



A new nanostructured material based on fluorophosphate incorporated into a zinc–aluminium layered double hydroxide by ion exchange

EL HASSAN ELKHATTABI¹, MOHAMED LAKRAIMI², MOHA BERRAHO¹,
AHMED LEGROURI^{3,4,*}, RADOUAN HAMMAL⁵ and LAYLA EL GAINI¹

¹Faculté des Sciences Semlalia, Cadi Ayyad University, BP 2390, 40000 Marrakech, Morocco

²Ecole Normale Supérieure, Cadi Ayyad University, BP 2400, 40000 Marrakech, Morocco

³International University of Grand-Bassam, BP 564, Grand Bassam, Côte d'Ivoire

⁴Al Akhawayn University, BP 104, 53000 Ifrane, Morocco

⁵Faculté des Sciences, Chouaib Doukkali University, BP 20, 24000 El Jadida, Morocco

*Author for correspondence (legrouri.a@iugb.edu.ci)

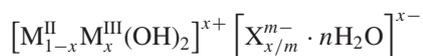
MS received 24 April 2016; accepted 16 September 2016; published online 25 July 2017

Abstract. Layered double hydroxides (LDHs), also called anionic clays, consist of cationic brucite-like layers and exchangeable interlayer anions. These hydrotalcite-like compounds, with Zn and Al in the layers and chloride in the interlayer space, were prepared following the coprecipitation method at constant pH. The effect of pH, aging time and anion concentration on the intercalation of fluorophosphate (PO_3F^{2-} , FP) in the [Zn–Al] LDH was investigated. The best crystalline material, with high exchange extent, was obtained by carrying out the exchange at 25°C in a 0.03 M FP solution at pH 7 with at least 42 h of aging time. A mechanism for the FP intercalation was confirmed by X-ray diffraction, infrared spectroscopy and thermogravimetry (TG) analyses (TG and DTG curves).

Keywords. Nanostructures; precipitation; Fourier-transform infrared spectroscopy; X-ray diffraction; electron microscopy.

1. Introduction

Layered double hydroxides (LDHs) date back to the discovery of the mineral hydrotalcite, whose chemical formula was determined in 1915 by Manasse [1]. Its structural features were first elucidated in the 1960s by Allman [2] and Taylor [3,4] using single-crystal X-ray diffraction (XRD) technique. These materials are also referred to as hydrotalcite-like compounds or anionic clays [5–7]. The basic structure of their layers is similar to that of brucite, $\text{Mg}(\text{OH})_2$, with some hydroxide ion–octahedrally coordinated cations (M^{II}) being isomorphously substituted by trivalent metal ions (M^{III}) [2–4]. The positive charge acquired by the layers is then balanced by intercalation of anions, which are usually hydrated, between the layers. Their chemical formula may be represented by:



and abbreviated as $[\text{M}^{\text{II}} - \text{M}^{\text{III}} - \text{X}]$.

The interlayer exchangeable species may be simple or complex organic or inorganic anions. Their intercalation may be achieved by directed synthesis, ion exchange or by reconstruction from thermally treated LDHs, which is based on the memory effect of these compounds.

The diversity and the proportions of di- and tri-valent cations as well as the intercalated anions lead to a large variety of materials with diverse formulations. This has opened the door for a wide range of applications and these materials continue to be the subject of investigations dealing with the preparation, modification and characterization of novel LDHs as well as the exploration of innovative applications, particularly as functional nanomaterials. The versatility of LDHs and the possibility to tailor them allowed for their use in a vast number of potential applications, mainly in the form of powders or thin films, such as in catalysis, drug delivery, separation technology, biomaterials, environment protection, polymer additives, flame retardants, etc.

The research activities in the area of LDHs continue to expand and the number of related papers and patents continues to grow at an exponential rate. Figure 1 presents the evolution of the number of articles and patents produced during the last 40 years according the Google Scholar website. The search, carried out by one of the authors on 8 October 2015, used all three words ‘layered double hydroxide’. In addition, several books and review papers were devoted to these promising materials [5–13].

