

XRD investigation of the intercalation of nacrite with cesium chloride

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ABSTRACT: An homogenous intercalated compound of dioctahedral 1:1 clay mineral with cesium chloride was prepared by immersing an homogeneous 8.4 Å hydrated nacrite in a CsCl-saturated solution. The nacrite/CsCl complex obtained was studied using X-ray diffraction and thermogravimetric analysis (TGA). The best agreement between the observed and the simulated $\rho(z)$ ($R = 7\%$) was obtained with one Cl^- ion, one Cs^+ ion and one water molecule (per half-unit cell). The cation was located near the oxygen atom plane, while the anion was located near the hydroxyl groups of the adjacent layer. The number of the species intercalated in nacrite/CsCl was confirmed by TGA analysis. The best agreement between the calculated and the experimental hkl reflections, with h and/or $k \neq 0$, corresponded to a stacking of 70% and 30% for $T_1 = -0.35a - 0.20b + 10.50n$ and $T_2 = +b/3 + 10.5n$, respectively. These results indicate that the surface hydroxyls form hydrogen bonds with Cl^- ions. The Cs^+ ions are situated near the ditrigonal cavities of the tetrahedral sheet and they interact with the surface oxygen atoms whereas the H_2O molecules interact with the intercalated species.

KEYWORDS: intercalation, nacrite, hydrated nacrite, nacrite/CsCl complex, XRD.

Minerals of the kaolin group are important raw materials in a variety of industrial processes and in environmental protection, used, in particular, as adsorbents, molecular sieves, ion-exchangers and catalysts (Murray *et al.*, 2000; Bergaya *et al.*, 2006). Kaolinite, with the chemical composition $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ is the most abundant mineral of the kaolin group which includes dickite, nacrite and halloysite. It is a dioctahedral 1:1 clay mineral formed by the superposition of silicon tetrahedral sheets and aluminium octahedral sheets (Brigatti *et al.*, 2006).

Advances in the preparation of hybrid organic–inorganic materials by the intercalation of organic molecules into kaolinite have presented new opportunities for developing new and interesting materials

(Gardolinski & Lagaly, 2005; Detellier & Letaief., 2006; Cheng *et al.*, 2013). Recently, kaolinite has been studied more widely because of its unique physico-chemical characteristics and versatile industrial applications (Ming, 2004).

The intercalation of alkali halides into kaolinite has been attempted in different ways. The mechanochemical method, *i.e.* the soft grinding of kaolinite crystals in a small amount of water containing the salt to be intercalated, destroys the kaolinite structure and leads to delamination of the material (Yariv *et al.*, 1999). With CsCl, the X-ray diffraction (XRD) pattern of the compound obtained by such treatment (Yariv *et al.*, 1986; Michaelian *et al.*, 1991a) indicates the absence of intercalation. In fact, the characteristic reflection at 7.2 Å disappears and no other reflections arise. For all cesium halides, intercalation only occurs when an additional thermal treatment ($>150^\circ\text{C}$) is applied (Yariv *et al.*, 1986; Michaelian *et al.*, 1991a,b).

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Intercalation of alkali halides is successful when kaolinite is first intercalated with hydrazine, dimethylsulfoxide (DMSO), ammonium acetate (Michaelian *et al.*, 1991b; Lapidès *et al.*, 1997; Yariv *et al.*, 2000) or water (Naamen *et al.*, 2004; 2006). Then, the intercalation of alkali halides may be obtained by two methods: (1) by immersion in alkali halide solutions; and (2) by soft grinding and heating. The immersion of first-intercalated kaolinite in alkali halide solutions (Weiss *et al.*, 1966; Michaelian *et al.*, 1991a,b, 1998; Lapidès *et al.*, 1997; Yariv *et al.*, 2000) fails with KI, CsI and KBr.

In contrast, grinding of intercalated kaolinite with alkali halides in air or in water, followed by heating at various temperatures allows the intercalation of all alkali halides (Yariv, 1975; Michaelian *et al.*, 1991a; Lapidès *et al.*, 1997; Naamen *et al.*, 2003). The hydrated salts penetrate the interlayer space of the kaolinite layers inducing a change in the basal spacing. For example, with a DMSO kaolinite as a starting material, the d_{001} value varies from 11.2 Å to 10.5 Å for CsCl. Yariv *et al.*, (2000) suggested that the hydrated kaolinite/CsCl complex does not show long-range periodicity without heating. After heating at 250°C, periodic stacking of the 1:1 layers is obtained. On the other hand, in all these works concerning the intercalated kaolinite with alkali halides, XRD measurements were only used to identify the newly formed complexes.

