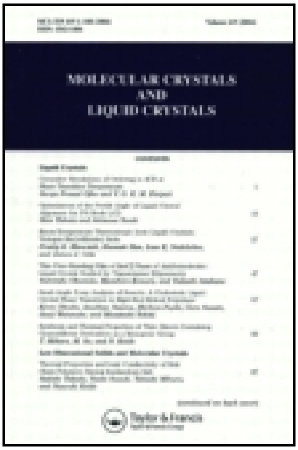

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Lamellar Double Hydroxides

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Lamellar Double Hydroxides

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A general overview on Lamellar Double Hydroxides (LDHs) is given, includind discussions about the structure and preparative methods. A tentative development strategy illustrated by examples is suggested.

Keywords: Lamellar Double Hydroxide; Anionic Clay; Hydrotalcite; Lamellar compounds; Pillared Layered Compounds; Hybrid materials

INTRODUCTION

The term of Lamellar Double Hydroxides (LDHs)[1] is used to designate synthetic or natural lamellar hydroxides with two kinds of metallic cations in the main layers and interlayer domains containing anionic species. This wide family of compounds is also referred to as anionic clays, by comparison with the more usual cationic clays whose interlamellar domains contain cationic species. LDHs are also reported as hydrotalcite-like compounds by reference to one of the polytypes of the corresponding [Mg-Al] based mineral. More seldom are they named pyroaurite-like compounds, lamellar hydroxides of transition metals, mixed metallic hydroxides, double layer hydroxides, hybrid layer structures.

Such minerals are reported since the beginning of this century[2] and the preparation of synthetic phases is generally based on the controlled precipitation of aqueous solutions containing the metallic cations and began with the early work of Feitknecht[3].

Since the end of the sixties, an increasing interest is given to LDHs in the fields of structural characterisation, preparation of new compounds and new preparative methods, anionic exchange properties, electrochemical and magnetic properties, heterogeneous catalysis, pharmaceutical applications, ... Several review papers and references therein give current trends on this subject.[4,5]

The aim of this paper is to picture a general overview on LDHs but we shall mainly point out some particular features about the structure of these compounds, their preparative methods and give a tentative development strategy illustrated by some examples.

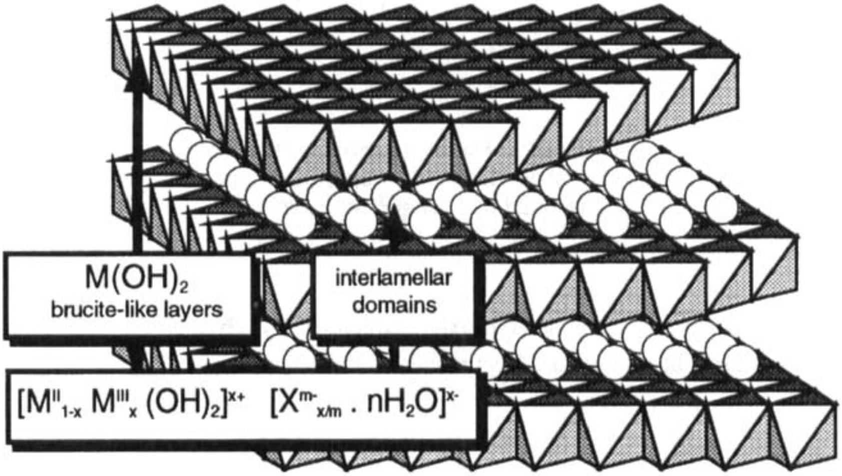

FIGURE 1 Schematic view of the LDH structure and general formula.

STRUCTURAL DESCRIPTION

The LDH structure is based on $M(OH)_6$ octahedral units sharing edges in order to build $M(OH)_2$ brucite-like layers. These octahedral units contain both divalent and trivalent metallic cations; the main layers are therfore positively charged, and the charge density is proportionnal to the trivalent metal ratio $x=M^{III}/(M^{II}+M^{III})$. The whole structure is constituted of the stacking of such layers, intercalating charge-balancing anionic species and water molecules as shown in figure 1 where is also given the heavy general chemical formula, shortened as [M^{II}-M^{III}-X].

LDHs exhibit a high charge density on the main layers. For example, a **x**=1/3 trivalent metal ratio corresponds to one charge for 50Å^2 on each side of the layer, leading to one charge for 25Å^2 in the interlamellar domains.

Trivalent metal ratio

Most of LDH systems accomodate a relatively wide range of trivalent ratios but it is not reported that it could vary from 0 to 1 without main structural changes. The most reliable limits, while larger ranges are sometimes given, are based for example on a clear evolution of lattice parameters and correspond approximatively to $0.2 \leq x \leq 0.4$ (Figure 2). Some authors describe systematically LDHs by the divalent versus trivalent ratio **R**=M^{II}/M^{III}, generally with an integer value (for example **R**=2, **R**=3), corresponding to the relative proportions of metallic cations in the reactants during the preparation. In all cases, it is not obvious that a pure LDH phase is always obtained while the global composition of the precipitate corresponds to the expected value but contains secondary phases such as hydroxides or basic salts of the divalent or trivalent metal.

