JOURNAL OF Materials CHEMISTRY

Preparation of a new stable hybrid material by chloride–2,4-dichlorophenoxyacetate ion exchange into the zinc–aluminium–chloride layered double hydroxide

Mohamed Lakraimi,†[a] **Ahmed Legrouri,***[b] **Allal Barroug,**[a] **André De Roy**[c] **and Jean Pierre Besse**[c]

[a]*Laboratoire de Chimie-Physique, Faculté des Sciences Semlalia, Université Cadi Ayyad, B.P. 2390, Marrakech 40001, Morocco*
[b]*School of Science and Engineering, Al Akhawayn University, P.O. Box 1871, Ifrane 53000, Morocco. E-mail: a.legrouri@alakhawayn.ma*
[c]*Laboratoire des Matériaux Inorganiques, UPRES-A 6002, Université Blaise Pascal, 63177 Aubière cedex, France*

Received 16th November 1999, Accepted 19th January 2000
Published on the Web 29th February 2000

A new hybrid material with the composition $[Zn_{1.9}Al(OH)_{5.8}][Cl_2C_6H_3OCH_2CO_2{\cdot}2.83H_2O]$ has been synthesised *via* ion exchange of chloride by ions of a molecule belonging to the pesticide family, 2,4-dichlorophenoxyacetate (2,4D). The ion exchange in the zinc–aluminium–chloride layered double hydroxide, [Zn–Al–Cl], was investigated by X-ray diffraction and infrared spectroscopy. The effects of the anion concentration in solution, the 2,4D/[Zn–Al–Cl] molar ratio, the ageing time and the temperature on the ion exchange were studied. The best sample, in terms of crystallinity and extent of ion exchange, was obtained at 100 °C in a 0.004 M 2,4D solution in which the 2,4D/[Zn–Al–Cl] molar ratio was equal to 11, with 24 h of stirring time. This hybrid material was further characterised by chemical analyses and its thermal behaviour was also studied.

Introduction

Increasing attention is being paid to the layered double hydroxides, also called anionic clays or hydrotalcite-like compounds,[1] owing to their layered structure and their high anion exchange capacity[2,3] which make them potential materials for technical applications in various domains, such as catalysis, electrochemistry, separation technology and medicine.[4–10]

Their structural units are made from stacks of positively charged octahedral sheets. The net positive charge, which is due to substitution of trivalent by divalent metal ions in the brucite-like metal hydroxide $M(OH)_2$, is balanced by an equal negative charge from the interlayer solvated anions. The anionic clays can be represented by the general formula[11,12] $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}[X^{m-}_{x/m}{\cdot}nH_2O]^{x-}$, abbreviated as $[M^{II}–M^{III}–X]$, where, $M^{II} = Mg^{2+}$, Zn^{2+}, Mn^{2+}, ...; $M^{III} = Al^{3+}$, Cr^{3+}, Fe^{3+}, ...; and $X^{m-} = Cl^-$, NO_3^-, CO_3^{2-}, PO_4^{3-}, ...

This study forms part of a wider investigation undertaken to study the anion exchange ability of anionic clays[13,14] and their use as sorbents for undesirable organic and inorganic anions.[8,15] We report here on the results obtained in the case of pesticides, which are present in many agricultural and industrial water streams,[16–18] in particular the intercalation of an ion from a molecule belonging to the pesticide family, 2,4-dichlorophenoxyacetic acid, abbreviated as 2,4D, in [Zn–Al–Cl] by ion exchange, leading to the formation of a new stable hybrid LDH. A review of the various syntheses of organic anion-containing LDHs has been published by Carlino.[19] The effects of the anion concentration in solution, the 2,4D/[Zn–Al–Cl] molar ratio, the ageing time and the temperature on the ion exchange were studied in order to determine the optimum conditions under which an intercalated clay is obtained with good crystallinity and high extent of exchange. Both the [Zn–Al–Cl] precursor and the exchanged phases were characterised by powder X-ray diffraction (PXRD) and Fourier transform infrared spectroscopy (FTIR). The best sample, in terms of crystallinity, obtained in the series was further characterised by chemical analyses, thermogravimetry (TG) and differential thermal analysis (DTA).