Michaelian *et al.* (1991a) used IR spectroscopy to identify the structure of the kaolinite/CsCl complex where the water molecule, coordinated with the Cs^+ cation, shares one proton with a 1:1 surface layer oxygen while the other proton interacts with the halide anion Cl^- , which itself accepts a proton from the surface hydroxyl group of the adjacent layer. This structure suggests that the Cs^+ cation, the Cl^- anion and the water molecule are located at the same z-coordinate normal to the (ab) plane of the layers in the interlamellar space.

In spite of the previous works, the exact structure of the kaolinite/alkali halide complexes has not been defined completely because, so far, only qualitative results have been used to describe the structure of such complexes. The objective of the present study, therefore, was to study the formation and structural features of well-ordered nacrite intercalation compounds with cesium chloride.

MATERIALS AND METHODS

Samples and preparation procedure

Nacrite has previously shown behavior similar to that of kaolinite during the intercalation mechanism.

The present study was carried out using Jbel Sлата nacrite for two reasons: (1) because the intercalation of the sample by water and an organic molecule is almost complete in this nacrite (Ben Haj Amara, 1997b); and (2) because the first-intercalated nacrite with water, which was used for the preparation of the alkali halide complex, is well ordered (Naamen *et al.*, 2004, 2006). CsCl salt was chosen for intercalation because it can be localized accurately in the interlamellar space of nacrite due to the large atomic X-ray diffusion factors of the Cs^+ (54) and Cl^- (18) ions (Bergaya *et al.*, 2006).

Hydrated nacrite was obtained by the method described in a previous study (Ben Haj Amara *et al.*, 1997a): 2 g of clay mineral were ground and kept in 20 mL of a saturated potassium acetate solution for several days until intercalation was complete. The resulting nacrite/potassium acetate complex was washed with water and air dried in order to obtain 8.4 Å nacrite.

The nacrite/CsCl complex was synthesized by immersing the 8.4 Å hydrated nacrite in a saturated CsCl solution. In order to determine the optimum CsCl concentration to obtain the greatest intercalation rate (τ), a starting hydrated nacrite mass was placed in the CsCl solution with a concentration which varied between 0.1 and 3 N. Figure 1 is a plot of τ vs. the normality where τ represents the proportion of intercalated nacrite and is given by the following relation:

$$\tau = \frac{I_{001}(\text{int})}{I_{001}(\text{hn}) + I_{001}(\text{int})}$$

where $I_{001}(\text{int})$ and $I_{001}(\text{hn})$ are the intensities of the nacrite intercalated by CsCl and the nacrite hydrate,

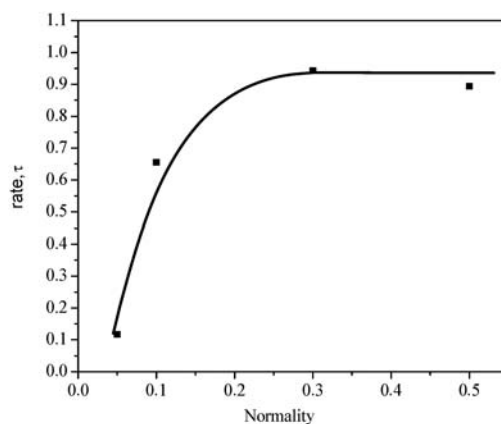


FIG. 1. Plot of the rate of intercalation of CsCl (τ) as a function of the normality.

respectively (Ben Haj Amara *et al.*, 1995). The optimum intercalation rate corresponds to $N \geq 0.3$ (Fig. 1).

X-ray diffraction analysis

The nacrite/CsCl complex was studied by means of XRD analysis. X-ray patterns of oriented powder were obtained using a Bruker D8-Advance diffractometer equipped with a vertical goniometer with $\text{CuK}\alpha_1$ radiation, using a step size of $0.02^\circ 2\theta$ with a 100 s acquisition time per step.

The hkl reflections (with h and/or $k \neq 0$) were obtained with an Inel diffractometer using $\text{MoK}\alpha_1$ radiation in transmission mode. The samples were placed in a glass capillary tubes in order to obtain powders which were thoroughly disoriented.

