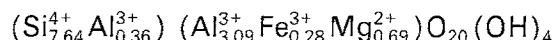# Swelling of lanthanide (La, Nd, Gd) montmorillonites heated in air and under vacuum

M. M. TOBÍAS, J. POYATO, J. M. TRILLO*
Department of Inorganic Chemistry, Institute of Materials Science, University of Seville, C.S.I.C., P.O. Box 874, Seville, Spain

A sodium-montmorillonite from Almeria (Spain), with the structural formula

$$(Si^{4+}_{7.64} Al^{3+}_{0.36})\ (Al^{3+}_{3.09} Fe^{3+}_{0.28} Mg^{2+}_{0.69}) O_{20} (OH)_4$$

has been used as starting material for the preparation of samples saturated with lanthanum, neodymium and gadolinium. By application of the Greene–Kelly Li^+ - test the inability of the sample to re-expand with glycerol, has been observed, in agreement with the existence of a predominant charge in the octahedral sheet. The effect of heating at 300° C, in air and under vacuum, on the swelling capacity of the lanthanide montmorillonites has been studied. Prolonged re-expansion in water after thermal treatment in air is necessary to reproduce the initial basal spacing of the samples. From Fourier transform infrared spectra it is concluded that the interlamellar hydrated lanthanide cation concentration decreases on heating, which agrees with the decrease in the cation exchange capacity claimed in the literature. The mechanism of exchangeable ion migration into octahedral vacant sites with thermal treatments, advocated in the case of lithium-saturated montmorillonite, does not seem to occur in the case of lanthanide-saturated samples. The partial hydrolysis of the interlamellar hydrated cations to polyhydroxycations is proposed as the only mechanism for explaining the loss or exchangeable 4f ions.

1. Introduction

Storage of high-level nuclear wastes in continental or marine repositories usually involves a clay-bearing packing material that acts as a physicochemical barrier. Geochemical data indicate that montmorillonite will be the major component responsible for ion sorption [1].

The interaction of rare earth ions with the clay minerals has attracted much attention in order to establish the safety of those repositories [2]. Lanthanide ions replace actinides in these studies; lanthanum and neodymium are suitable from their properties to simulate americium and curium. The major barrier for preventing waste movements should be the fixation of radionuclides by the clays surrounding the canister. It is known that heating above 160° C causes a reduction in the exchangeable 4f cations from montmorillonite saturated with them [3, 4]. An explanation greatly accepted for the loss of exchangeable lithium when lithium-saturated montmorillonite is heated (200 to 300° C) is the migration of lithium ions into vacant octahedral sites; this has been recently reviewed and its contribution estimated, together with the entrapments of lithium in collapsed interlayers and the deprotonation of structural hydroxyl groups [5]. A similar mechanism would be of great importance in

order to irreversibly fix 4f cations by montmorillonite. Miller *et al.* [4] have examined the sorption of Eu (III), Ho (III) and Yb (III) on montmorillonite from Upton, Wyoming, with temperature. In Miller *et al.*'s work it is claimed that some migration of the studied 4f tervalent exchangeable ions into octahedral holes can occur. It is of importance concerning the disposal of high-level radioactive nuclear waste, because of the possibility of irreversible fixation through prolonged periods of sorption. The aim of this paper is to determine the mechanism of interaction of tervalent ions from the first half of the lanthanide series; La (III), Nd (III) and Gd (III) having been selected.

The clay-bearing packing materials surrounding nuclear wastes may react with ground water, the swelling of smectite clays also being a property of fundamental importance for the use of such barrier materials. The effect of heating on the swelling capacity of the lanthanide montmorillonites has also been studied.

2. Experimental details

X-ray powder diffraction diagrams were obtained with a Siemens Kristalloflex D-500 instrument, using $CuK\alpha$ radiation and a nickel filter, 36 kV and 26 mA. Basal spacings, $d(0\ 0\ 1)$, were examined using oriented aggregate preparations on glass microscope slides.

*Author to whom all correspondence should be addressed.

As is customary, the *b*-dimension was computed from (0 6 0) reflections. Air-dried samples of homoionic montmorillonites were confined in the window of a specially loaded powder munt partially to overcome preferred basal orientation. Quartz powder was used as an internal standard to correct the results for any geometrical diffractometer aberrations. The mean square error was ± 0.0003 nm for *b*.

Infrared spectra were recorded in a Fourier Transform Nicolet 5 DXE spectrometer. Samples were water suspended and allowed to sediment on to plastic slides; the suspensions were evaporated to dryness overnight and the resulting oriented aggregate films were peeled from the foil.

Results and discussion

3.1. Materials

A Trancos smectite mineral from Gador, Almeria (Spain) was used [6]. Minerals of the smectite group are among the most finely divided of the clay minerals. The $< 2\,\mu$m fraction was collected after water suspension. Air-dried samples were successively treated with pH 5 NaOAc–HOAc buffer to dissolve carbonates and 6% H_2O_2 to remove organic matter. They were then water resuspended and saturated with sodium by using 1 N solution of NaCl. This sample, Na–Mt, was selected as the starting material. The X-ray powder diffractograms show the sample to be a smectite.

