^{III}\text{-}X]^{d}_{ss}$. We prepared compounds belonging to the [Zn-Cr-SO_4], [Zn-Al-SO_4] and [Cu-Cr-SO_4] systems. In this paper, we present structural results about two phases of the [Zn-Cr-SO_4] system.

EXPERIMENTAL

Synthesis

The studied compounds were prepared by the coprecipitation method (2); an aqueous solution of metals salts is slowly added into a reactor containing a large excess of sodium sulfate solution maintained at pH=4.5 by controlled addition of sodium hydroxide under mechanical stirring. The obtained compound is then washed with carbonate-free water to avoid intercalation of carbonate anions. Related to the washing process, we obtained two phases with basal spacing of respectively 8.9Å and 11Å for the main sheets. The "11Å" phase is obtained by direct filtration of the suspension percolated with a few ml of water; the "8.9Å" phase is obtained by a series of centrifugation-washing cycles until the resistivity of washing water is higher than $10^4\Omega$.cm.

The sulfate anions remain exchangeable for the two [Zn-Cr-SO_4] compounds. For example, it is easy to obtain the well known [Zn-Cr-Cl] phase by anionic exchange. We

performed also the synthesis with the sodium sulfate replaced by potassium sulfate; the basal spacing of the "11Å" increases up to 11.3Å.

Chemical Analysis

The two phases display very similar ratios between divalent and trivalent metallic cations. On the opposite they differ by their hydration state and sulfate content. The "11Å" phase contains also sodium while in the "8.9Å" phase only traces were found. The analytical data agree with the following abbreviated formulas:

"11Å" phase: $^{1.47}_{0.32}[\text{Zn-Cr-SO}_4\ \text{Na}_{0.098}]^{11.06}$,

"8.9Å" phase: $^{0.68}_{0.32}[\text{Zn-Cr-SO}_4]^{9.92}$.

Characterisation by PXRD

At this time only LDH minerals could be studied on single crystals (3,4), synthetic LDH are at best microcrystalline, that's why the structural study was performed from PXRD data. The diffractograms were obtained on a Siemens D501 with Cu K_α radiation fitted by a backwards monochromator. The measurements were made in the range 5 - 105° (2θ) with an integrating time of 20s for each 0,04° step. These data were processed by the Rietveld method with a Fourier series representation for the profiles of diffraction lines (6,7).

RESULTS AND DISCUSSION

Structure of the "8.9Å" Phase

Lattice and Space Group

LDH present hydroxylated sheets of hexagonal symmetry with a basal periodicity $a_0 \approx 3{,}1$Å corresponding to the distance of two neighbouring metallic cations. Perpendicular to the sheet, the c_0 parameter corresponds to the distance of two successive sheets and is closely related to the content of interlamellar domains.

All the diffraction line of the "8.9Å" phase can be indexed in an hexagonal lattice of parameters $a_0=3.1202(2)$Å and $c_0=8.922(1)$Å. This lattice agrees with a 1H stacking sequence of the hydroxylated compact planes (AB-AB...). The alternative 2H stacking (AB-BA-AB...) as in sjögrenite-like minerals (4,5), corresponding to $c=2c_0$ has also to be considered. On the opposite, the rhombohedral 3R stacking is excluded. The best results were obtained with a 2H stacking and $P6_3/mmc$ space group.

Fitting of the Structure

Metallic cations are randomly distributed on the 2(a) Wyckoff position. The 4(f) position with $z \approx 0{,}06$ is then the only suitable to generate their octahedral hydroxylated environment.

At this stage a Fourier synthesis shows the presence of interlamellar atoms in a 12(k) position corresponding to atomic triplets at about 2.4Å each another and about 2.9Å of the hydroxyl groups of the main sheets. They were attributed to three oxygen atoms belonging to the same SO_4 group; by geometrical considerations, the sulphur and fourth oxygen atoms are located in 4(e) positions. This disposition generates pair of sulfate groups which fit into each other and thus exclude one another. During the fitting, the occupancy of the 12(k) position increases far beyond the value corresponding to the oxygen atoms of the sulfate groups. So we considered that the oxygen atoms of the interlamellar water molecules were located on the same positions. The reliability coefficients are then $R_I=6{,}1\%$ et $R_{WP}=13{,}2\%$. The structural parameters are reported in Table 1, the Figure 1 displays the observed, calculated, and difference diffractograms.