Experimental

Materials

All experiments were carried out under a stream of N_2 in order to avoid, or at least minimise, contamination by atmospheric CO_2.

The anionic clay [Zn–Al–Cl], with a [Zn]/[Al] ratio equal to 2, was synthesised by coprecipitation at a constant pH of 9.0.[8] Mixtures of molar $ZnCl_2$ and $AlCl_3$ aqueous solutions were slowly introduced into the reactor, where the pH was maintained by the simultaneous addition of 1.0 M NaOH solution. The resulting slurry was then left under stirring for 34 h at room temperature. The precipitate was filtered, washed several times with water and then dried at 30 °C.

Exchange reactions were carried out at a pH around 7. 200 mg of [Zn–Al–Cl] suspended in the anion containing solution (500 mL) was stirred and then centrifuged. The reactions were carried out under reflux for temperatures higher than room temperature.

The influence of the [2,4D]/[Zn–Al–Cl] ratio on the anion exchange was examined at room temperature with 24 h of ageing time in a 0.004 M 2,4D solution. The other three parameters were studied with a [2,4D]/[Zn–Al–Cl] molar ratio equal to 11.

The effect of the anion concentration in solution was investigated at room temperature with 24 h of continuous stirring. The influence of ageing time was studied at room temperature in a 0.004 M 2,4D solution. Experiments were also

---

†Permanent address: Ecole Normale Supérieure, B.P. S41, Marrakech 40001, Morocco.

DOI: 10.1039/a909047i

carried out at different temperatures in a 0.004 M 2,4D solution under stirring for 24 h.

Methods

Chemical analyses were effected by atomic absorption spectroscopy at the "Service Central d'Analyses" of the CNRS at Vernaison (France).

The XRD equipment used was a Siemens D 501 diffractometer. Samples of unoriented powder were exposed to Cu-Kα radiation ($\lambda = 1.5405$ Å). Measurement conditions: 2θ range: 2–76°; step size: 0.08° 2θ; step counting time: 4 s. Data acquisition was effected on a DACO-MP microcomputer. Unit cell parameters were calculated using a least squares refinement.

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

DTA and TG experiments were performed in air on a Setaram 92 instrument. Curves were recorded at a rate of 5 °C $\mathrm{min^{-1}}$ using 14.5 mg test samples.

Results and discussion

Characterisation of the [Zn–Al–Cl] precursor

The PXRD pattern for [Zn–Al–Cl] (Fig. 1), which shows good agreement with those found for other hydrotalcite-like compounds,[11,20] indicates that the solid consists of a well crystallised single phase with large constituting crystallites. The lattice parameters, refined on the hexagonal setting with a rhombohedral symmetry (space group: R-3m), are: $a = 0.3060$ and $c = 2.334$ nm ($d = c/3 = 0.7789$ nm).

The IR spectrum of the sample (Fig. 2) presents profiles which resemble those exhibited by all hydrotalcite-like phases.[20,21] Typical of this spectrum are the strong absorbance at 3450 $\mathrm{cm^{-1}}$ and the band at 1650 $\mathrm{cm^{-1}}$ which correspond to the valence vibrations of hydroxyl groups and the bending vibration of water, $\delta(H_2O)$, respectively. The bands observed in the low-frequency region of the spectrum correspond to the lattice vibration modes and can be attributed to M–O (841 and 647 $\mathrm{cm^{-1}}$) and O–M–O (435 $\mathrm{cm^{-1}}$) vibrations.[8,13] It is noteworthy that, despite the precautions taken during the materials syntheses, the IR spectrum shows some contamination by CO_3^{2-} (1360 $\mathrm{cm^{-1}}$) in the solid. However, CO_3^{2-}, which is known to form stable anionic clays,[22] is only present in trace amounts, since no carbonate clay phase is visible in the PXRD pattern.