Chemical analysis of the starting material by X-ray fluorescence was carried out, yielding the structural formula

$$(Si_{7.64}^{4+}Al_{0.36}^{3+})\,(Al_{3.09}^{3+}Fe_{0.28}^{3+}Mg_{0.69}^{2+})O_{20}(OH)_4$$
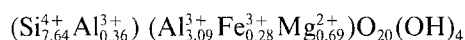
with a calculated charge deficit per unit cell of 0.87 (0.36 + 0.51). The theoretical value of the cation exchange capacity (CEC) amounts to 119 meq per 100 g clay; the experimental value, obtained by saturation with ammonium acetate, was 100 meq per 100 g, giving the usual level of agreement.

The Greene-Kelly test [7, 8] was applied which differentiates between montmorillonites and beidellite. However, ideal montmorillonites and beidellites are rare in nature and most of them possess some tetrahedral and octahedral charge, respectively. In the present case, an inability of the Na–Mt samples to re-expand with glycerol after lithium-saturation and air heat treatment at 300° C for 24 h has been observed. This indicates that the predominant charge of the mineral is in octahedral sheets and that the migrating Li^+ ions effectively neutralized this octahedral charge. Greene-Kelly [8] claimed that some expansion occurs with glycerol solvation if the sample contain $> 30\%$ tetrahedral substitution or $> 70\%$ Li^+ ions in the interlayer spaces. The Na–Mt samples contain 41% tetrahedral substitution. Surprisingly, as shown by Malla and Douglas [9], none of the workers dealing with this topic referred to the importance of the absolute values of the tetrahedral and octahedral charges, but to their relative percentages; Malla and Douglas found that for complete expansion with alkylammonium, which is more effective in penetrating the collapsed layers than glycerol, a tetrahedral charge > 0.24 per half unit cell is required. The present
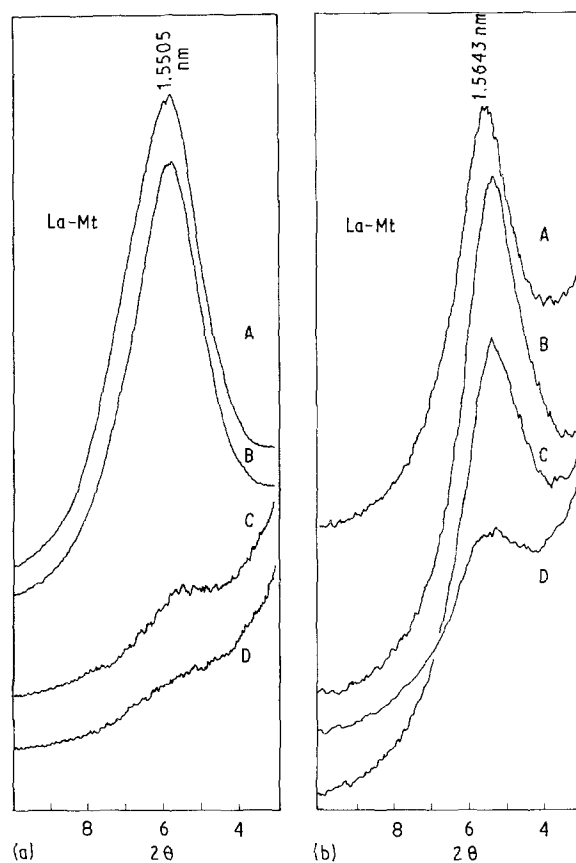

Figure 1 (a) XRD pattern of lanthanum-montmorillonite at 60% r.h. after heating 24 h at (A) 20° C in air, (B) 110° C in air, (C) 300° C under vacuum, and (D) 300° C in air. (b) XRD pattern of lanthanum-montmorillonite dried at 60% r.h., after 24 h treatment at 300° C (A) under vacuum or (B to D) in air, and water resuspension for (A) 1 min, (B) 8 d, (C) 5 min and (D) 1 min.

sample shows a tetrahedral charge of 0.18 per half unit cell.

The sodium montmorillonite has been used, as mentioned above, for the preparation of lanthanide-montmorillonites, Ln–Mt (Ln = La, Nd, Gd), according to the method described by Miller *et al.* [4], except that the samples were washed with water up to the elimination of excess Ln (III).

3.2. X-ray powder diffraction (XRD) analysis

The basal spacing of lanthanide-montmorillonites prior to heating pretreatment is ~ 1.5 nm, curves A Figs 1a to 3a, for samples equilibrated at 60% r.h. over 24 h; this interlamellar spacing is almost constant over a wide range of humidities and corresponds to a double-sheet complex. Early studies on smectites [10, 11] showed what appeared to be a continuous variation of $d(0\,0\,1)$ with water content, but it is now clear that this variation results from random interstratification of two or more successive hydrates, yielding rather broad bands in the XRD diagrams. The occurrence of steps in the basal spacing of swelling smectites, as a function of water content, is now a generally accepted phenomenon.