Description of the structure

The hydroxylated framework is constituted of octahedra in C_{3i} symmetry; the corresponding inter atomic distances and angles are given in Table 2.

To dispose the interlamellar species we put forward a strongly statistical distribution. Related to horizontal main sheets, the same portion of space is occupied either by a SO_4 tetrahedra in C_{3v} symmetry with an upward apex, or by a SO_4 tetrahedra with a downward apex, or by interlamellar water molecules.

Table 1: Atomic positions of the "8.9Å" phase

Atom	position	x	y	z	B_{11} (Å^2)	B_{33}
0.680 Zn/0.320 Cr	2(a)	0	0	0	0.12(1)	2.9(5)
OH	4(f)	1/3	2/3	0.0563(2)	0.29(1)	2.9(5)
0.111 H_2O/0.083 O(2)	12(k)	0.2488(2)	0.4976(4)	0.2989(2)	6.8(5)	2.7(4)
0.083 O(1)	4(e)	0	0	0.1861(2)	3.5(3)	1.3(5)
0.083 S	4(e)	0	0	0.2648(2)	6.7(5)	-2.7(8)

Table 2: Inter atomic distances and angles of the "8.9Å" phase

6 Zn/Cr - OH = 2.07Å	OH - Zn/Cr - OH = 180°	OH - OH = 4.13Å
	OH - Zn/Cr - OH = 81.9°	OH - OH = 2.71Å
	OH - Zn/Cr - OH = 98.1°	OH - OH = 3.12Å
3 S - O(2) = 1.44Å	O(2) - S - O(2) = 108.1°	O(2) - O(2) = 2.33Å
1 S - O(1) = 1.40Å	O(1) - S - O(2) = 110.9°	O(2) - O(2) = 2.34Å
OH - H_2O/O(2) = 2.76Å	OH - H_2O/O(2) = 2.71Å	OH - O(1) = 2.93Å

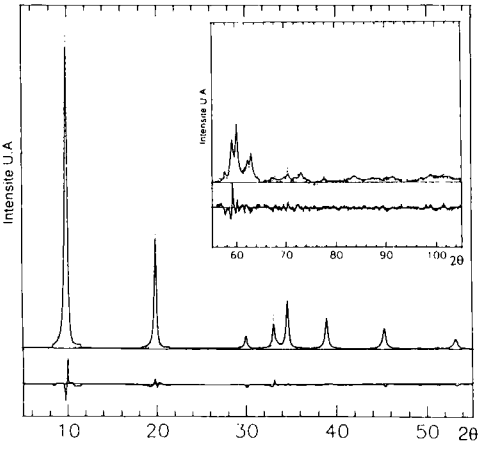

FIGURE 1:
Diffractogram of the "8.9Å" phase.

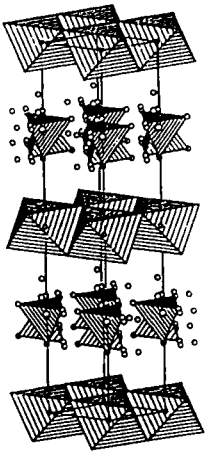

FIGURE 2:
Schematic view of the "8.9Å" phase.

Structure of the "11Å" Phase

Lattice and Space Group

This phase displays supplementary reflections that could only be indexed by taking in account a superstructure with $a=a_0\sqrt{3}=5.407(4)$Å and $c=c_0=11.058(4)$Å corresponding to a 1H stacking. With this lattice all of the reflections are indexed, apart a weak line at 29.6° (2θ). As previously, we considered the 1H and 2H stackings. The best results were obtained with the 2H stacking corresponding to $c=2c_0$; the space group is $P6_3/mcm$.

Disposition of Metallic Cations

The only convenient position for these atoms are the 2(b) and 4(d) Wyckoff positions. The stoechiometry being very close to a $M^{II}/M^{III}=2$ ratio, we first considered that an

ordered disposition of the divalent and trivalent metallic cations on these two crystallographic sites could account for the superstructure $a=a_0\sqrt{3}$. This hypothesis which leads to calculated intensities incompatible with experimental data is also inconsistent with the crystallo-chemical behavior of this phase. So, we considered a disordered disposition of metallic cations.