The outcome and extent of ion exchange in LDHs is governed by several concomitant phenomena and experimental conditions. Some of these are the layer composition (anion

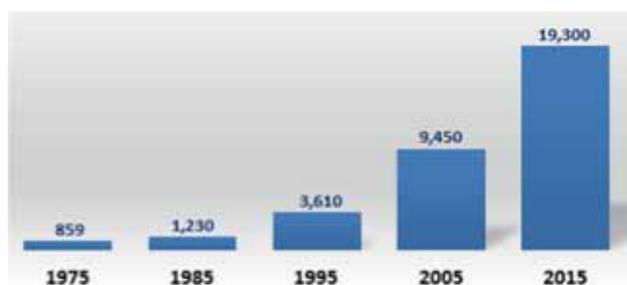


Figure 1. Number of articles and patents given by Google Scholar Search using all the keywords 'layered double hydroxide' on 24 April 2016.

exchange capacity), the affinity for the incoming anion, the nature of the exchange medium, the pH, the temperature, the anion-LDH contact time, etc. Like in natural hydrotalcite, LDHs have a great affinity for the carbonate ion and their manipulation needs to occur under inert atmosphere to avoid reaction with atmospheric CO_2 .

This paper presents the investigation carried out on the interaction between a chloride containing [Zn-Al] LDH and the fluorophosphate ion (PO_3F^{2-} , FP). This work constitutes a continuation of research activities carried out on the interaction between phosphates and LDHs [14,15]. The main objective is to obtain the value of phosphates, for which Morocco is the largest producer in the world. In addition, the understanding of the mechanisms of LDH-phosphate interaction may lead to environmental applications. In a previous research, the FP ion was intercalated directly and by ion exchange from a nitrate ion containing LDH [15].

The synthesis and characterization of an FP-intercalated LDH, [Zn-Al-FP], prepared by ion exchange via a chloride precursor, are presented. Data on the effect of pH, aging time and anion concentration on this intercalation are discussed. The optimization of the intercalation process and the localization of the phosphate ion in the interlayer space are studied by XRD, infrared spectroscopy (IR) and thermogravimetry (TG) and discussed in light of the induced interlayer spacing change.

2. Experimental

2.1 Materials

The [Zn-Al-Cl] precursor was prepared by coprecipitation at a constant pH from a homogeneous mixture of ZnCl_2 and AlCl_3 aqueous solutions, with a molar ratio of 0.33. The mixture was slowly introduced under stirring into a reactor containing 250 ml of freshly decarbonated water. The pH of the solution was maintained at 9 by the simultaneous addition of 1.0 M NaOH solution. The precipitate obtained was filtered, washed several times with water and then dried at room temperature. The experiments were carried out under a

stream of N_2 in order to avoid, or at least minimize, contamination by atmospheric CO_2 .

Exchange reactions were carried out with 100 mg of [Zn-Al-Cl] suspended in 100 ml of 0.1 M $(\text{NH}_4)_2\text{PO}_3\text{F}$ solution under continuous stirring. The experiments were achieved under the following conditions: pH 7, 25°C , and 42 h of aging time. The solids were filtered, washed several times with water and then dried in air at ambient temperature.

2.2 Methods

The XRD equipment used was an XPERT-MPD diffractometer. Samples of unoriented powder were exposed to copper K_α radiation ($\lambda = 0.15415$ nm). Measurement conditions were as follows: 2θ range, 5° – 70° ; step size, $0.08^\circ 2\theta$ and step counting time, 4 s. Data were acquired on a DACO-MP microcomputer. Unit cell constants were calculated using a least-square refinement.

Absorbance IR spectra were recorded on a Perkin-Elmer 16 PC spectrophotometer, at a resolution of 2 cm^{-1} and averaged over 100 scans, in the range 400 – 4000 cm^{-1} . Samples were pressed into KBr discs.

Scanning electron microscopy (SEM) examination was carried out on samples in the form of a dry powder sprinkled onto the surface of a very thin adhesive layer. They were then coated with gold by vacuum deposition in order to minimize the severe charging effects that proved to be characteristic of this type of materials. They were run on a Cambridge Stereo scan 360 microscope operated at an accelerating voltage of 5 kV.

A Pentafet Oxford apparatus was used for X-ray microanalysis of samples pressed into small discs. The results obtained constitute a mean of several analyses done on different points of the disc.

Thermogravimetric (TG) and DTG studies were performed with a SETARAM TG-DSC 92 instrument. Curves were recorded on 20 mg of the sample over a temperature range of up to 1200°C at a heating rate of 5°C min^{-1} . The weights were corrected for the small effect of the gas flow as a function of temperature.