In spite of the difference in hydration enthalpy between the divalent alkaline earth cations and the lanthanides, the swelling behaviour of montmorillonites saturated with both is the same over a wide range of humidities [12]. From EPR spectra [13] of calcium-
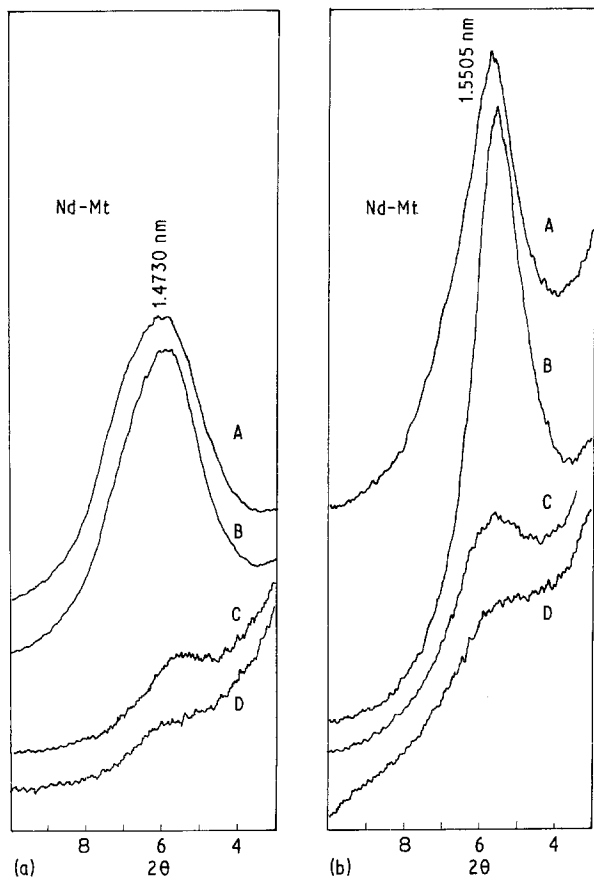
Figure 2 (a) XRD pattern of neodymium-montmorillonite at 60% r.h. after heating 24 h at (A) 20° C in air, (B) 110° C in air, (C) 300° C under vacuum, and (D) 300° C in air. (b) XRD pattern of neodymium-montmorillonite dried at 60% r.h., after 24 h treatment at 300° C (A) under vacuum or (B to D) in air, and water resuspension for (A) 1 min, (B) 8 d, (C) 1 h and (D) 5 min.

Figure 3 (a) XRD pattern of gadolinium-montmorillonite at 60% r.h. after heating 24 h at (A) 20° C in air, (B) 110° C in air, (C) 300° C under vacuum, and (D) 300° C in air. (b) XRD pattern of gadolinium-montmorillonite dried at 60% r.h., after 24 h treatment at 300° C (A) under vacuum or (B to D) in air, and water resuspension for (A) 1 min, (B) 8 d, (C) 1 h, and (D) 5 min.
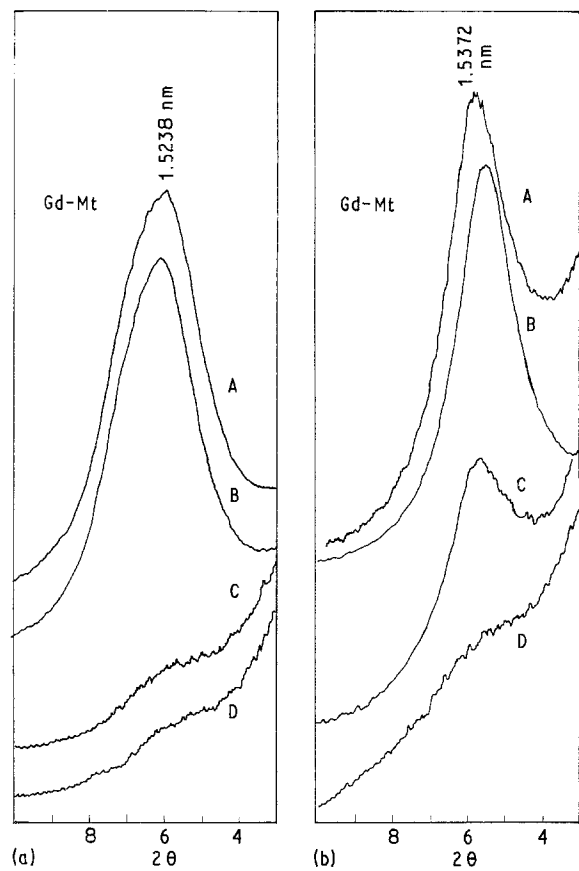
montmorillonite containing manganese the existence of $Mn(H_2O)_6^{2+}$ complexes in two-layer sheets; $Mn(H_2O)_6^{2+}$ in three-layer sheets and Mn^{2+} ions in hexagonal cavities has been suggested. Lanthanide cations in aqueous solution show higher coordination numbers in their first hydration spheres [14], but the configuration and orientation in the interlayer region should allow the observed basal spacing. The swelling of lanthanide-montmorillonites is limited as for divalent saturating ions, going up to 2 nm in water, Fig. 4, prior to heating. This value is slightly higher than that for divalent cations [12].