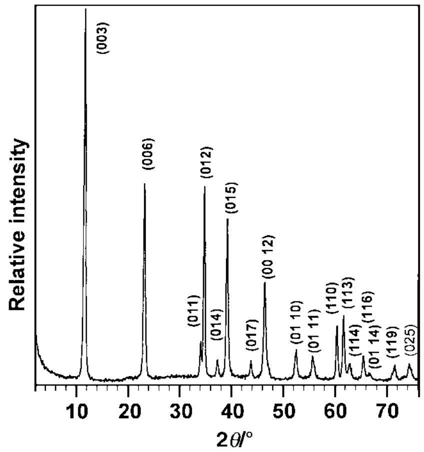

Fig. 1 PXRD pattern of [Zn–Al–Cl].

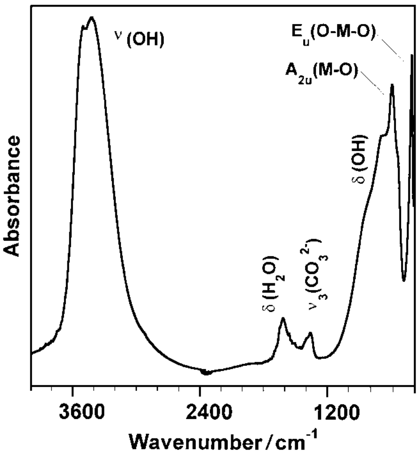

Fig. 2 FTIR spectrum of [Zn–Al–Cl].

Characterisation of the exchanged phases

PXRD patterns for [Zn–Al–2,4D] LDHs prepared with different 2,4D/[Zn–Al–Cl] molar ratios, different 2,4D ion concentrations, different ageing times, and at different temperatures present some common features (Fig. 3–6). The layered structure of the material is preserved upon exchange. However, as in the case of hybrid LDHs,[23,24] the crystallinity is lowered, as attested to by the elimination of some (hkl) reflections, the widening of the remaining PXRD lines and the decrease in their intensity. In addition, the ion exchange is observed to cause a little broadening of the (110) reflection, indicating a certain amount of disorder in the layers, which could be due to electrostatic interactions between the 2,4D ion and the layers of the host matrix. However, this disorder could also be due to the typical turbostratic effect caused by a decrease of the ordering along the stacking axis of the layers which in turn is induced by the loss of the van der Waals interactions between adjacent layers and the absence of a densely packed interlayer space formed by high charge density anions, such as halides or oxo-anions. A displacement of (00l) lines denoting an increase in the interlayer distance, which is due to the exchange of chloride by 2,4D, was also observed.

The 2,4D/[Zn–Al–Cl] molar ratio (abbreviated as R) plays an important role in the exchange process (Fig. 3). When this ratio is very small ($R = 0.14$) no exchange is observed. Increasing this ratio leads to a mixture of phases corresponding to the precursor and an 2,4D-exchanged phase ($R = 1$ and 5). Total exchange is observed when this ratio is equal to 11.

The study of the effect 2,4D concentration indicates that the best extent of ion exchange is obtained for the concentration

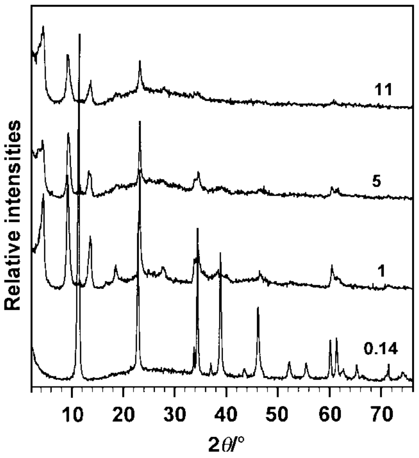

Fig. 3 PXRD patterns of [Zn–Al–2,4D] phases obtained in solutions with different 2,4D/[Zn-Al-Cl] molar ratios.