3. Results and discussion

3.1 XRD

The XRD pattern of the [Zn-Al-Cl] precursor (figure 2) indicates that the sample consists of a very-well-crystallized single phase made of large crystallites. This pattern is in agreement with that found for crystallites of the hydrotalcite-like minerals. The XRD powder data, refined on the hexagonal setting with a rhombohedral symmetry (space group: $R(-3)m$), provided the lattice parameters for the sample: $a = 0.307(5)$ nm and $c = 2.334(4)$ nm.

The interlayer distance, $d = 0.778(6)$ nm, is in accordance with that of a chloride-containing LDH [14,16].

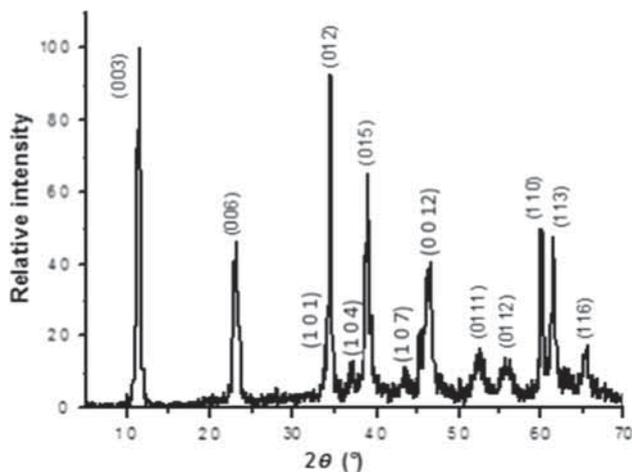


Figure 2. XRD pattern of [Zn–Al–Cl] precursor.

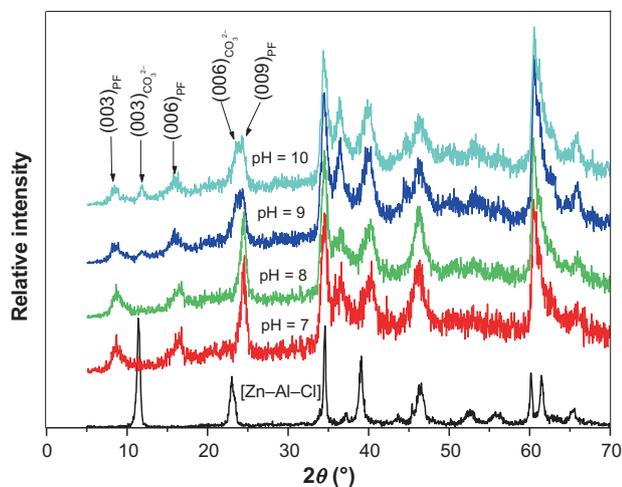


Figure 3. XRD patterns of FP-exchanged phases obtained in solutions with different pH values.

The chloride precursor was used for the preparation of the FP-containing LDH by ion exchange. The separate effects of pH, initial FP concentration and aging time were investigated in order to determine the optimum conditions for the complete exchange and the best-crystallized compounds.

The XRD patterns of the solids obtained by ion exchange, leading to [Zn–Al–PF] LDHs, correspond to that of a hydrotaalcite-like material (figures 3–5). The layered structure of the material is preserved after intercalation. However, the crystallinity is lowered, as attested by the broadening of the lines and the decrease of their intensity. In addition, intercalation is observed to cause a displacement of the (003) line, denoting an increase in the interlayer space, which is due to the exchange of chloride ions by the larger FP ions [14,15,17–19].

3.1a *Effect of pH:* Figure 3 presents the XRD patterns for [Zn–Al–Cl] and the intercalated phases, [Zn–Al–PF], at