Air-heating 24 h at 110° C produced no change in the basal spacing, curves B Figs 1a to 3a, as expected. After heating for 24 h at 300° C, in air and under vacuum, the samples equilibrated at 60% r.h. did not show a more distinct aqueous two-layer configuration, curves C and D Figs 1a to 3a. However, prolonged re-expansion in water again gave the predominant ~ 1.5 nm spacing. In the case of heating under vacuum the re-expansion with water occurred immediately, while in air a period of days was necessary. At the same time, the re-expansion was easier as the lanthanide was lighter, Figs 1b to 3b.

The re-expansion of the same montmorillonite saturated with lithium is shown in Fig. 5 for comparative purposes. According to the Hofmann–Klemen effect [15], no two- nor mono-layered sheets are observed. The effect of heating a lithium-montmorillonite under

vacuum is the same as in air, which supports the mechanism of lithium migration to octahedral vacant sites, as generally accepted, because hydrolysis of the hydrated interlamellar Li^+, the alternative mechanism, should be largely inhibited at the low water pressure on the sample ($< 10^{-4}$ torr).

The lanthanide montmorillonites swell in water after heating in air, if re-expansion is later forced by wetting for a few days, to give the maximum basal spacings 2.2636 nm (La–Mt), 2.1294 nm (Nd–Mt) and 2.1020 nm (Gd–Mt), Fig. 4.

It is known that heating above 160° C causes a reduction in the exchangeable 4f cations from montmorillonites saturated with them [3, 4]. Miller *et al.* [4] have studied the sorption of Eu (III), Ho (III) and Yb (III) on a montmorillonite from Upton, Wyoming, with temperature. On the basis of this study, the hydrolysis of hydrated lanthanide ions and migration into octahedral holes are claimed as likely mechanisms for 4f ion fixation, with a prevalence of the latter. However, a rather high Fe (III) content presented difficulties in examining the migration mechanism by infrared spectroscopy. The Fe (III) content of the montmorillonite, used here is such that this difficulty is avoided as it will be shown later.

The knowledge of possible 4f ion fixation through a migration mechanism is of great importance concerning the disposal of high-level radioactive nuclear waste in the continental or marine ecosystem. Lanthanum
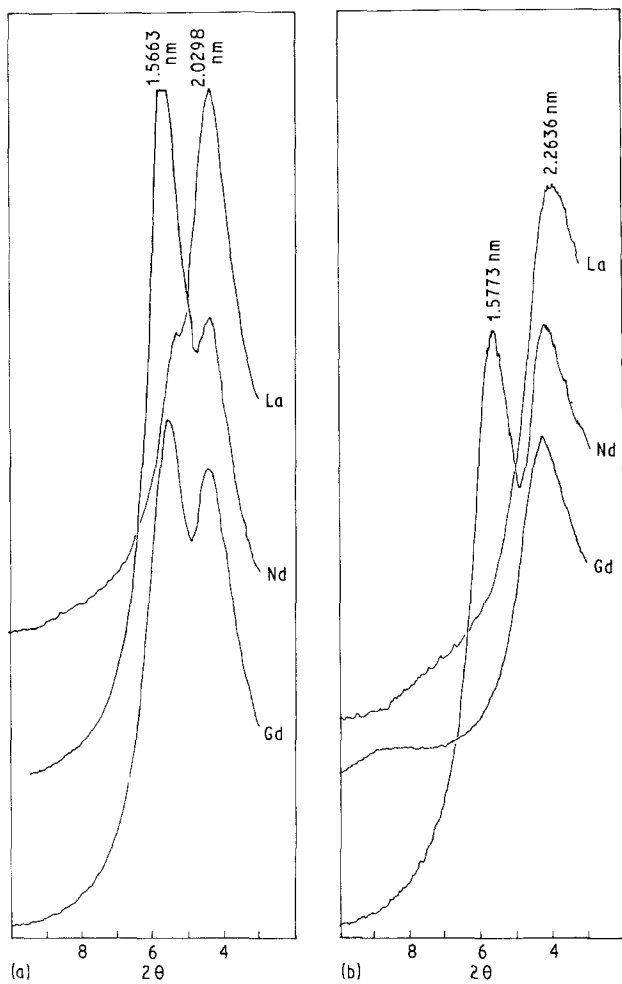
Figure 4 XRD pattern of lanthanum-, neodymium-, and gadolinium-montmorillonite wetted orientated aggregates. (a) Samples resuspended 8 d in water. (b) Samples air-heated 24 h at 300°C and further resuspended for 8 d in water.