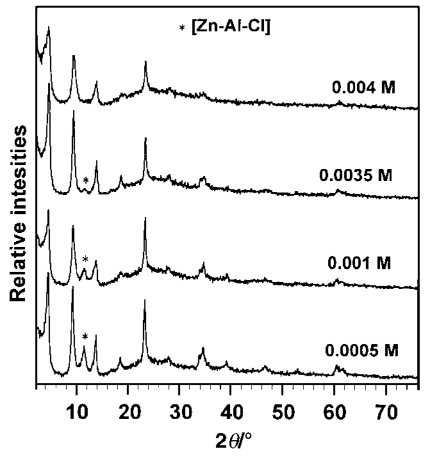

Fig. 4 PXRD patterns of [Zn–Al–2,4D] phases obtained in solutions with different 2,4D concentrations.

corresponding to the solubility limit of 2,4D in water, which is 0.004 M. Below this concentration, the PXRD patterns present some lines corresponding to the chloride phase. The important background noise observed between 20 and 30° in 2θ can be attributed to amorphous $Al(OH)_3$.[25]

For ageing times below 24 h, the PXRD patterns (Fig. 5) present lines corresponding to both the precursor and the exchanged phase. For times longer than 24 h, the crystalline phase undergoes degradation with an increase in the amount of the amorphous phase. This lowering of crystallinity might be due to the mechanical effects of the stirring, which favours turbostratic disorder.

Temperature was observed to cause a slight improvement in the crystallinity for the exchanged phase, as shown by the (00l) lines which become less broad and more intense when the temperature is increased (Fig. 6).

Characterisation of the optimised phase

It can be concluded from the preceding investigations that the best exchanged phase with high extent of ion exchange is obtained at 100 °C in a 0.004 M 2,4D solution in which the 2,4D/[Zn–Al–Cl] molar ratio is equal to 11 with 24 h of stirring time.

The XRD powder data obtained for a phase prepared under these conditions were refined on the hexagonal setting (space group: $P6_3/mmc$). The cell parameters were $a = 0.3060$ and $c = 1.906$ nm. The intercalation of the organic ion in the layered host structure is clearly evidenced by the net increase in the basal spacing from 0.7789 nm for [Zn–Al–Cl] to 1.906 nm for the organic derivative.

The intercalation is also confirmed by IR (Fig. 7). All stretching and bending vibration modes of the organic anion are observed in the spectrum, besides the absorption bands of the hydroxylated layers. The band at 1620 cm^{-1} can be attributed to the carboxylate ion vibrations and masks the deformation vibration of water molecules in the interlayer domain which appear in the spectrum of the parent material at 1650 cm^{-1}. The C=C bond vibrations of the aromatic nuclei appear around 1490 and 1420 cm^{-1}. The bands observed at 1280 and 1060 cm^{-1} correspond to the antisymmetric and symmetric vibrations of C–O–C, respectively. The band at 860 cm^{-1} can be assigned to the C–Cl vibration and those at 770 and 800 cm^{-1} to C–H deformation vibrations out of the benzenic plane.[26,27]

Chemical analyses of the [Zn–Al–2,4D] phase confirm the chloride–2,4D ion exchange and show that the exchange is almost total (Table 1). The average composition of the phase corresponds to the formula $[Zn_{1.9}Al(OH)_{5.8}][Cl_2C_6H_3OCH_2CO_2\cdot 2.83H_2O]$.

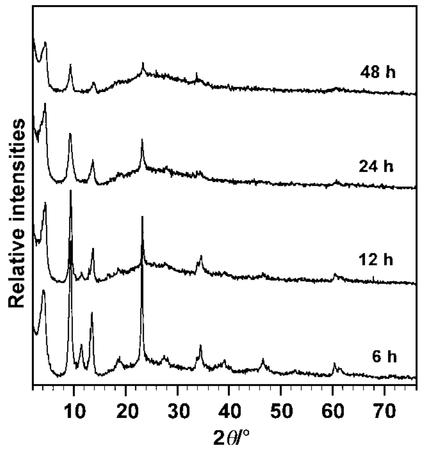

Fig. 5 PXRD patterns of [Zn–Al–2,4D] phases obtained with different ageing times.