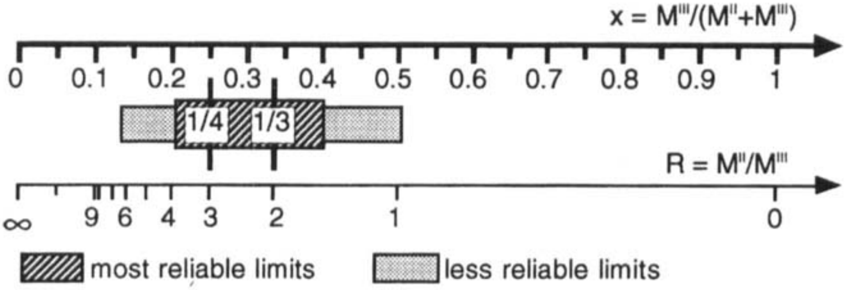

FIGURE 2 Comparison of trivalent metal ratio **x** scale and divalent versus trivalent **R** scale, and corresponding limits for LDH compositions.

The upper limit of trivalent ratio is generally attributed to electrostatic repulsion between neighbouring trivalent metals in the layers which is unavoidable if **x**>1/3 and also to repulsion between the charge-balancing anionic interlamellar species. The lower limit could correspond to a too high main distance between these interlamellar anions leading to a collapse of the interlamellar domains. The structure of the α-variety of divalent metals hydroxides with neutral $M(OH)_2$ sheets and interlamellar domains containing salts or basic salts and water molecules seems to be close to a LDH structure with **x**=0 but, as far as we know, compared to regular LDH structures there is a solution of continuity in the values of **x**.

The metallic cations are arranged in the layers on an hexagonal framework of $\mathbf{a}_0$ parameter. For particular values of **x**, superstructures can be expected by ordering of divalent and trivalent cations. In hexagonal symmetry, the solutions are given by the relation $1/\mathbf{x}=(\mathbf{a}/\mathbf{a}_0)^2$ where **a** is any metal-metal distance in the hexagonal framework. The first solutions are **x**=1/3, 1/4, 1/7, 1/9, 1/12, 1/13, ... The survey of experimental data show that the existence of such superstructures seem clearly evidenced only in a few cases. In other cases, the use of a stoechiometric formula is only a simplified formalization and in fact, the studied compounds are essentially nonstoichiometric with a random distribution of metallic cations in the layers. On the contrary, a particular value can be systematically observed in some systems, for example **x**=1/3 in [Zn-Cr] based LDHs. Such particular values are also often reported in minerals, mainly with **x**=1/3 and **x**=1/4 (figure 2).

Metallic cations in the layers

The divalent and trivalent metallic cations found in LDHs belong mainly to the third and fourth periods of the periodic classification of the elements:

- divalent cations	Mg, Mn, Fe, Co, Ni, Cu, Zn,
- trivalent cations	Al, Mn, Fe, Co, Ni, Ga.

The ionic radius are in the range 0.65 - 0.80 Å for divalent cations and 0.62 - 0.69 Å for trivalent ones (with the main exception, Al: 0.50Å).

Higher ionic radius (Ca, Cd and Sc, La) seem to be incompatible with the formation of true brucite-like layers. LDHs can also be obtained with a Li-Al monovalent-trivalent and Co-Ti divalent-tetravalent associations or with more than two different cations in the layers; this is also generally observed in LDH minerals containing more or less minor elements.

Structure of the layers

In LDHs, the octahedral environment of metallic cations is far from the regular polyhedron. The octahedra are strongly flattened along the stacking direction, lowering the symmetry from O_h to D_{3d}, as illustrated on figure 3 for a [Zn-Al] based LDH. The higher is the mean metallic ionic radius, the more flattened are

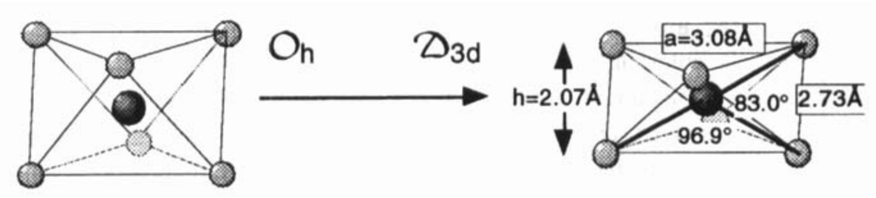

FIGURE 3: Flattening of the $M(OH)_6$ octahedron in a [Zn-Al] LDH.

the octahedra with a lowering of the layer thickness **h** and an increase of the distance **a** between metals — which is the same as between OH groups on same side of the layer. This evolution is illustrated in table I with results from X-ray Rietveld structure refinement, for two [Zn-Al] and [Zn-Cr] based LDHs. The comparison of calculated and observed M-OH distances show that a simple geometrical model based on ionic radius is not able to give quantitative predictions. It also appears clearly that the hydoxyl groups on each side of the main layer do not build a really close-packing layout with such high OH-OH distances (≈3.1Å).

TABLE I Structural data about the layers of two [Zn-Al] and [Zn-Cr] based LDHs; distances are in Å and angles in degrees.

composition of main layers	$Zn_{3/4}Al_{1/4}(OH)_2$	$Zn_{2/3}Cr_{1/3}(OH)_2$
mean M^{II}-M^{III} ionic radius	0.68	0.72
M-OH distance (calc. / obs.)	2.04 / 2.053	2.08 / 2.053
a (mean M-M distance)	3.083	3.120
h (along C_3 axis)	2.071	2.020
OH-OH distance (same / alter. side)	3.083 / 2.729	3.120 / 2.707
OH-M-OH angle (same / alter. side)	96.9 / 83.0	98.1 / 81.9

If the radius of one of the metallic cations becomes too high, the octahedral coordination is lost by opening of one side of the octahedron on the interlamellar domain leading to additional coordination with one interlamellar water molecule. The symmetry around the metal is lowered from D_{3d} to C_{3v}. Such a behaviour is observed in minerals from the hydrocalumite group. For [Ca-Al] based layers, three different distances in a short range of are observed around calcium: 3 Ca-OH at 2.375Å, 3 Ca-OH at 2.455Å, and 1 Ca-OH_2 at 2.497Å.