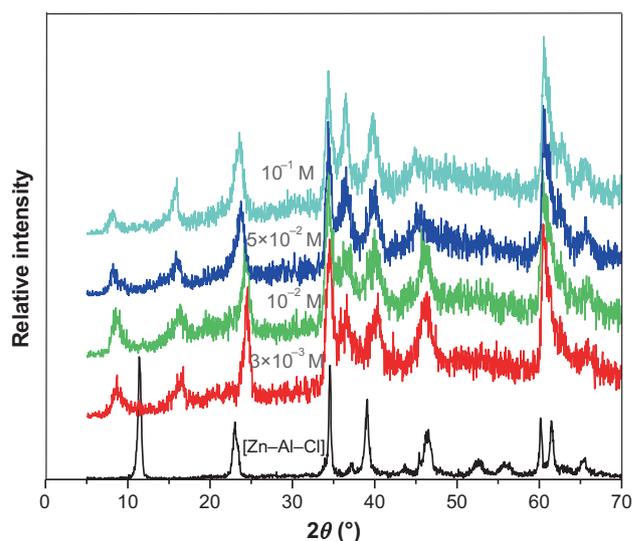


Figure 4. XRD patterns of FP-exchanged phases obtained in solutions with different FP concentrations.

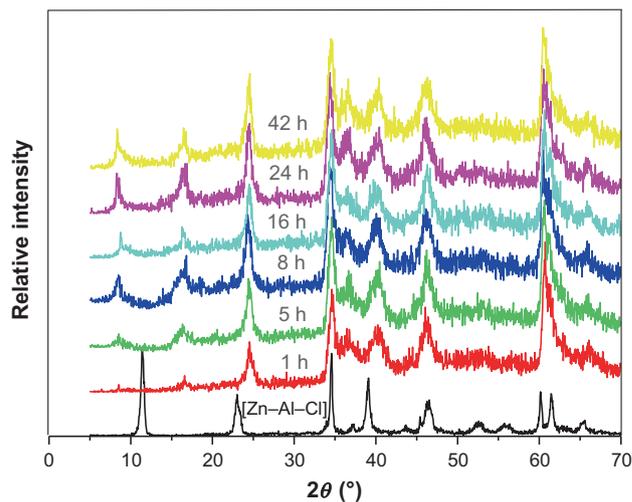


Figure 5. XRD patterns of FP-exchanged phases obtained in solutions with different aging times.

different pH values, with an FP concentration of 0.1 M. The shift of the position of (00 l) diffraction lines, in particular, indicates the dependence of the interlayer distance on the size of the intercalated anion.

The phases obtained at pH values of 7 and 8 are pure with complete exchange between the two anions. The exchange phases obtained at pH 9 and 10 are contaminated by carbonate ions, which have great affinity for LDHs [20].

3.1b *Effect of concentration:* The study of the effect of FP concentration indicates that the best phase, in terms of crystallinity, is obtained for 0.003 M (figure 4). The exchange can be considered as complete, since the lines of the chloride-containing LDH have disappeared.

When the concentration increases, the intensity of the (00 l) lines of exchanged phases decreases. The increase of the (006) line intensity relative to the (003) line may be due to an increase in the quantity of the material in the middle of the sheets.

3.1c Effect of contact time: The effect of aging time was investigated in solution with an FP concentration of 0.003 M at pH 7. The evolution of the precipitate (figure 5) indicates that both the first lines, which correspond to (003) and (006) reflections, vary in intensity. The ion exchange occurs after 5 h of aging time.

This shows that the exchange takes place by staging and rearrangement of the matter. The shift of (003) and (006) lines towards higher interlayer distances may be attributed to the anion orientation and to the amount of anions in the interlayer space. These results indicate that the most preferred time for well-crystallized phase formation is within a range of 8–42 h.

For a period of agitation greater than or equal to 24 h, the interlayer distance d increases from 0.778 to 1.153 nm. This increase of the c parameter may be explained by an increase in the exchange rate of chloride ions by the FP ions. This complete exchange is confirmed by the absence of the (00 l) lines of the host matrix. The broadening and asymmetry of the diffraction lines reflect the turbostratic nature of the phases obtained after exchange. It may also be due to some interstratification of different orientations of the FP ion between the layers, as predicted by Mering [21] and described by Manohara and Kamath [22] for the benzoate-intercalated Ni–Al LDH.

3.2 IR spectroscopy

The results of IR spectroscopy are consistent with those obtained by XRD. The comparison between [Zn–Al–Cl] and [Zn–Al–FP] spectra is illustrated in figure 6. It can be noted that the lattice vibrations of the sheets are preserved and the new bands imply the presence of the FP anion between the sheets. The absorption centred at 3448 cm^{-1} , which results from the stretching vibration of hydroxyl groups and water molecules, is appreciably broadened by the presence of FP anion. This may be attributed to the interaction of the anion with water molecules as well as the interlayer matter disorder [23].