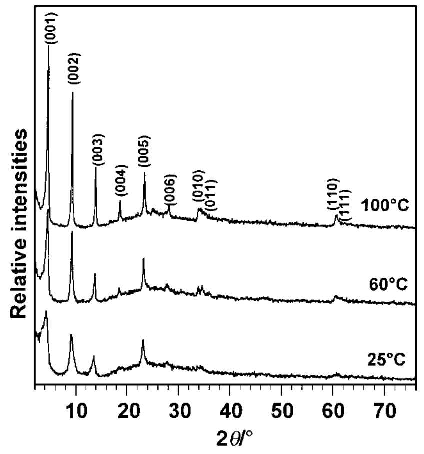

Fig. 6 PXRD patterns of [Zn–Al–2,4D] phases obtained at different temperatures.

TG and DTA curves obtained for the [Zn–Al–2,4D] phase are reported in Fig. 8. The thermal evolution under air takes place in four consecutive stages with weight losses for which the inflection points coincide with the temperatures corresponding to minima and maxima in the DTA trace. The first weight loss (*ca.* 10%), which begins as soon as heating is applied with a first intense endothermic effect at 85 °C and a shoulder at 40 °C, is attributed to the loss of adsorbed and interlayer water molecules. The amount of these molecules, calculated from the TG curve, corresponds to the elimination of 2.96 mol water

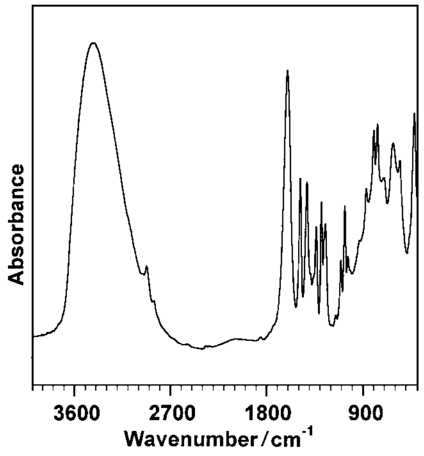

Fig. 7 FTIR spectrum of the [Zn–Al–2,4D] phase obtained under optimum experimental conditions.

Table 1 Chemical analyses of the exchanged phase [Zn–Al–2,4D]

	Layers	Anionic species			
	Zn/Al	C/Al	O/Al	Cl/Al	H/Al
Experimental	1.90	8.36	12.00	2.03	16.45
Theoretical	2.0	8.0	11.83	2.0	16.66

Calculated formula: $[Zn_{1.9}Al(OH)_{5.8}][Cl_2C_6H_3OCH_2CO_2 \cdot 2.83H_2O]$.

per mol Al, in agreement with the value obtained by chemical analyses. The second weight loss (*ca.* 9%), with an endothermic peak at 200 °C, is assigned to the dehydroxylation of the brucite-like layers as well as the removal of carbon dioxide from interlayer carbonate anions which are only present in trace amounts, since no carbonate-LDH phase is seen on the XRD pattern. These two first stages are similar to those previously reported for hydrotalcite-like materials.[4,20,28–31] The third and fourth weight losses (*ca.* 30 and 11%), with two exothermic signals at 380 and 510 °C, respectively, arise from decomposition of the organic anions by combustion reactions in two steps; extraction of the dichlorophenol fragment followed by the elimination of the acetate fragment. Supplementary analyses are presently being performed, by linking a mass spectrometer to the TG–DTA apparatus, in order to elucidate the decomposition mechanism of the host matrix and the organic entity.