Interlamellar anions

In LDHs, the interlamellar domains contain anions, water molecules and sometimes other neutral or charged moieties. One major characteristic of LDHs is that, in most cases, only weak bondings occur between these interlamellar ions or molecules and the host structure. A great variety of anionic species can therefore take place between the layers, during the formation of the lamellar structure, or by further anionic exchange.

These anions can belong to:

- halides:	fluoride, chlorides,...
- oxo-anions:	carbonates, nitrates, sulfates, bromates, ...
- oxo & polyoxo-metallates:	chromates, dichromates, $(Mo_7O_{24})^{6-}$, $(V_{10}O_{28})^{6-}$, ...
- anionic complexes:	ferro & ferricyanide, $(PdCl_4)^{2-}$, ...
- organic anions:	carboxylates, phosphonates, alkyl sulphates, ...

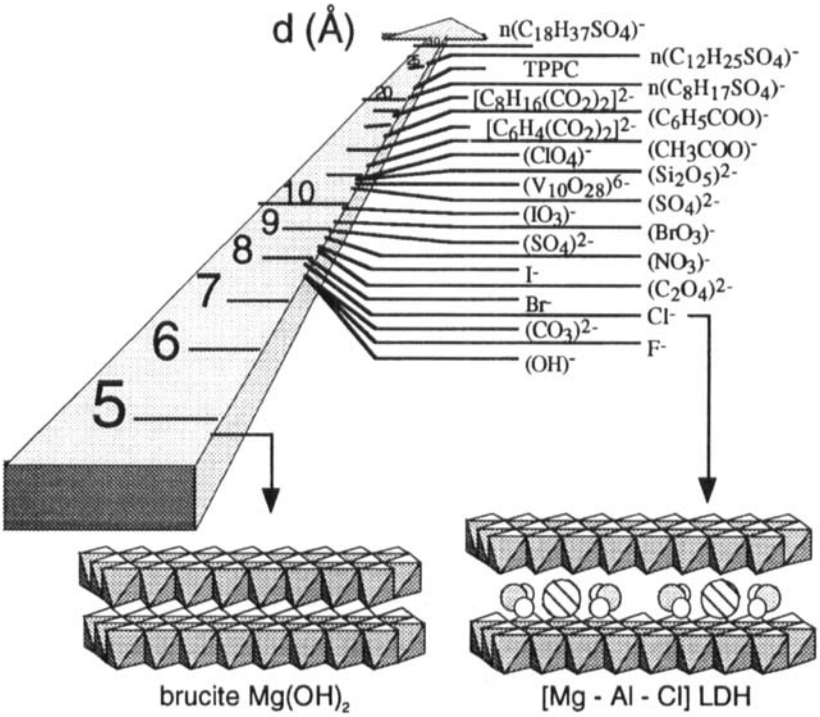

FIGURE 4 Evolution of the basal spacing with intercalated anions.

In relation to the size, charge and layout of these interlamellar species, the basal spacing of the layers is dramatically modified as shown in figure 4 which gives a selection of inorganic and organic species. The most remakable features are:

- the large gap between brucite and the smallest basal spacings in LDHs, corresponding to the intercalation of an interlamellar monolayer,
- the small distance range for a series of small anions — hydroxyl, fluoride, carbonate, chloride, attributed to a "levelling" effect of water molecules,
- the clear separation between inorganic anions intercalated LDHs with basal spacings lower than 15Å, even for species such as the decavanadate, and hybrid LDHs intercalating organic anions and displaying distances higher than 15Å.

Interlamellar structure

The structure of interlamellar domains is more difficult to characterize than the main layers. With small anionic species, such as halides and carbonates, and up to sulphate-containing LDHs with a basal spacing of 11Å, a regular stacking of the layers is observed on X-ray diffractograms. With bulky anions, in most cases the stacking of the layers displays no more long-range ordering (turbostratic effect) and the diffractograms show only lines relative to the basal spacing and to the structure of the main layers.

TABLE II Rietveld structure refinement of a [Zn-Cr-Cl] LDH.

space group R-3m	a = 3.124 Å	reliability: R_I = 4.53 %
3R stacking	c = 23.29 Å	R_{WP} = 13.25 %

atoms	site	x	y	z	B_{11}(Å^2)	B_{33}(Å^2)
2 Zn, 1 Cr	3 (a)	0	0	0	2.4 (2)	5.2 (4)
6 OH	6 (c)	0	0	0.3810 (2)	3.6(2)	4.8(2)
1 Cl, 2 H_2O	18 (g)	0.269 (3)	0	1/2	15.7 (4)	2.45 (3)

We give here as an example, the results of X-ray Rietveld structure refinement on a [Zn-Cr-Cl] LDH (table II). The same R-3m space group was used for the first structural resolution on a monocrystalline LDH mineral.[6] This space group is very "low cost" with only one refinable atomic position parameter for the main layers and one more for the interlamellar domain where chloride and oxygen of water molecules are randomly distributed on a high multiplicity position around the C_3 axis. As reported on figure 5, the hydroxyl groups are facing one another between two succesive layers and the layout of interlamellar species is in agreement with hydrogen-bonding onto the main layers.