Disposition of the Hydroxyls

The octahedral environment of metallic cations is obtained with the 12(k) particular position. The construction of octahedra of the same size in C_{3i} symmetry and M-O length in agreement with the ionic radius, implies moreover x=1/3 and z≈0.046. In fact a fit starting at these initial co-ordinates shows only a weak evolution.

Disposition of the Interlamellar Atoms

A Fourier synthesis performed at this step displays the presence of atoms close to the hydroxylated sheets (z≈0.16) in a 12(k) position. As in the preceding structure, they are attributed to triplets of oxygen atoms O(2) belonging to the same SO_4 group. The sulphur atom is then located in 4(e) with z≈0.19. The fourth oxygen of the SO_4 group can be located in 4(e) with z≈0.25 or 2(a) (0,0,1/4); we choosed this last position. This disposition generates pairs of sulfate groups with one common apex O(1). Such positions exclude each another and are thus randomly occupied. During the fit, the occupancy of the O(2) position increases far beyond the expected value. We attributed this behavior to oxygen atoms of water located in a position close to O(2). The fitting was then carried on with an O(2) occupancy fixed at the expected value and oxygen of water molecules in general position 24(l). After this new step of the fit the Fourier synthesis displays a residual maximum in 2(a) already partly occupied by the O(1) atom; it was attributed to the sodium cation not yet introduced in the structure. The final reliability coefficients are then R_I=5.2% and R_{WP}=12.3%. The structural parameters are reported in Table 3, the Table 4 presents the inter atomic distances and angles and the Figure 3 displays the observed, calculated, and difference diffractograms.

Table 3: Atomic positions of the "11Å" phase

Atom	position	x	y	z	B_{11} (Å^2)	B_{33}
(0.680 Zn/0.320 Cr)(1)	2(b)	0	0	0	0.7(1)	4.9(4)
(0.680 Zn/0.320 Cr)(2)	4(d)	1/3	2/3	0	1.0(4)	5.3(7)
OH	12(k)	0.3365(3)	0	0.0458(8)	1.2(5)	5.9(9)
0.320 O(2)	12(k)	0.2507(7)	0	0.8376(3)	3.1(4)	2.9(4)
0.640 O(1)/0.300 Na	2(a)	0	0	1/4	3.7(4)	2.5(4)
0.320 S	4(e)	0	0	0.1851(4)	5.0(2)	3.1(4)
0.330 H_2O	24(l)	0.3728(6)	0.1329(4)	0.1781(2)	5.1(2)	1.6(6)

Table 4: Inter atomic distances and angles in the "11Å" phase

6 (Zn/Cr)(1) - OH = 2.08Å	OH - (Zn/Cr)(1) - OH = 180°	OH - OH = 4.17Å
	OH - (Zn/Cr)(1) - OH = 81.7°	OH - OH = 2.72Å
	OH - (Zn/Cr)(1) - OH = 98.3°	OH - OH = 3.15Å
6 (Zn/Cr)(2) - OH = 2.06Å	OH - (Zn/Cr)(2) - OH = 179.2°	OH - OH = 4.12Å
	OH - (Zn/Cr)(2) - OH = 81.5°	OH - OH = 2.69Å
	OH - (Zn/Cr)(2) - OH = 82.8°	OH - OH = 2.73Å
	OH - (Zn/Cr)(2) - OH = 97.9°	OH - OH = 3.11Å
3 S - O(2) = 1.45Å	O(2) - S - O(2) = 108.6°	O(2) - O(2) = 2.37Å
1 S - O(1) = 1.44Å	O(1) - S - O(2) = 110.4°	O(1) - O(2) = 2.35Å
6 Na - H_2O(1) = 2.38Å	H_2O - Na - H_2O = 166.0°	H_2O - H_2O = 4.72Å
	H_2O - Na - H_2O = 80.2°	H_2O - H_2O = 3.07Å
	H_2O - Na - H_2O = 91.7°	H_2O - H_2O = 3.41Å
	H_2O - Na - H_2O = 109.8°	H_2O - H_2O = 3.92Å
OH - O(2) = 3.12Å	OH - H_2O = 3.05Å	

Description of the Structure

The hydroxylated brucite-like sheets are constituted of two kinds of octahedra. As we postulate a random distribution of metallic cations, the small difference of shape is attributed to the presence of sulfate anion near the octahedra centred on 2(b).