Figure 5 XRD pattern of lithium-montmorillonite samples at 60% r.h., after heating 24 h at (A) 20°C in air, (B) 110°C in air, (C) 300°C under vacuum, and (D) 300°C in air. Samples (E) and (F) have been water resuspended for 8 d and dried at 60% r.h. after 24 h heating at 300°C under vacuum and in air, respectively.

and neodymium simulate americium and curium in studies on the interaction of the latter with clay minerals. This topic will be examined later through the b-dimension of the montmorillonite unit cell and infrared spectroscopic measurements.

The data mentioned above on the basal spacings show that even in the case of 4f migration by heating at 300°C, the exchangeable cations remaining are sufficient to allow swelling. The observed inertia of expansion on heating can be associated with that for desorbing the 4f ions from the hexagonal cavities in the tetrahedral sheets; the ratio of the cation size to that of the hole is appropriate to stabilize a sort of crown-ether complex, which the lanthanide trivalent ions are known to give [16].

In a previous paper [17] on the thermal dehydration of lanthanide montmorillonite, we reported partial hydrolysis of interlamellar hydrated 4f cations by anchoring to the montmorillonite sheets of the resulting polyhydroxycations, through a condensation reaction by H_2O elimination. Both the protons obtained during the hydrolysis and the interlamellar polyhydroxycations can explain the observed high basal spacing in water, in the range 2.1 to 2.2 nm. These poly-cations could be precursors of pillars. Plee *et al.* [18] observed a more ordered distribution of pillars in the case of smectites rich in tetrahedral substitution, which is
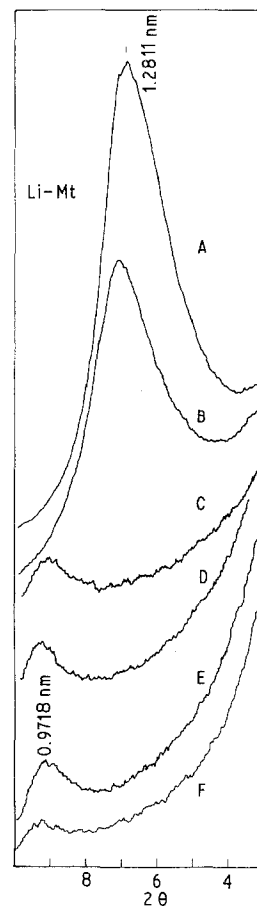
ascribed to the specific linkages between Al_{13}-polyhydroxypolymer and the clay's tetrahedral layer.

The b-dimension of the montmorillonite unit cell is well known to be a function of the water content, the isomorphous substitutions and the exchangeable cations. Table I shows the b-dimension of the montmorillonites, measured as mentioned above. Column 2 shows the values for samples prior to heating; there is no observable dependence on the nature of the exchangeable ion, the variation being smaller than the limit of error. Ravina and Low [19] obtained values for air-dried montmorillonites which changed slightly with the monovalent cation exchange – 0.8969 nm (Na), 0.8966 nm (Li) – and remained constant with the divalents – 0.8960 nm (Be, Mg, Ca, Sr, Ba).

The b-dimension values for the samples air heated for 24 h at 300°C and dried after cooling at 60% r.h. are shown in Column 3. Afterwards, the samples were wetted for a few days, dried at 60% r.h. and the b-dimension measured again, Column 5. Except for the lithium-montmorillonite, the initial values were practically reproduced after rehydration. The same effects were observed when the samples were previously heated for 24 h at 300°C under vacuum, Columns 4 and 6, respectively.