This 3R rhombohedral stacking is also reported with other interlamellar halides or with carbonates. For LDHs intercalating anions of tetrahedral shape such as sulphate, the structures are described in hexagonal space groups ($P6_3/mmc$ and $P6_3/mcm$) leading to a 2H stacking of the layers.[7]

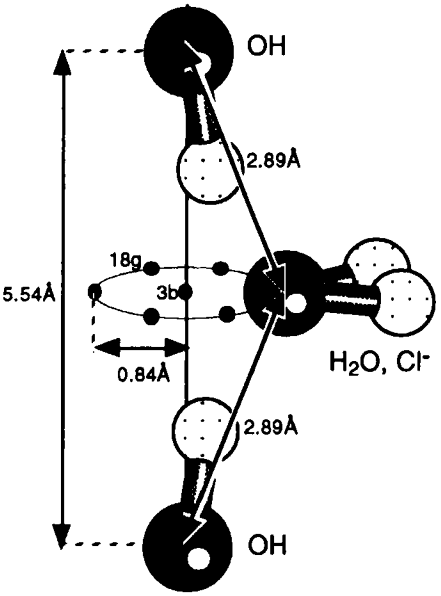

FIGURE 5 Disposition of interlamellar species in a [Zn-Cr-Cl] LDH.

A nomenclature for LDHs

A LDH phase is mainly described by its chemical formula, the basal spacing of the layers and the symmetry of the stacking sequence. We have shown that the heavy general formula given in figure 1 could be shortened as $[M^{II}\text{-}M^{III}\text{-}X]$. We propose now an extended symbolic notation ${}^{n}_{x}[M^{II}\text{-}M^{III}\text{-}X]^{d}_{ss}$ constituted of three parts:
- the qualitative chemical data between brackets, with divalent-trivalent anion symbols, in this order and separated by hyphens,
- on the left side, quantitative chemical data: trivalent metal ratio **x** and hydration state **n** based on a $M(OH)_2$ formula,
- on the right side, structural data: basal spacing **d** of the layers in Å and their stacking sequence ss (3R, 2H, ...).

A great adaptability can be expected from this notation by the use of all or part of the full symbol, for example in a ${}_{0.33}$[Zn-Cr-Cl] phase, the [Zn-Cr] symbol refers to the framework regardless to the nature of the interlamellar anion.[4]

PREPARATION OF LDHs

LDHs exist as minerals with names depending on their composition and the symmetry of polytypes[8] for example:

- Hydrotalcite, Manasseite	Mg, Al
- Sjögrenite, Pyroaurite, Coalingite	Mg, Fe
- Stichtite, Babertonite	Mg, Cr
- Takovite	Ni, Al or Ni, Ni
- Reevesite	Ni, Fe
- Woodwardite	Cu, Al

where interlamellar anions are mainly carbonates, and sometimes sulphates or chlorides. Their composition is generally complex with minor elements and associated phases; it is therefore necessary to prepare synthetic phases for an extensive study of LDHs.

Coprecipitation method

This is the most common preparative method of LDHs. It is based on the slow addition of a mixed solution of divalent and trivalent metals salts in adequate proportions into a reactor containing water. A second solution (alkaline solution) is added in the reactor in order to maintain the pH at a selected value leading to the coprecipitation of the two metallic salts. A schematic experimental device is given on figure 6 — all of the sub-systems are not required for every experiment.

Mechanism of coprecipitation

The mechanism of coprecipitation is ideally based on the condensation of hexa aqua complexes in solution in order to build the brucite-like layers with a distribution of both metallic cations and with solvated interlamellar anions. The look of the precipitates and X-ray diffraction characterizations show that the co-formation of the main layers and interlamellar domains takes place at a very early stage of the process without clear "delaminated" state of the layers.

Origin of interlamellar anions

If obviously the metallic cations in the obtained LDH phase are issued from the metallic salts solution, the origin of interlamellar anions has to be discussed. If these anions are the counter-anions of the metallic salts they come

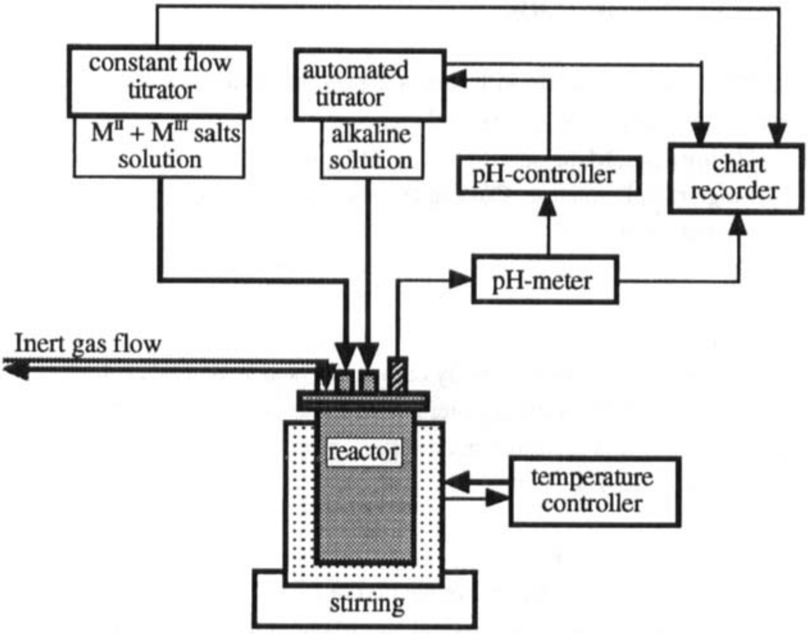

FIGURE 6: Exprimental device for the preparation of LDHs by the coprecipitation method.