The structural characterization was achieved in two steps: (1) determination of the number and positions of the water molecules and the Cs^+ and Cl^- ions along the normal to the (ab) plane, by modelling the experimental electronic density obtained from the $00l$ reflections; and (2) determination of the in-plane positions of the water molecules and the Cs^+ and Cl^- ions by modelling the hkl reflections. The theoretical XRD patterns were calculated using the nacrite atom coordinates given by Zheng & Bailey (1994) while the unit-cell origin was placed on the oxygen surface.

Thermal analysis

The transition temperature of the samples was measured by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) using a SETARAM instrument. About 10 mg of each of the samples was heated at a rate of $10^\circ\text{C}/\text{min}$ from room temperature to 1000°C .

EDAX analysis

A Tecnai G2 transmission electron microscope was used for imaging and local mode analysis. Thin

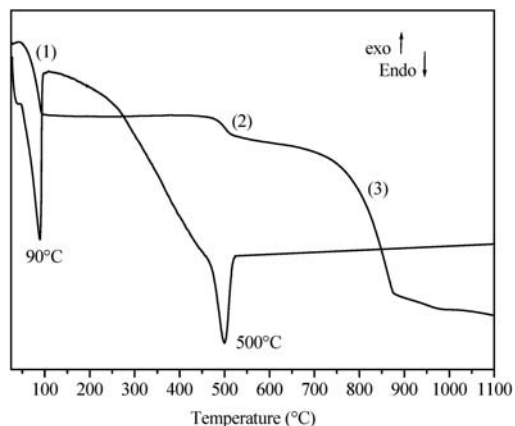


FIG. 2. Results of the thermal analysis of the nacrite/CsCl complex.

specimens were prepared simply by crushing the sample into fine fragments (Ben Haj Amara, 1997a) in a mortar under butanol. A drop of the dispersions was placed on a holey carbon film supported by a copper grid.

RESULTS

Chemical and thermal analysis

The TG curve of the intercalated nacrite/CsCl/ H_2O complex showed three steps of mass loss (Fig. 2): (1) The first was due to the dehydration of the complex at close to 90°C . The corresponding mass loss, without taking into account the free hydrated salt in the structure, is of the order of one water molecule per $\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4$ (Table 2). (2) The second step was at $\sim 500^\circ\text{C}$ and corresponded to the dehydroxylation of the sample. (3) The third step between 500 and 700°C should be related to the evolution of HCl, formed from the thermal hydrolysis of CsCl in the presence of traces of water (Yariv *et al.*, 1994, 2000). This result has been confirmed by the EDAX chemical analysis of the

TABLE 1. Parameters of apparent coherent domain, basal spacing for $00l$ reflections and experimental I_{001}/I_{001} ($l = 1, 2, 3, 4, 5, 6, 7, 8, 9$ and 10) ratios of the nacrite/CsCl complex.

$00l$	002	004	006	008	010	012	014	016	018	020
I_{001}/I_{001}	1	0.78	0.71	2.01	1.84	25.5	9.32	14.26	35.35	54.97
$(ld_{001})_{\text{app}}$	10.54	10.52	10.50	10.50	10.5	10.5	10.49	10.49	10.49	10.50
M	46	46	46	48	46	47	47	48	48	48

TABLE 2. Number of molecules intercalated using the TG analysis.

$\Delta m/m$	Experimental	Theoretical	Events
Loss 1	4.32%	4.33%	$-1\text{H}_2\text{O}$
Loss 2	10.75%	10.75%	$-2\text{H}_2\text{O}$
Loss 3	18.56%	18.55%	-1Cs^+
Total	33.52%	33.63%	

nacrite/CsCl complex heated at 800°C under the same conditions as the TG analysis (Fig. 3). Indeed, the sample contains larger amounts of cesium whereas chlorine is absent.