Structural model

The experimental results show that the 2,4D anion is intercalated in the interlayer space and bound to the host matrix by electrostatic interactions and hydrogen bonding with an interlayer distance of 1.906 nm. Knowing the layer thickness (0.21 nm) and the hydrogen-bond distances between guest and host (0.27 nm), gives the interlayer space available for the anion as 1.60 nm. Comparison with the size of the 2,4D anion (0.886 nm) indicates an opposite and perpendicular orientation for the anion, as shown in Fig. 9.

Conclusions

2,4D-intercalated [Zn–Al] anionic clay phases were prepared from a chloride precursor, which was obtained by the coprecipitation method at constant pH, *via* an exchange reaction in a 2,4D-containing solution. The effects of the anion concentration and temperature on the exchange were studied in order to determine the optimum conditions under which the intercalated clay is obtained with a good crystallinity and high extent of exchange.

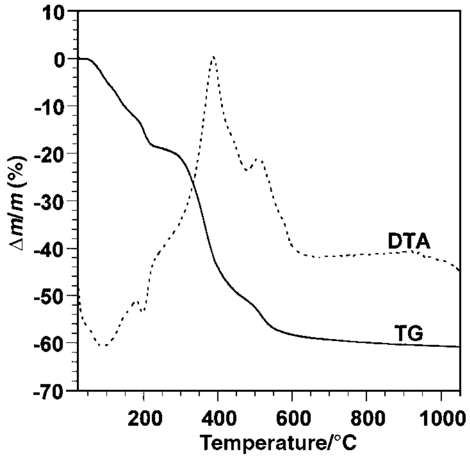

Fig. 8 TG and DTA curves for the [Zn–Al–2,4D] phase obtained under optimum experimental conditions.

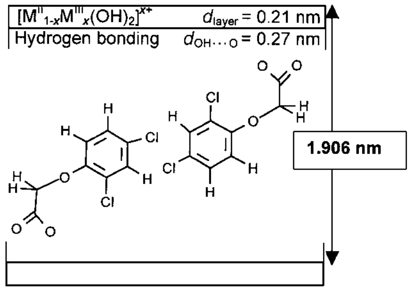

Fig. 9 Model for the orientation of the 2,4D anion between the hydroxylated layers.

PXRD revealed that, in all cases, the crystallinity of the intercalated phases is lower than that of the precursor. Intercalation was also observed to cause a certain degree of disorder in the layers without destruction of the layered structure of the material or degradation of the pesticide anion. The best crystalline material, with a high extent of exchange, was obtained by carrying out the exchange at 100 °C in a 0.004 M 2,4D solution in which the 2,4D/[Zn–Al–Cl] molar ratio was equal to 11 with 24 h of stirring time.

The intercalation of the organic ion in the layered host structure was clearly evidenced on a phase prepared under these conditions by the net increase in the basal spacing from 0.7789 nm for [Zn–Al–Cl] to 1.906 nm for the organic derivative. This intercalation was also confirmed by IR, with all stretching and bending vibration modes of the organic anion being present on the spectra, besides the absorption bands of the hydroxylated layers.

Chemical analyses of the intercalated phase obtained under the optimum conditions confirmed the anion exchange and provided the average composition of the sample, which corresponds to the formula $[Zn_{1.9}Al(OH)_{5.8}][Cl_2C_6H_3OCH_2CO_2 \cdot 2.83H_2O]$.

Thermal treatment of the optimised [Zn–Al–2,4D] phase led to the loss of adsorbed and interlayer water, as well as to dehydroxylation of the layers below 300 °C. The decomposition of the organic anion by combustion reactions was observed after this point.

Acknowledgements

The authors wish to thank the "Comité Mixte Interuniversitaire Franco-Marocain" for financial support (Action intégrée no. 95/856).