from the same solution. If the preparation is performed at very high pH values, the interlamellar anion can be the hydroxyl anion coming from the alkaline solution. When the alkaline solution is a sodium or potassium carbonate solution, the intercalated anion is the carbonate because of its high selectivity for LDHs interlamellar domains. Moreover, when the preparation is performed at relatively high pHs, one have to work under CO_2-free conditions in order to avoid carbonate contamination. Another way to intercalate a given anion is to prepare a solution of this anion in the reactor prior to the beginning of the coprecipitation.

So,we see that there is often competition between several anionic species and the control of experimental conditions can lead to the selective intercalation of one of them as the primary interlamellar anion. Secondary interlamellar anions can replace them by further treatments such as anionic exchange (*vide infra*).

Experimental parameters

Depending on the precipitation conditions, one can generally obtain well crystallized LDH phases or quasi amorphous materials. Some of these experimental parameters are obvious like:

- temperature in the reactor,
- pH of the reactive medium,
- concentration of metallic salts solution,
- concentration of alkaline solution,
- flow rate of reactants,
- aging of the precipitate,

other parameters are less obvious, such as:

- accumulation of electrolytes in the reactive medium,
- hydro-dynamics of the dilution of reactive species, related to the stirring mechanism, geometry of the reactor including reactants injection pipes,
- complexation state of the metallic cations which, depending on the previous history of the metallic salts solutions, can give rise to a great number of different $M(OH_2)_u(OH)_vX_w$ charged monomers and also to oligomers.

We actually perform in collaboration with the LURE *in situ* XAFS measurements during the preparation of LDH phases in order to characterize the evolution of the environment around metallic cations.

In order to obtain well organised phases, the operating conditions have to be optimized for each system. In all cases synthetic LDHs are obtained as microcrystalline platelets generally aggregated in a "rose des sables" morphology as shown by SEM. The low BET surface measurements (15-18 m^2g^{-1}) are in good agreement with the external surface of the platelets.

Other preparative methods and comparison

Induced hydrolysis

The induced hydrolysis[9] is a two step method. The trivalent metal hydroxide is first precipitated by an alkaline solution. The second step consist in the slow addition of this precipitate on the divalent metal salt at constant pH inducing a controlled release of trivalent metal species and formation of the LDH phase.

Salt - oxide method

This method[10] is based on the slow addition of a solution of trivalent metal salt (acidic species) on an aqueous suspension of the divalent metal oxide (basic species). The slow dissolution of divalent oxide induce here a controlled release of divalent metal species and formation of the LDH phase. No control of the pH is needed here; this is a main simplification of the experimental device.

Comparison of preparative methods

While the three methods — coprecipitation, induced hydrolysis and salt-oxide, seem to be quite different, the mechanism for the construction of the LDH structure is probably the same; this can also be extended to the reconstruction method described later. In all cases the aim is to obtain in the reactive medium each constituent of the future LDH structure in the most appropriate concentration and association state. The "best method" does not exist; depending on the studied system and the final use of the product, one or another method can be chosen.

DEVELOPMENT STRATEGY FOR LDHs

LDHs are used in several fields from catalysis to medical use. They present in fact a much broader spectrum of potential applications related to their membership to the more general family of compounds designated as Pillared Layered Structures[11] (PLS), besides smectite clays, pillared phosphates and phosphonates, layered oxides and oxy-halides, ...

The major interest of PLS and particularly LDHs lies in the fact that these phases are a good example of materials by design whether by modification of the host-structure chemical composition, or by chemical or structural modification of the guest-species domains. Relating to the degrees of freedom given by the nature and proportions of metallic cations in the layers, nature of interlamellar anionic species, structural an textural modification, LDHs appear as a huge "reservoir" of new materials at this time very partly explored where the continuous ranges of compositions lead to tunable chemical and physical properties.

LDHs can be used "as prepared" for their intrinsic physical or chemical properties, or after further treatements that we shall call "post-synthesis modifications".

Use of as prepared LDHs

LDHs are used for their acido-basic properties for example as antacids for medical use and as additive in polymers for acid-residue scavenging.

The controlled release of active species is generally related to the anionic exchange properties and concern mainly interlamellar organic anions, but main layers metallic cations are also involved as for iron deficiency medical treatment.

Anionic exchange properties are also used for anionic pollutant trapping. Interesting results are actually obtained for the removal of Cr^{VI} traces in water while the surface absorption appears to play the main part.

The physical properties of LDHs have also applications: related to their particular rheological properties, LDHs are used as additives in drilling fluids.

Another main physical property of LDHs is their high ionic (mainly protonic) conductivity related to the high mobility of interlamellar water molecules *via* the hydrogen-bonding network with the main layers hydroxyl groups (figure 5). An application is the realization of low cost humidity sensors[12] by the screen printing technique with a [Zn-Al-Cl] based ink as shown on figure 7.