Analysis of the XRD data

Analysis of the 00l diffraction maxima. The degree of orientation in an oriented particle might be characterized by the σ^* parameter defined by Reynolds (1986) as the standard deviation of an assumed Gaussian distribution, describing the probability of occurrence of particles whose normal is tilted by an angle ω from the mean orientation. This σ^* parameter, which ranges from 4 to 30° for oriented clay-mineral particles, may be determined using the protocol described previously (Taylor & Norrish, 1966). A plot of $\text{Ln}[I(\omega)]$ vs. ω^2 , using the 006 reflection for the nacrite/CsCl complex, shows a straight line confirming that the orientation function was indeed Gaussian (Fig. 4). These results are in agreement with those of previous works, in which it was concluded that a Gaussian function explains the orientation state of well oriented clay-mineral samples (Taylor & Norrish, 1966; Lippmann,

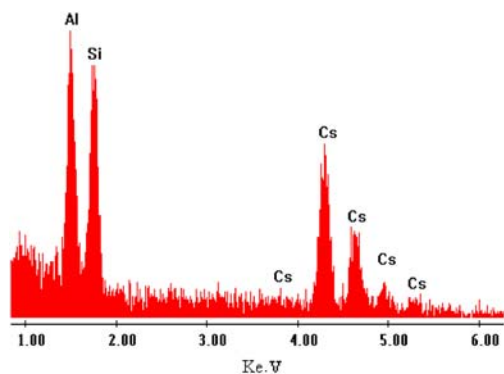
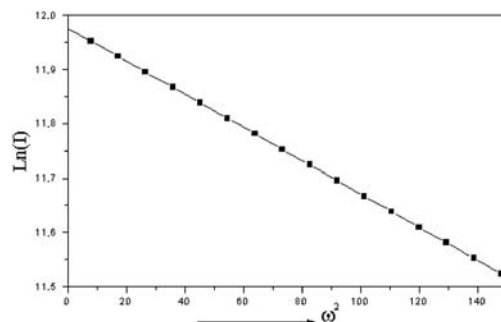


FIG. 3. EDAX spectrum of the nacrite/CsCl complex heated at 800°C.

FIG. 4. Plot of the intensity as a function of tilt angle $\text{Ln}[I(\omega)]$ vs. ω^2 . The standard deviation from the assumed Gaussian distribution of the orientation function (σ^*) was obtained from the slope of the straight line.

1970; Zheng & Bailey, 1994; Ben Haj Amara *et al.*, 1998). The value of σ^* obtained from the slope of the straight line is 11.7° (Fig. 3) which is characteristic of a well oriented sample (Reynolds, 1986; Ben Haj Amara, 1997).

The qualitative analysis of the XRD pattern of the nacrite/CsCl complex shows ten 00l reflections (Fig. 5) with rational positions (Table 1), and basal-spacing values of 10.51 ± 0.02 Å (Naamen *et al.*, 2004, 2006). There are no anomalies in terms of the width at half-maximum intensities (FWHM) for any 00l reflections, which lead to a mean number of layers per stacking $\bar{M} = 47 \pm 1$. These results indicate that the complex is homogeneous. A small amount of non-intercalated nacrite can be detected (weak reflection at 7.2 Å in Fig. 5).

The number of 00l reflections is sufficient to determine the composition of materials of the mono-dimensional electron density projection, $\rho(z)$, along the normal to the layers, using a Fourier transform (Ben Haj Amara *et al.*, 1998). The same formula is applied to the observed and calculated $\rho(z)$ (XRD, Plançon, 1981; Ben Haj Amara *et al.*, 1995, 1997a,b):

$$\rho(z) = \frac{8}{V_c} \sum_{l=0}^N |F_{00l}| \cos\left(\frac{2\pi z}{d_{002}} l - \alpha_{00l}\right)$$

where F_{00l} is the structural factor for the 00l reflections and takes into account the structural formula (Table 3) (Ben Haj Amara *et al.*, 1998). The number of Cl^- , Cs^+ ions and H_2O per unit-cell and their z coordinates (Å) along the perpendicular to the layer plane were determined using 00l reflections analysis.

α_{00l} corresponds to the structural factor phase. For the observed electron density projection, α_{00l} represents the calculated factor phase.