The absorption at 1637 cm^{-1} is assigned to the bending vibration of water. The characteristic vibrations of FP groups appear at 1200, 1023, 780, 617 and 550 cm^{-1} for $\nu(\text{NH}_4^+)$, $\nu_3(\text{P-O})$, $\nu(\text{P-F})$, $\nu_2(\text{P-O})$ and $\nu_1(\text{P-O})$, respectively [24]. The band at 1363 cm^{-1} , whose intensity increases after exchange, is assigned to the carbonate ion. The presence of such bands confirms the existence of the FP anion and the ammonium cation between the LDH layers.

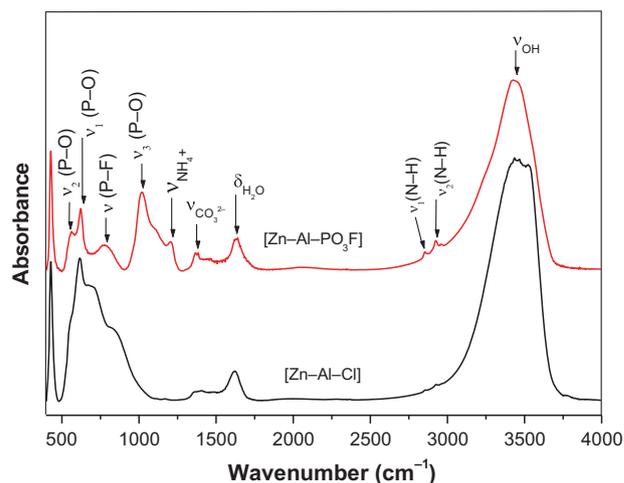


Figure 6. IR spectra of [Zn–Al–Cl] and [Zn–Al–FP] phases.

3.3 SEM and microanalysis

The examination of the precursor and the FP-intercalated materials by SEM (figure 7) reveals that the crystals present almost the same morphological features. They tend to result from the superposition of several leaflets with dimensions of the particles being about 6 μm for [Zn–Al–Cl] and 4 μm for [Zn–Al–FP]. These particles consist of crystallites whose average sizes are 1.2×1.4 and $1.0 \times 0.4 \mu\text{m}^2$, correspondingly. The small morphological alteration of the layers, upon exchange, may be due to the turbostratic effects, leading to the decrease in crystallinity observed in XRD analyses.

The X-ray microanalysis of the samples, before and after exchange, was carried out on separate points of the same crystal for each phase. The spectrum of the precursor material exhibits characteristic emissions for zinc, aluminium and chloride, while that of the intercalated sample presents, in addition to the emissions of zinc and aluminium, only those of fluorine and phosphorus (figure 8), confirming the Cl–FP total ion exchange.

3.4 TG analysis

TG and DTG curves obtained for [Zn–Al–PF] are reported in figure 9. The thermal evolution in air takes place in five consecutive stages with weight losses, for which the inflexion points coincide with temperatures, corresponding to minima and maxima in the DTG trace.

The first weight loss, which begins as soon as heating is applied, with the first effect at 174°C, is attributed to the loss of adsorbed water molecules and interlayer water. It corresponds to a weight loss of 9.14%.

The second loss, at 318°C, is of 13.0% of the total mass of the exchanged phase and may be attributed to the dehydroxylation of the brucite-like layers. This destruction of the hydroxylated sheets occurs at the same temperature for the