LDHs are also interesting materials to study for their tunable magnetic properties. For example in a [Ni-Cr] LDH, anti-ferro and ferromagnetic interaction are expected between cations of the same layer (intra-layer interactions) and also between cations belonging to different layers (inter-layer interactions). An evolution from a ferromagnetic to a ferrimagnetic behaviour coud be observed with increasing x trivalent ratio values.[13]

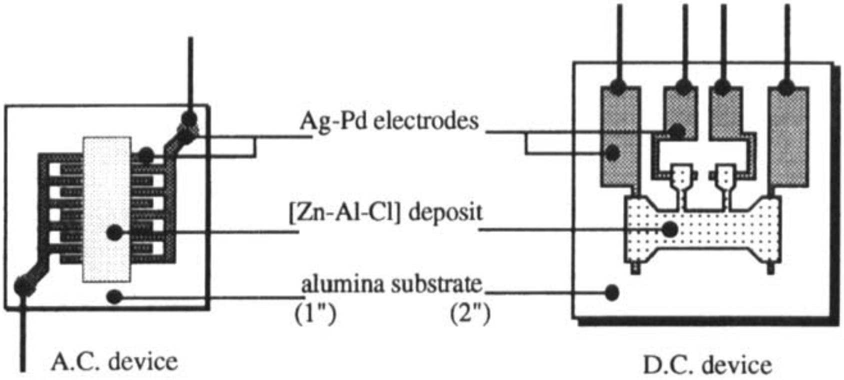

FIGURE 7 Screen-printed [Zn-Al-Cl] based humidity sensors.

Post-synthesis modifications of LDHs

Subsequent treatements can modify as prepared LDHs. The most obvious is anionic exchange, but moderate thermal treatements and even washing and drying processes can also give rise to new materials.

Anionic exchange

The LHD is stirred with a solution containing the new anion to intercalate. There is generally no co-intercalation of two different anionic species and the selectivity of a LDH host structure for a couple of anions display the behaviour observed on figure 8 with only two discrete values for the basal spacing and a sharp variation in the composition of solid.[14] The small amount of foreign anion out of the hysteresis loop can be attributed to surface absorbed species. For others systems, a more progressive evolution is evidenced.[15]

Some exchange reactions are difficult to complete an two phases with different basal spacings can remain while increasing the exchange time and renewing the exchange solution. This is an indication of possible heterogeneity in the primeval LDH phase.

For some anions, the exchange solution pH is of outstanding importance: the nature of polyoxometallates is generally pH-dependent, for example $(CrO_4)^{2-}$ /$(Cr_2O_7)^{2-}$ equilibriums; intercalated carbonates are generally very difficult to exchange but the reaction is favoured at low pH. In all cases it is however

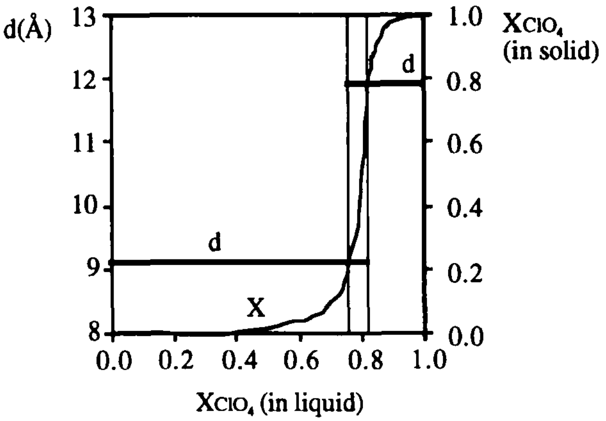

FIGURE 8 Evolution of basal spacing d and anionic composition $X_{ClO_4}=ClO_4/(ClO_4+NO_3)$ of a [Zn-Cr] LDH with anionic composition of the surrounding liquid phase (from [14]).

obvious that the acido-basic properties of the exchange solution on one hand, and of the interlamellar medium on the other hand, are not the same.

Washing and drying process

After preparation, the LDH precipitate has to be separated from the reactive medium, washed and dried. The following example corresponding to $_{0.33}$[Zn-Cr-SO$_4$] phases (figure 9) shows that the operating conditions can strongly modify the obtained LDH.

In the 3D diagram where are reported the basal spacing **d**, the temperature of thermal treatment **t** and the relative humidity at room temperature **%RH**, five structural varieties could be identified.

- a 2H "11Å" phase which intercalate the sulphate groups and also alkaline cations (sodium or potassium) surrounded by water molecules,
- a 3R "10.9Å" phase without alkaline cations obtained by wahing of the previous one,
- a 2H "8.9Å" phase corresponding to a partial dehydration of interlamellar domains,
- a 3R "8.3Å" phase corresponding to severe dehydration at room temperature.

All of these phases can be reversibly obtained. This points out that the washing and drying processes can be considered as post-synthesis treatments. In this example, the "as-prepared" phase in the reactive medium is always the 2H "11Å" phase.

Grafting of anions onto LDH layers

The last 3R "7.1Å" phase on figure 9 diagram corresponds to an irreversible transformation of the structure with no more rehydration or further anionic exchange capacity.