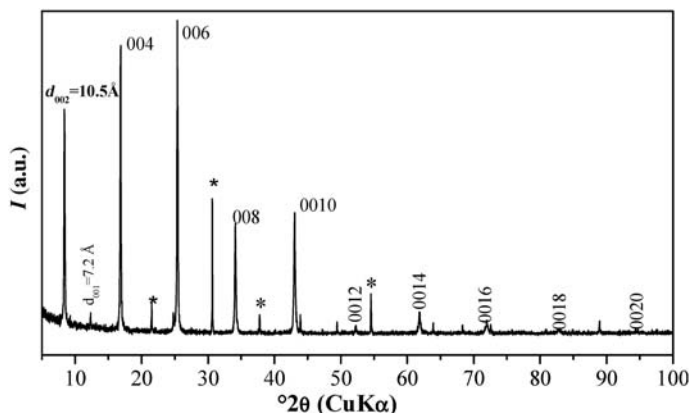


FIG. 5. XRD pattern of the nacrite/CsCl intercalated complex. * Denotes excess CsCl present in the sample.

The validity of the model is evaluated by the reliability factor:

$$R = \frac{\sum |F_{\text{cal}}| - |F_{\text{obs}}|}{\sum |F_{\text{obs}}|}$$

where F_{obs} and F_{cal} are the structural factors of the observed and calculated $00l$ reflections, respectively.

The best agreement between experimental and calculated profiles of electronic density for the nacrite/CsCl complex is illustrated in Fig. 6. The best reliability factor ($R = 7\%$) is obtained per half unit cell

TABLE 3. Atomic coordinates for nacrite, calculated on an orthogonal basis, from those refined by Zheng & Bailey (1994).

Atoms	x (Å)	y (Å)	z (Å)
O ₁	0.2439	0.7499	0.0690
O ₂	0.2855	0.2470	0.0072
O ₃	0.0165	0.4417	0.000
O ₄	0.1723	0.4385	2.1800
O ₅	0.3648	0.011	2.2605
OH ₁	-0.0211	0.0118	2.3300
OH ₂	0.3587	0.6342	4.3530
OH ₃	-0.204	0.6296	4.3340
OH ₄	0.1709	0.2066	4.3352
Si ₁	0.1817	0.470	0.6050
Si ₂	0.3525	0.983	0.6050
Al ₁	0.0023	0.3198	3.4007
Al ₂	0.3375	0.3245	3.3980
Vacant octahedron	0.1778	-0.1752	3.4000

using: one Cs⁺ cation placed at $z = 8.30 \pm 0.01$ Å, one Cl⁻ anion placed at $z = 6.36 \pm 0.01$ Å, and one H₂O molecule placed at $z = 7.26 \pm 0.01$ Å.

These results indicate that: the Cs⁺ cation is located near the basal oxygens of the nacrite layer, interacting with the oxygen atoms of a surface layer. This result is in agreement with those suggested by (Yariv *et al.*, 1986; Michaelian *et al.*, 1991b). The Cl⁻ ion is located near the surface hydroxyl ($z = 4.41$ Å), interacting with the OH groups of the surface of the adjacent layer. The H₂O molecule is situated in the middle of the interlamellar space, interacting only with the salt ions. This differs from the interaction given by Michaelian *et al.* (1991a) who suggested an interaction between the intercalated H₂O molecule and the oxygens at the surface of the tetrahedral sheet.

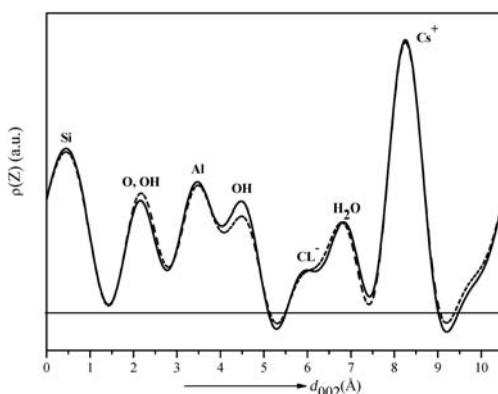


FIG. 6. Agreement between the calculated (solid trace) and experimental (dashed-line trace) electronic density for the nacrite/CsCl complex.