Isomorphic substitution in layer silicates leads to changes in the b-dimension. Empirical formulae have been proposed from which this dimension can be
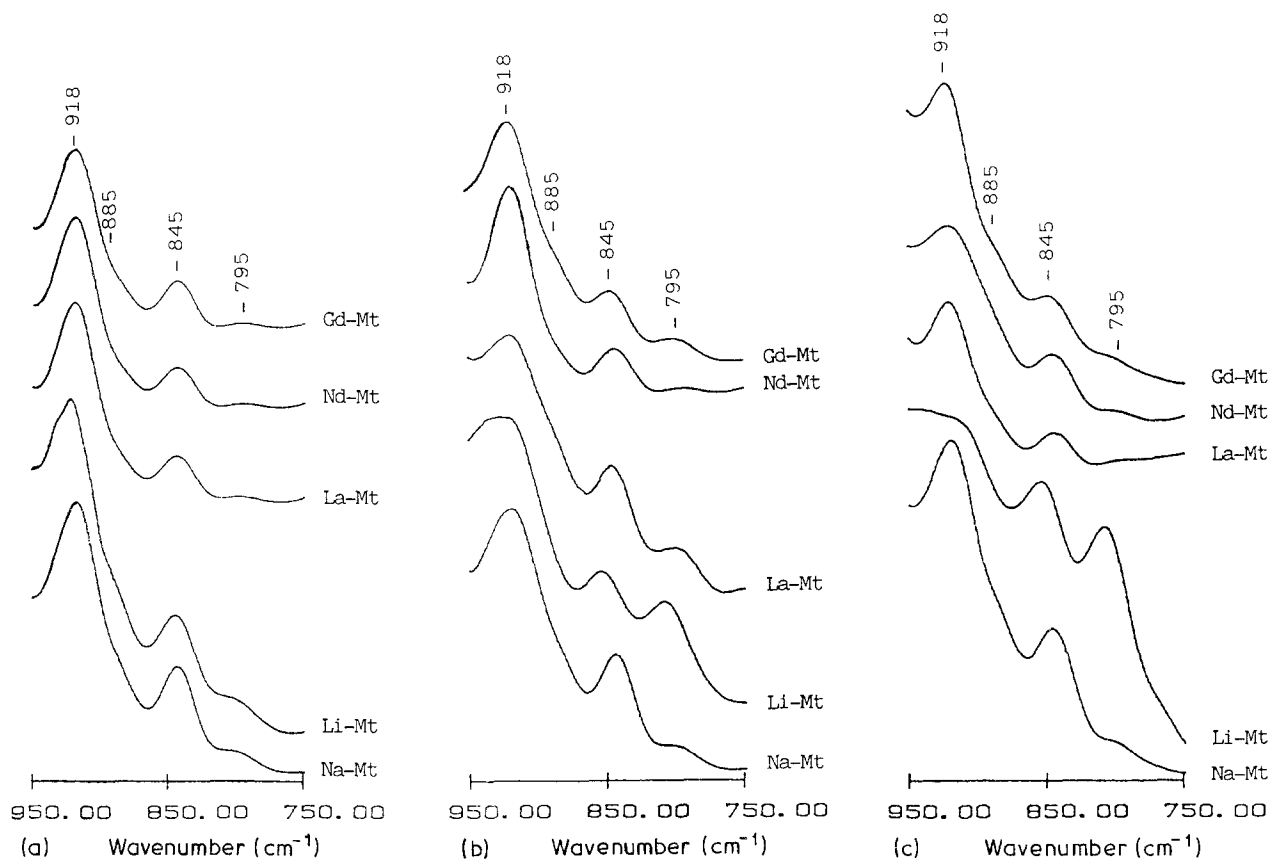
Figure 6 FT-IR spectra of sodium-, lithium-, lanthanum-, neodymium- and gadolinium-montmorillonite. (a) The initial samples, (b) the air-heated (300° C, 24 h) samples and (c) the vacuum heated (300° C, 24 h) samples.

calculated [20, 21]. From the values in Columns 5 and 6 it can be deduced that heating of the lanthanide montmorillonites at 300° C, in air or under vacuum, does not produce any increase in the cell unit parameter, which is not consistent with the Ln (III) migration into vacant octahedral sites.

The influence of hydration on the *b*-dimension has been studied for montmorillonite in the range from oven-dry to air-dry [22] and from air-dry to maximum swelling [19]. In the former range a decrease in *b*-dimension with hydration was observed; in the latter an increase with water content from air-dried sodium-montmorillonite (0.8968 nm) to 3.0 g H_2O/g clay (0.8980 nm), was found the *b*-dimension remaining constant up to 24 g H_2O/g clay. Data in Table I agree with this effect of water content on the *b*-dimension and with a long induced period of time for re-expansion of the lanthanide montmorillonites after heating; the rehydration of the samples needs to be forced by prolonged wetting.

3.3. Infrared (FT–IR) spectroscopy analysis

The FT–IR spectra in the region 950 to 750 cm^{-1} of the sodium-, lithium- and lanthanide-saturated montmorillonites are shown in Fig. 6. Four absorption bands due to OH-bending modes at 918 cm^{-1} (AlAlOH), 885 cm^{-1} (AlFe (III) OH), 845 cm^{-1} (AlMgOH) and 795 cm^{-1} (MgMgOH) are observed. Heating for 24 h at 300° C, in air or under vacuum, keep the positions of the four bands constant for all the prepared montmorillonites, except for that saturated with lithium. The migration of exchangeable cations into the vacant octahedral sites should be accompanied by a shift in the OH bending frequencies [23]. Therefore, the migration from their exchangeable positions to the octahedral sites of the tervalent ions belonging to the first half of the lanthanum series, can be rejected. The relative intensity of the (AlFe (III) OH) absorption band is smaller than given by Miller *et al.* [4], so that the shift of the OH bending frequencies should be observable here.