To dispose the interlamellar species, as for the "8.9Å" phase, a strongly statistical distribution has to be used. When a SO_4 tetrahedra is present near an hydroxylated plane, it is separated from the other hydroxylated plane by water molecules.

The sodium ion, in the middle of the interlamellar domain has an environment constituted of water molecules distributed on six pairs of positions excluding one another. Depending on the selected positions, this average environment of six water molecules can be described as a right prism or an irregular octahedra; the inter atomic distances and angles corresponding to this second hypothesis are reported in Table 4. Figure 4 shows a schematic view of the structure pointing out the brucite-like layers and the sulfate groups.

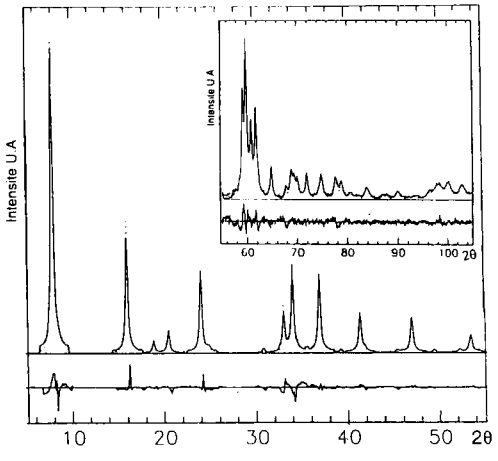

FIGURE 3:
Diffractogram of the "11Å" phase.

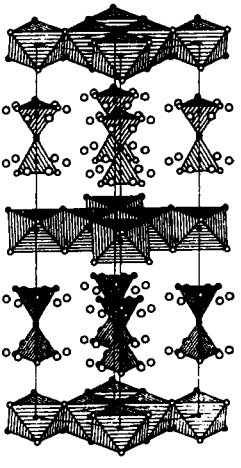

FIGURE 4:
Schematic view of the "11Å" phase.

DISCUSSION - CONCLUSION

Disorder in the Interlamellar Domains

The structural study points out a strong dynamical disorder in the interlamellar domains. This disorder is evidenced by the distribution of the corresponding atoms on positions of low occupancy and the sharing of the same site by several different species (oxygen/water or oxygen/sodium).

It is theoretically possible to distinguish these different species by the use of close but separate positions. We only could perform this process for the positions $O(2)/H_2O$ of the "11Å phase; for the "8.9Å phase, the fit became unstable. It is also possible to suggest an ordering in the interlamellar domains by the use of superstructures of higher order but in the actual state of crystallisation of the studied compounds, the experimental PXRD data does not allow to verify the significance of such hypothesis.

The Superstructure in the "11Å" Phase

In the "8.9Å" phase, the statistical distribution of the metallic cations M^{II} et M^{III} is imposed by the symmetry. For the "11Å" phase, we could not obtain good results with an ordered disposition. Moreover this superstructure appears and disappears reversibly by anionic exchange of sulfate by chloride or by washing out the intercalated sodium sulfate; this is a strong indication of the topotactic nature of these exchange reactions which preserves the random distribution of the metals in the main sheets. The existence of a short range order on metallic cations is however probable for both phases; the experimental PXRD data giving only access to an average structure.

The superstructure in the "11Å" phase is thus attributed to the disposition of interlamellar species and especially the water molecules environment of the sodium ion. The distances between the sodium ion and the water molecule are consistent with those reported for other sodium salts. The size of alkaline ion is a sensitive parameter; the replacement of sodium by potassium causes an expansion of the basal spacing of the sheets; this confirms the localization of the alkaline cation in the interlamellar domains. With potassium, the superstructure is maintained but the crystallinity decreases and we could never obtain a similar phase with lithium ions.

Disposition of the Sulfate Groups

In the two structures, the sulfate groups are disposed in the same way in a C_{3v} symmetry with three oxygen atoms equally close to an hydroxylated sheet. The fourth oxygen atom is in the middle of the interlamellar domain ("11Å" phase), or near the opposite sheet ("8.9Å" phase). The inter atomic distances between the hydroxyl groups of the sheets and the interlamellar oxygen atoms are compatible with the existence of hydrogen bonding.

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