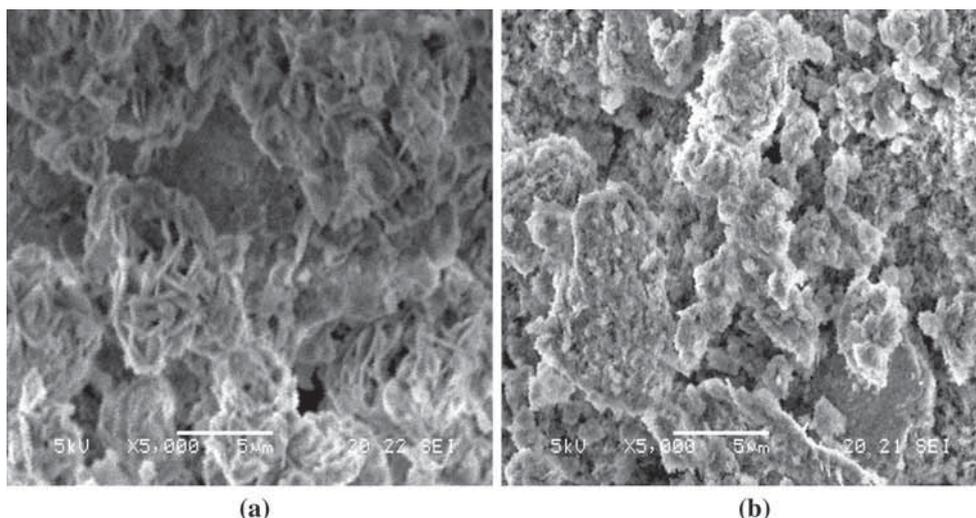


Figure 7. SEM photographs of (a) [Zn–Al–Cl] and (b) [Zn–Al–FP] obtained in a solution of pH 7.

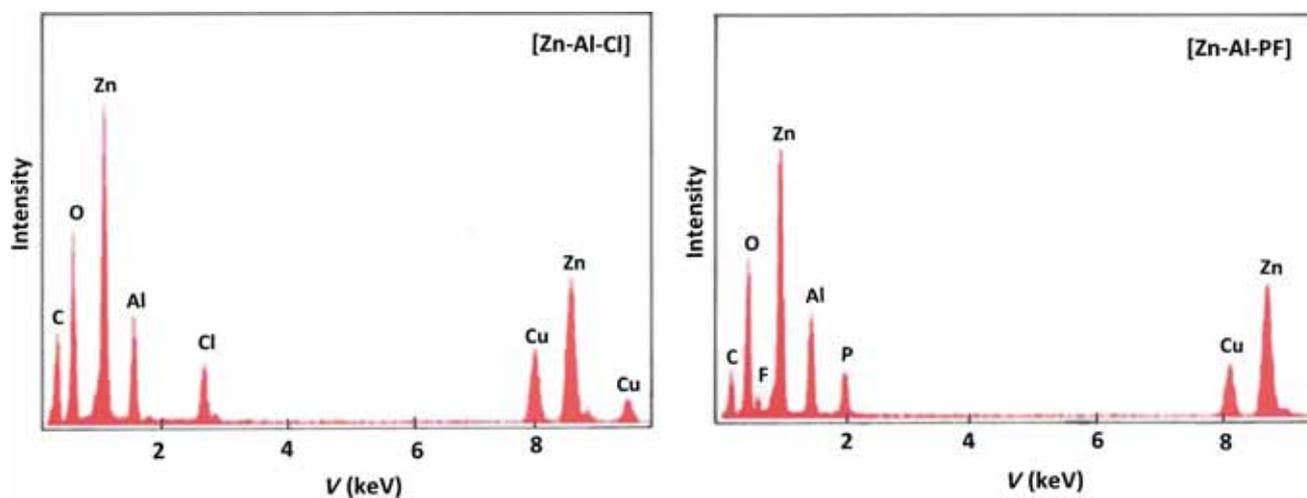


Figure 8. X-ray microanalysis spectra of [Zn–Al–Cl] and [Zn–Al–FP] obtained in the solution of pH 7.

[Zn–Al–Cl]. These first stages are similar to those previously reported for hydrotalcite-like materials [7,25].

The third loss of 1.59 wt% is rapid and occurs between 513 and 698°C. This loss matches the behaviour of ammonium-containing LDHs and confirms the results of XRD and IR spectroscopy.

The fourth and fifth losses represent 7.94 wt% and occur between 698 and 1192°C. They correspond to the loss of the two gases, F₂ and PF₅ [26]. The rest of the decomposition may correspond to the formation of orthophosphate, zinc oxide (ZnO) and the spinel, ZnAl₂O₄.

3.5 Structural model

Before proposing an orientation of the FP anion between the layers, we determined the value of the length of FP and ammonium by the molecular orbital semi-empirical method with the

Gaussian 03 software. The calculated value for a vertical position FP ion is 0.204 nm. Figure 10 shows the orientation of FP intercalated between the sheets of the LDH.