Such transformations are related to moderate thermal treatments of several LDHs intercalating tetrahedral oxo-anions such as sulfates, selenates, phosphates, chromates and dichromates, ... The low basal basal spacing is incompatible with the presence of "free" $(XO_4)^{2-}$ anions. The only consistent hypothesis is the grafting[16] of the anions onto the LDH layers with elimination of water molecules leading to neutral layers. The new phase has to be considered as a layered oxy-hydroxy-salt and belongs no longer to the LDHs family. This behaviour was also recently evidenced by XAFS.[17]

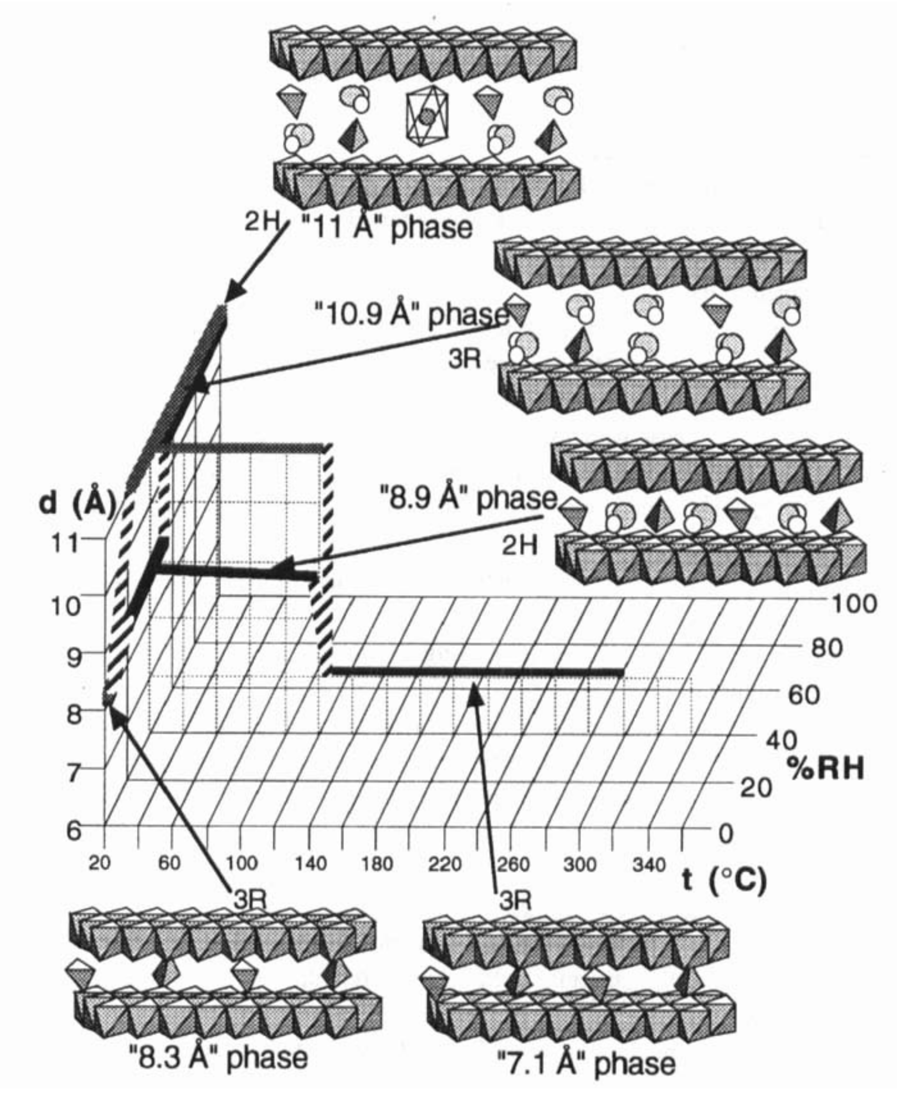

FIGURE 9 Structural transformations of a $_{0,33}$[Zn-Cr-SO$_4$] LDH related to the washing process, the relative humidity of atmosphere **%RH**, and the thermal treatment **t** °C.

Similar grafting reactions were also evidenced on [Zn-Cr] and [Zn-Al] LDHs intercalating silicic acid anionic layers.[18] In this case, interlamellar polymerization of anionic species and grafting on the main layers occur simultaneously.

Hybrid LDHs

LDHs intercalating organic anions are prepared by anionic exchange or by direct synthesis. In this particular case is obtained an hybrid stacking of inorganic-organic layers.

For organic molecules with one anionic function such as alkyl sulfates or sulfonates, or with aromatic rings (naphtalene or anthraquinone sulfonates) one obtain hydrophobic double layers. Inbetween these organic domains may be intercalated neutral organic species such as alcohols, giving rise to a subsequent interlamellar swelling.[10]

With one anionic function at each end of an organic molecule, for example dicarboxylates such as succinate, adipate, sebacate, ..., the interlamellar anion acts as a pillar and the observed evolution of basal spacings for a series of different anions is in good agreement with the calculated values.

This pillaring effect is also observed with macrocyclic molecules such as *para*-tetracarboxylate-phenylporphyrins[19] (pTCPP) with a 22.5Å basal spacing as shown on figure 10; for the ortho-subtituted molecule (oTCPP), the basal spacing is reduced to 18.5Å and a different layout is suggested.

Such hybrid materials are very promising for applications such as:

- nanoscale reactors with stereoselective reactivity,
- substrates for catalytically active species and electro-active molecules,
- templates for interlamellar bidimensionnal polymerization.