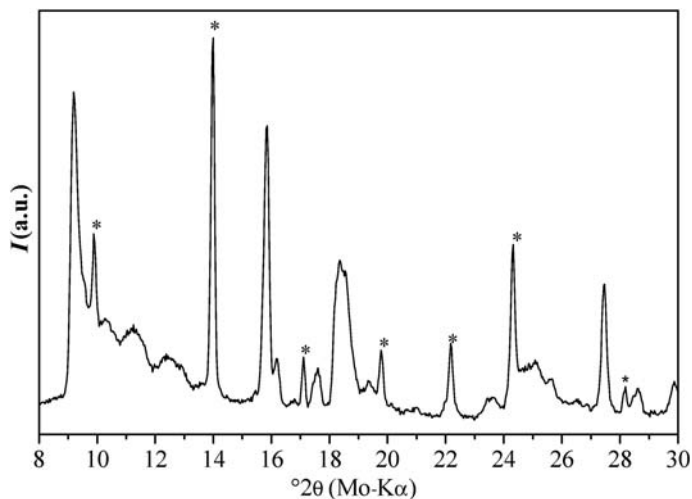


FIG. 7. Experimental XRD pattern (transmission mode) of the nacrite/CsCl intercalated complex. *Denotes excess CsCl present in the sample.

The Cs^+ cation is inserted deeply into the ditrigonal cavity. The keying of the cation is of the order of 0.15 Å. The Cl^- anion is placed above the hydroxyl surface of the adjacent layer and forms a hydrogen bond. The model proposed by Yariv *et al.* (1994, 2000) for the anhydrous kaolinite intercalated with CsCl, which suggested the same z coordinates for both Cl^- and Cs^+ , has not been verified here. This suggests that the nacrite/CsCl intercalated complex is almost a hydrated complex and not anhydrous as suggested by Yariv *et al.* (1994).

Analysis of the hkl reflections. The stacking mode of the layers and the in-plane positions of the intercalated molecules were determined from modeling of the hkl reflections of a randomly oriented powder. The theoretical XRD intensities were calculated using the matrix formalism (Plançon, 1981; Ben Rhaïem *et al.*, 1998, 2000). The structural model depends on the number of the different kinds of layers, the stacking mode along the normal and in the plane of layers, the size of scattering coherent domains and the particle orientation (Plançon, 1981; Naamen *et al.*, 2003).

The qualitative analysis of the XRD patterns corresponding to the natural and treated samples, demonstrates clearly an evolution from an ordered structure (Ben Haj Amara *et al.*, 1997b) to a disordered one (Fig. 7).

The quantitative analysis of the hkl reflections was carried out using the results obtained from the 00 l reflections. The (x, y) positions deduced from analysis of the hkl reflections correspond to the middle of the

octahedral vacancy at a distance of 3.35 Å from the hydroxyl surface of the octahedral sheet (Fig. 8). In order to determine the distribution of Cs^+ , the ionic radius of the ions ($r_{\text{Cs}^+} + r_{\text{Cl}^-} = 3.5$ Å) was calculated. Then the Cs^+ was placed above the Cl^- lattice along the normal (n) going through the gravity centre of the anions. This situation corresponds to two sites designated 1 and 2 in Figure 8. For the two locations, the distance between the Cs^+ and Cl^- ions is of the order of 3.50 Å. The Cs^+ is keyed in the ditrigonal hole and interacts with the oxygen surface of the tetrahedral sheet. This involves two translation possibilities between the adjacent layers:

$T_1 = -0.35a - 0.20b + 10.50n$ or $T_2 = +b/3 + 10.50n$ for the sites 1 and 2, respectively. The H_2O molecule is placed in the middle of the interlamellar space within one of the sites unoccupied by Cs^+ cations (Fig. 9a,b). The distances between the H_2O molecule and the Cs^+ and Cl^- ions are 3.25 Å and 3.35 Å, respectively. The best agreement between the experimental and simulated patterns was obtained by placing 70% of Cs^+ in site 1 and 30% in site 2 (Fig. 10).

DISCUSSION AND CONCLUSION

The present study illustrates the complete intercalation of nacrite with an aqueous solution of CsCl. The quantitative analysis of the XRD profiles allowed the structural characteristics of the hydrated complex to be determined. The structural parameters for the intercalated species are summarized in Table 4.