The interlayer distance, determined experimentally, which is 1.153 nm, suggests a vertical orientation of the anion (perpendicular to the planes of the sheets) in the interlayer space:

$$d = 0.21 + 0.26 + 0.26 + 0.204 + 0.204 + 0.015 = 1.153 \text{ nm.}$$

The same result was found for the exchange of nitrate ions by FP [15].

The orientation of the FP anion between the layers of the LDH in the presence of ammonium ions confirms the existence of a sur-structure as observed by Mostarih and De Roy [27] on sulphate-intercalated LDHs in the presence of sodium ions.

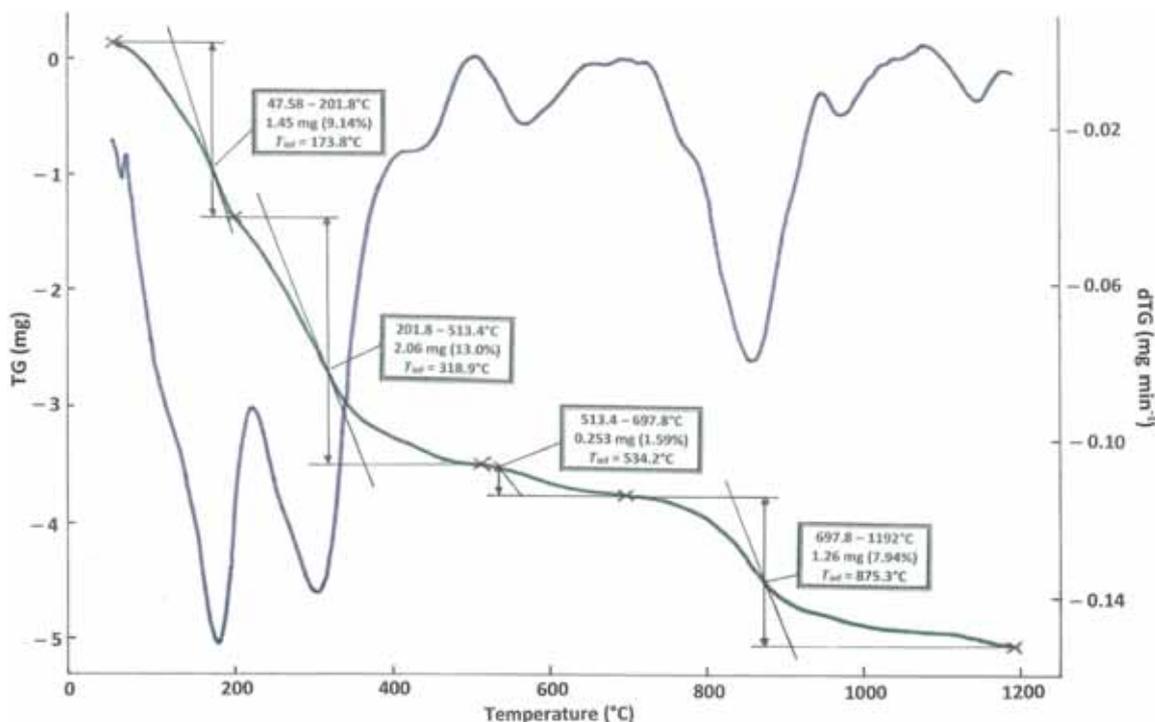


Figure 9. TG and DTG curves for [Zn-Al-FP].

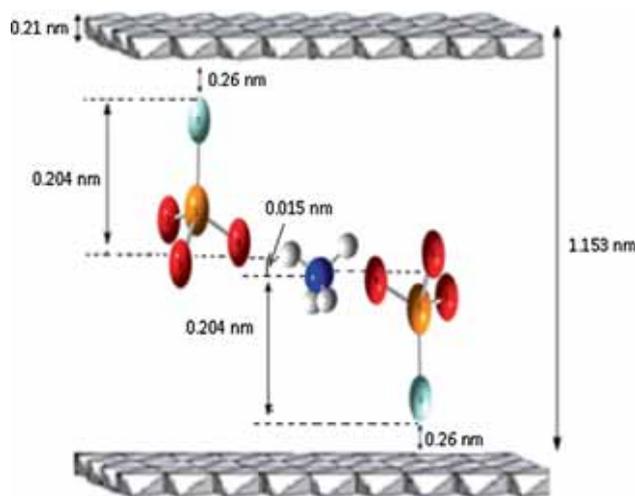


Figure 10. Schematic representation proposed for [Zn-Al-FP, NH₄] phase.