TABLE I *b*-dimensions of M-montmorillonites measured on air-dried samples at 60% r.h.

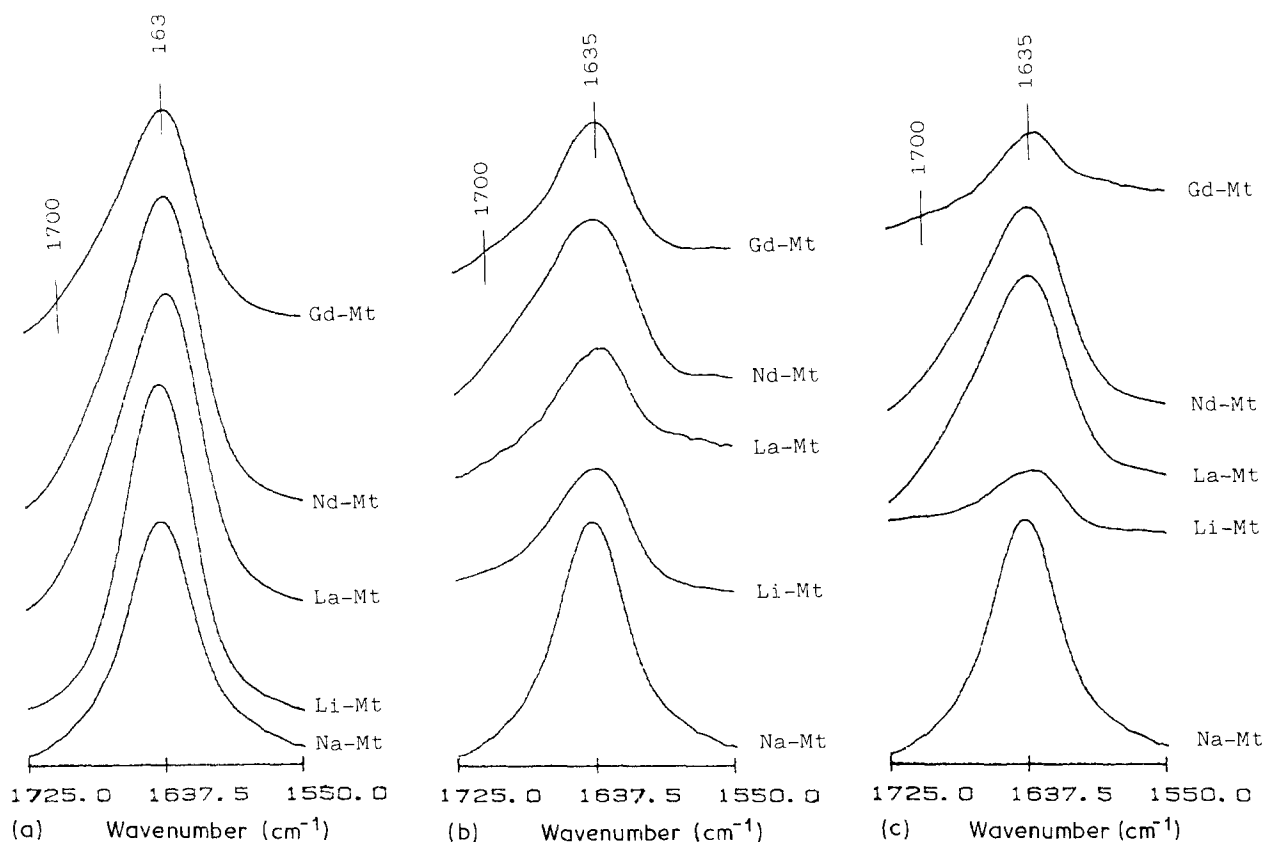| Sample	*b* (nm)				
	Unheated	Air-heated (24 h, 300° C)	Vacuum-heated (24 h, 300° C)	Re-expanded in water after air-heating	Re-expanded in water after vacuum heating
Na-Mt	0.8973	0.8975	0.8980	0.8973	0.8974
La-Mt	0.8975	0.8982	0.8983	0.8971	0.8976
Nd-Mt	0.8975	0.8982	0.8983	0.8970	0.8973
Gd-Mt	0.8971	0.8980	0.8984	0.8972	0.8970
Li-Mt	0.8973	0.8988	0.8996	0.8989	0.8995

Error: ± 0.0003 nm.

Figure 7 FT-IR spectra of sodium-, lithium-, lanthanum-, neodymium- and gadolinium-montmorillonite. (a) The initial samples, (b) the air-heated (300°C, 24 h) samples and (c) the vacuum heated (300°C, 24 h) samples.