A new challenge with hybrid LDHs is to graft the organic molecules onto

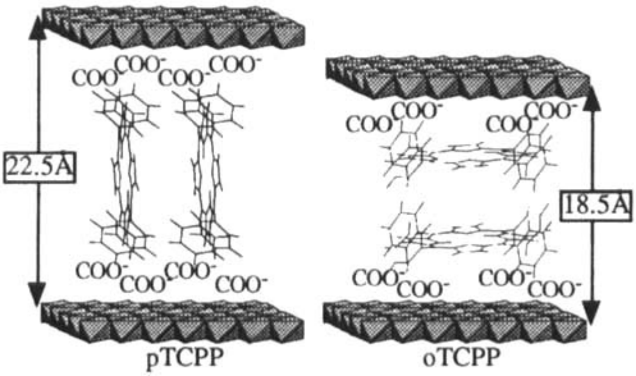

FIGURE 10 Two different layouts for *para* and *ortho*-tetracarboxylate-phenylporphyrins in [Zn-Al] LDHs.

the brucite-like layer by substitution of hydroxyl groups by the anionic function or by condensation with other functions. A model for such novel phases is, for example, the structure of the layered copper hydroxy-acetate.

Calcination and reconstruction

For most of LDHs, during progressive calcination, are first lost surface water molecules, interlamellar water molecules and last, roughly in the 200-350°C temperature range, water corresponding to the dehydroxylation of the main layers leading to the collapse of the structure. For some hybrid LDHs, this step takes place before the pyrolysis of organic species giving an hybrid layered compound with amorphous inorganic oxide layers.

Depending on the nature of interlamellar species, they can definitively remain (phosphates or oxo-metallates), or be removed at more or less high temperatures (sulphate or chloride), or lost at relatively low temperature, during the dehydroxylation step, such as carbonates.

After dehydroxylation are obtained quasi-amorphous mixed oxides which crystallize progressively at higher temperatures generally as a $M^{II}M^{III}_2O_4$ spinel-like phase and divalent metal oxide. The ill-organized mixed oxides display generally three broad diffraction bands corresponding to the future strongest lines of the spinel-like phase; they are therefore called pre-spinel oxides and it is not impossible that the thansformation from the layered structure to this oxide phase could be topotactic. These mixed oxides display generally a relatively high specific surface (up to 150 m^2g^{-1}) compared to the as prepared LDHs (≈15 m^2g^{-1}). Higher specific surfaces (250 m^2g^{-1}) can be obtained by thermal treatment of LDHs intercalating anionic complexes or organic molecules.

After moderate calcination to pre-spinel oxide, a further step is the reconstruction of a LDH phase in a solution containing a new anion to be intercalated. By this method, polyoxometalates could be intercalated.[20] Some authors postulate a "memory-effect" of the previous structure, but this seems not absolutely needed since a LDH phase could be prepared from a mixture of divalent and trivalent metals.[21] The reconstruction process can also be performed in air, which supply water molecules and carbonates; in this case, the same anion being re-intercalated, the only interest is to modify the textural properties of the primitive LDH. The textural properties are also modified by reconstruction in solvents other than water, this evidences a template effect of the solvent on the spatial organization of the regenerated microcrystallites giving rise to meso-scale porosity.[22]

Redox modifications

We only give here a few examples.

LDHs can be involved in redox reactions by means of electroactive interlamellar species; electronic exchanges with adequate metallic cations could also occur.[23]

The optimisation of Cd-Ni batteries is of major industrial importance. LDH phases appearing during their cycling, the efficiency could be optimised by the use of materials containing additional metals, for example [Ni-Co,Al-CO_3] phases.[24]

LDHs can also be precursors for divided oxides and metals. For example, from [Ni-Cr-CO_3] nickel oxide and the spinel-like phase are obtained by calcination. By reduction under hydrogen or in ethylene-glycol, it is possible to prepare mixed metallic nickel and chromium III oxide as submicronic particles.

Cr^{III}-containing LDHs give rise to the formation of chromates by moderate heating, generally in the 200-350°C range, but we observed oxidation to Cr^{VI} from temperatures as low as 100°C in [Mg-Cr-CO_3].

The palladium chloride square planar complex $(PdCl_4)^{2-}$ could be intercalated in a [Zn-Al] matrix. Depending on the solvent (water or ethanol) nanoscale particles of metallic palladium could be obtained as a result of a slow hydrolysis process.

CONCLUSION

LDHs were identified as minerals at the beginning of the century and prepared as synthetic compounds more than fifty years ago. Succeeding to the first structural determinations of the late sixties and early seventies, an increasing interest is since given to these compounds leading to applications in various domains.

We have seen that LDHs are based on a very simple structural model, but many variations can occur around it.

The combination of different main layers compositions, different intercalated species, and different structural varieties constitute a very rich chemical and structural domain at this time very partly explored. This give rise to a great number of novel materials with tunable chemical and physical properties.

Moreover the concept of post-synthesis modification appears as very appropriate for LDHs; in fact, *via* different treatments, a LDH can be the precursor of another LDH or of another non-LDH phase or material of controlled texture and with a new set of physico-chemical properties.

When the layered structure is still present, a main goal to reach is a comprehensive wiew of the pillaring chemistry describing on one part, the interactions between the main layers and the guest species, and on the other part the interactions between these guest species.

In this context, the emergence of new classes of materials can be expected in the next few years.

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