4. Conclusion

A new stable FP-intercalated LDH has been prepared by ion exchange using [Zn-Al-Cl] as a starting material. The effects of the solution pH, the HP concentration and the solid solution contact time were studied in order to determine the optimum conditions under which a stable exchanged material is obtained with good crystallinity and large extent of exchange.

XRD patterns gave direct evidence for the FP intercalation in all cases with a noticeable increase of the interlayer distance, due to the larger size of FP compared with the chloride ion. The crystallinity of the intercalated phases is lower than that of [Zn-Al-Cl]. In addition, intercalation was observed to cause a certain degree of disorder in the layers without destruction of the layered structure. The best phase with high extent of ion exchange can be obtained at pH 7, in a 0.003 M FP solution stirred continuously for 24 h.

Intercalation was evidenced also by IR, with all stretching and bending vibration modes of the phosphate ion being present on the spectra, besides the absorption bands of the hydroxylated layers.

References

- [1] Manasse E 1915 *Atti Soc. Toscana Sci. Nat. Proc. Verb.* **24** 92
- [2] Allmann R 1968 *Acta Crystallogr. B* **24** 972
- [3] Taylor H F W 1969 *Mineral. Mag.* **37** 338
- [4] Taylor H F W 1973 *Mineral. Mag.* **39** 377
- [5] Newman A C D 1987 *Chemistry of clays and clay minerals*, Mineralogical Society monograph vol 6 (New York: Wiley-Interscience) p 469
- [6] Evans D G and Slade R C T 2006 *Struct. Bond.* **119** 1
- [7] Cavani F, Trifiro F and Vaccari A 1991 *Catal. Today* **11** 173
- [8] Rives V 2001 *Layered double hydroxides: present and future* (New York: Nova Science)
- [9] Braterman P S, Xu Z P and Yarberry F 2003 In S M Auerbach, K A Carrado and Dutta P K (eds) *Handbook of layered materials* (New York: Marcel Dekker)

- [10] Duan X and Evans D G (eds) 2006 *Layered double hydroxides* (Berlin: Springer)
- [11] Zümreoglu-Karan B and Ay A N 2012 *Chem. Pap.* **66** 1
- [12] Rosenberg S P and Armstrong L 2013 D Donaldson and B E Raahauge (eds) *Essential readings in light metals: alumina and bauxite* vol 1 (Hoboken: John Wiley)
- [13] Fan G, Li F, Evans D G and Duan X 2014 *Chem. Soc. Rev.* **43** 7040
- [14] Badreddine M, Legrouri A, Barroug A, De Roy A and Besse J P 1999 *Mater. Lett.* **38** 391
- [15] Elkhatabi E, Badreddine M, Berraho M and Legrouri A 2012 *Bull. Mater. Sci.* **35** 693
- [16] Elkhatabi E, Lakraimi M, Badreddine M, Legrouri A, Cherkaoui O and Berraho M 2013 *Appl. Water Sci.* **3** 431
- [17] Ookubo A, Ooi K and Hayashi H 1993 *Langmuir* **9** 1418
- [18] Ookubo A, Ooi K and Tani F 1994 *Langmuir* **10** 407
- [19] Reichle W T 1986 *Solid State Ion.* **22** 135
- [20] Miyata S 1980 *Clay Miner.* **28** 50
- [21] Mering J 1949 *Acta Crystallogr.* **2** 371
- [22] Manohara G V and Kamath P V 2014 *Z. Anorg. Allg. Chem.* **640** 434
- [23] Bish D L and Brindley G W 1977 *Am. Mineral.* **62** 458
- [24] Durand J, Beys L, Hillaire P, Aleonard S and Cot L 1978 *Spectrochim. Acta A* **34** 123
- [25] Labajos F M and Rives V 1996 *Inorg. Chem.* **35** 5313
- [26] Gnanaraj J S, Zinigrad E, Asraf L, Gottlieb H E, Sprecher M, Aurbach D and Schmidt M 2003 *J. Power Sources* **119** 794
- [27] Mostarih R and De Roy A 2006 *J. Phys. Chem. Solids* **67** 1058