The asymmetric band centred around 3400 cm^{-1} is due to hydroxyl stretching or interlayer water molecules in a variety of environments, and it is generally taken as indicative of the extension of montmorillonite hydration, although the band at 1635 cm^{-1}, caused by H–O–H bending absorption, will be used here. Russell and Farmer [24] have distinguished two types of interlayer water in montmorillonites by infrared spectroscopy; one more labile with an infrared absorption pattern similar to that of liquid water, ascribable to water molecules in outer co-ordination spheres of the exchangeable cations, and another more firmly held. The latter makes an unusually strong contribution to the absorption band at 1635 cm^{-1} and is associated with molecules directly co-ordinated to the cations, in agreement with quasi-elastic neutron scattering experiments data on montmorillonite saturated with polyvalent cations [25]. From this it can be inferred that a decrease in the amount of interlamellar hydrated cations should result in a parallel decrease of the 1635 cm^{-1} band intensity. Fig. 7 shows the FT-IR spectra (1725 to 1550 cm^{-1}) of the diverse samples, (a) without thermal treatment, (b) after 24 h heating at 300°C at the air, and (c) under vacuum; the absorption scale has been kept constant for all the spectra. The spectra for the sodium-saturated montmorillonite has been included as a reference.

The spectra of the Li-Mt samples show a high decrease in the 1635 cm^{-1} band intensity with thermal treatment, in air and under vacuum. A quantitative comparison of the changes in air and under vacuum does not make sense because of the control of the

process by kinetic factors. In the cases of La-Mt and Nd-Mt a small decrease is observed on heating under vacuum, which corresponds to a lower magnitude of the hydrolysis reaction of the hydrated exchangeable cations. However, the intensity of the band for the montmorillonite saturated with gadolinium decreases greatly on heating under vacuum; this can be ascribed to the higher enthalpy of hydration of Gd (III), which leads to an appreciable level of hydration of it under the vacuum conditions used. The decrease for the Li-Mt sample on heating under vacuum cannot be explained in the same way, because of the difference in hydration enthalpy between Li (I) and La (III)-Nd (III).

The above discussion of the 1635 cm^{-1} absorption band leads to the conclusion that the behaviour of the montmorillonite saturated with lithium is different from that saturated with lanthanides when they are thermally treated at 300°C. Furthermore, spectra of air-dried films of H-montmorillonites show broad absorption bands at 2900 and 1700 cm^{-1} which are thought to be due to the hydronium ion [26]; the spectra of the Ln-Mt samples show, together with decrease in the intensity of the 1635 cm^{-1} band, the appearance of a shoulder centred around 1700 cm^{-1} as proof of the hydrolysis of the hydrated interlamellar cations. The possibility of a certain degree of hydrolysis in the lanthanide montmorillonites prior to heating may not be ruled out, because it is difficult to avoid this during the preparation process; so it is observed that the intensity of the 1635 cm^{-1} band for the Gd-Mt sample in Fig. 7a is smaller than the corresponding value for the La-Mt and Nd-Mt samples.

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4. Conclusions

The basal spacing of lanthanide montmorillonites is almost constant over a wide range of humidities and corresponds to a double-sheet complex. The swelling behaviour of montmorillonite saturated with lanthanide trivalent cations is the same over a wide range of humidities as those saturated with divalent alkaline earth cations, irrespective of the difference in hydration enthalpies between both kinds of ion. After heating for 24 h at 300° C, in air and under vacuum, the lanthanide montmorillonites equilibrated at 60% r.h. apparently lose their swelling capacity. However, prolonged re-expansion in water and further equilibration at 60% r.h. reproduces the double-sheet interlamellar complex. The re-expansion is easier for the sample heated under vacuum and for the lighter lanthanides.

The b-dimension of the montmorillonite unit cell is reproduced after rehydration for the lanthanide samples heated at 300° C, but not in the case of the lithium-montmorillonite. The FT–IR spectra in the region 950 to 750 cm^{-1} show shifts on heating of the OH bending frequencies only in the case of the lithium-montmorillonite. These results are not consistent with migration of the interlamellar lanthanide cations into vacant octahedral sites.

From observation of a noticeable decrease in the 1635 cm^{-1} band with the thermal treatment in the Li-Mt and Ln-Mt (Ln = La, Nd, Gd) samples, but not in the case of the Na-Mt one, it is concluded that there exists a parallel decrease in the interlamellar hydrated cations. This result supports the mechanism of charge reduction advocated by Hofmann and Klemen, in the case of the lithium-montmorillonite, which implies migration of exchangeable cation into octahedral vacant sites. However, the mechanism mentioned should not contribute in the cases of lanthanide montmorillonites, according to the XRD and FT-IR data shown above. The well-known decrease in the cation exchange capacity for the lanthanide montmorillonites having undergone thermal treatments, parallel to that observed here, in the intensity of the 1635 cm^{-1} band, must be ascribed exclusively to a hydrolysis mechanism. The interlamellar polyhydroxycations and the protons obtained during the hydrolysis causes a basal spacing in the wetted samples of 2.1 to 2.2 nm higher than that observed for the unheated ones, under the same conditions.

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