References

1 R. Allmann, *Chimia*, 1970, **24**, 99.
2 H. P. Bohem, J. Steinle and C. Vieweger, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 265.
3 A. De Roy, J. P. Besse and P. Bondot, *Mater. Res. Bull.*, 1985, **20**, 1091.
4 F. Cavani, F. Trifiro and A. Vaccari, *Catal. Today*, 1991, **11**, 173.
5 T. Kwon, G. A Tsigdinos and T. J. Pinnavaia, *J. Am. Chem. Soc.*, 1988, **110**, 3653.
6 E. Suzuki, M. Okamoto and Y. Ono, *Chem. Lett.*, 1989, 1485.
7 O. Clause, B. Rebours, E. Merlen, F. Trifiro and A. Vaccari, *J. Catal.*, 1991, **133**, 231.

8 B. Houri, A. Legrouri, A. Barroug, C. Forano and J. P. Besse, *J. Chim. Phys.*, 1999, **96**, 455.
9 A. C. Playle, S. R. Gunning and A. F. Llewellyn, *Pharm. Acta Helv.*, 1974, **49**, 298.
10 Y. Takagishi, K. Iwamoto and H. Mackawa, *Yakuzaigaku*, 1978, **38**, 166.
11 A. De Roy, C. Forano, K. El Malki and J. P. Besse, in *Synthesis of Microporous Materials*, ed. M. L. Occelli and H. E. Robson, Van Nostrand Reinhold, New York, 1992, p. 108.
12 M. A. Ulibarri, M. J. Hernandez and J. Cornejo, *Mater. Chem. Phys.*, 1986, **14**, 209.
13 M. Badreddine, M. Khaldi, A. Legrouri, A. Barroug, M. Chaouch, A. De Roy and J. P. Besse, *Mater. Chem. Phys.*, 1998, **52**, 235.
14 M. Badreddine, A. Legrouri, A. Barroug, A. De Roy and J. P. Besse, *Mater. Lett.*, 1999, **38**, 391.
15 M. Lakraimi, A. Legrouri, A. Barroug, A. De Roy and J. P. Besse, *J. Chim. Phys.*, 1999, **96**, 470.
16 A. Wettasinghe, *MSc Thesis*, Oregon State University, USA, 1992.
17 N. T. L. Tortensson, J. Stark and B. Goransson, *Research*, 1975, **15**, 159.
18 R. G. Wilson and H. H. Cheng, *J. Environ. Qual.*, 1978, **7**, 281.
19 S. Carlino, *Solid State Ionics*, 1997, **98**, 73.
20 S. Miyata, *Clays Clay Miner.*, 1975, **23**, 369.
21 M. J. Hernandez-Moreno, M. A. Ulibarri, J. L. Rendon and J. S. Serna, *Phys. Chem. Miner.*, 1985, **12**, 34.
22 S. Miyata, *Clays Clay Miner.*, 1980, **28**, 50.
23 S. Bonnet, C. Forano, A. De Roy, J. P. Besse, P. Maillard and M. Momenteau, *Chem. Mater.*, 1996, **8**, 1962.
24 V. Prevot, C. Forano, J. P. Besse and F. Abraham, *Inorg. Chem.*, 1998, **37**, 4293.
25 S. Bonnet, *Blaise Pascal University Thesis*, Clermont-Ferrand, France, 1997.
26 M. C. Van Oosterwyck-Gastuche, G. Brown and M. M. Mortland, *Clay Miner.*, 1967, **7**, 177.
27 D. L. Bish and G. W. Brindley, *Am. Mineral.*, 1977, **62**, 458.
28 M. Del Arco, C. Martin, I. Martin, V. Rives and R. Trujillano, *Spectrochim. Acta*, 1993, **49**, 1575.
29 F. M. Labajos and V. Rives, *Inorg. Chem.*, 1996, **35**, 5313.
30 B. Houri, A. Legrouri, A. Barroug, C. Forano and J. P. Besse, *Collect. Czech. Chem. Commun.*, 1998, **63**, 732.
31 M. Del Arco, P. Malet, R. Trujillano and V. Rives, *Chem. Mater.*, 1999, **11**, 624.

Paper a909047i