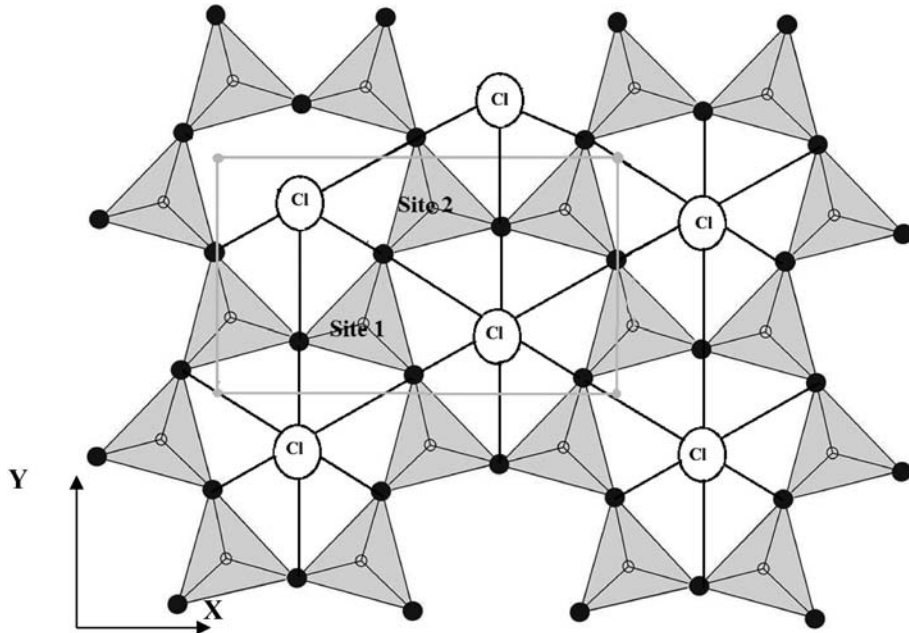


FIG. 8. Projection of the Cl^- anions and possible location of the Cs^+ cations on the nacrite basal surface.

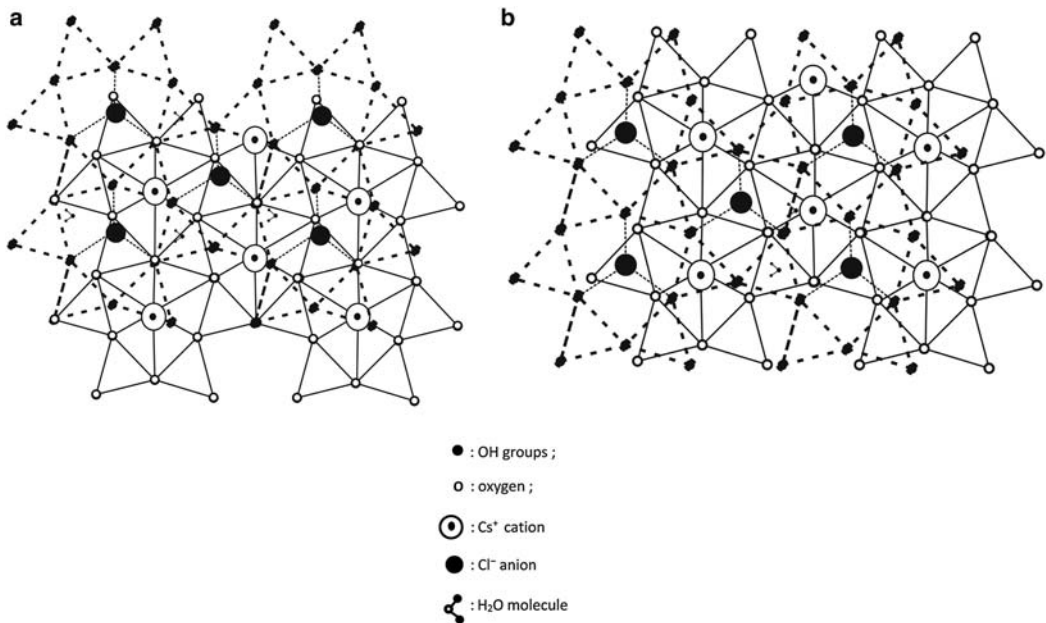


FIG. 9. (a) Projection in the ab plane of two adjacent nacrite layers. Projection of the Cl^- anion with surface hydroxyls when the Cs^+ occupies site 1 and the H_2O molecule occupies site 2. The interlayer translation involved in this occupation is designated T_1 . (b) Projection in the ab plane of two adjacent layers. Projection of the Cl^- anion on the surface hydroxyls when the Cs^+ occupied site 2 and the H_2O molecule site 1. The interlayer translation involved in this occupation is designated T_2 .

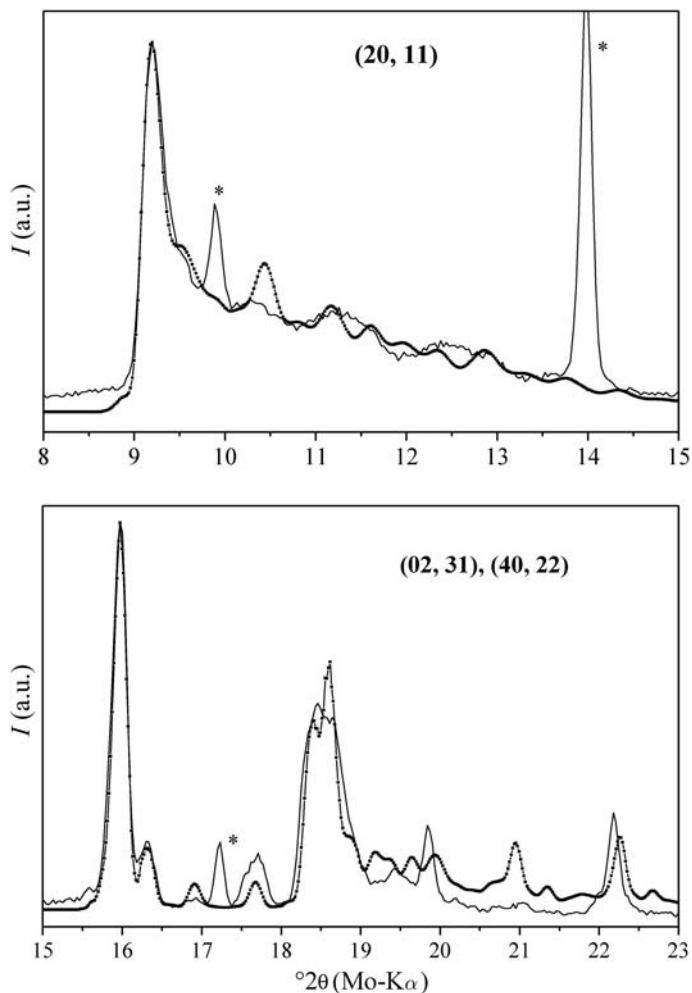


FIG. 10. Agreement between experimental (–) and calculated (bold line) hk reflections for the nacrite/CsCl complex. The calculated intensities are normalized to the experimental intensities. *Denotes excess CsCl present in the sample.

TABLE 4. Coordinates of the entities intercalated for the nacrite/CsCl according to the two translation possibilities between the adjacent layers.

Coordinates of the intercalated ions		Cs ⁺		Cl [–]		H ₂ O	
\vec{T}_1	x (Å)	0.15	0.65	0.66	0.15	0.5	0.0
	y (Å)	0.25	0.75	0.35	0.80	0.5	0.70
	z (Å)	8.30	8.30	6.36	6.36	7.26	7.26
\vec{T}_2	x (Å)	0.50	0.00	0.66	0.15	0.65	0.5
	y (Å)	0.85	0.35	0.35	0.80	0.75	0.2
	z (Å)	8.30	8.30	6.36	6.36	7.26	7.26

TABLE 5 The calculated distance between the different entities intercalated for the nacrite/CsCl complexes.

Bond length	
Cl ⁻ -H ₂ O	3.25 Å
Cl ⁻ -O	4.50 Å
Cl ⁻ -OH	2.80 Å
H ₂ O-OH ₂	4.38 Å
H ₂ O-O	5.02 Å
Cs ⁺ -H ₂ O	3.35 Å
Cs ⁺ -O	2.95 Å
Cs ⁺ -OH	4.02 Å

According to the interaction model proposed by Yariv *et al.* (1999) for the hydrated complex, the distances between: H₂O-Cl; H₂O-Cl⁻; H₂O-Cs⁺; H₂O-O and H₂O-OH are summarized in Table 5. These distances suggest that Cs⁺ entered the ditrigonal holes and interacted with the oxygen atoms. These bonds are electrostatic, whereas the Cl⁻ interacts with the surface OH and forms hydrogen bonds with the OH groups. These results are in agreement with the keying of the Cs⁺ cations with the O-plane, thus rejecting the interaction between Cl⁻ and the ditrigonal holes. Moreover, the intercalation of the salts in nacrite decreases the mean number of layers from 70 for the natural nacrite (Plançon, 1981) to 47 for the nacrite/CsCl complex, indicating partial delamination of nacrite.

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