

## Proton conductivity in Al-stevensite pillared clays

B. Rhouta, M. Amjoud, D. Mezzane, A. Alimoussa

*1 Laboratoire de Matière Condensée et Nanostructures (LMCN), Faculté des Sciences et Techniques Guéliz, BP 549, Marrakech, Maroc*

L. Daoudi

*2 Laboratoire de Géosciences et Géoenvironnement, FST Gueliz, BP 549, Marrakech, Maroc.*

E. Ech-chamikh

*3 Laboratoire de physique du solide et des couches minces, Faculté des sciences semlalia, BP : 2390, Marrakech, Maroc*

H. Kaddami

*4 Laboratoire de Chimie Bioorganique et Macromoléculaire, Faculté des Sciences et Techniques Guéliz, BP 549, Marrakech, Maroc*

Fine stevensite mineral fraction ( $< 2 \mu\text{m}$ ) has been extracted from natural Moroccan ghassoulite clay. Thereafter, it has been pillared by  $\text{Al}_{13}$  polycations species. Physico-chemical characterization, performed using X-ray diffraction (XRD), thermal analysis (TG-TDA) and Scanning Electron Microscopy (SEM) equipped with X-ray Energy Dispersion (XED) analysis, has proved that stevensite pillaring has been successfully achieved. Electrical impedance measurements, carried out onto samples before and after pillaring operation, have shown an increase in proton conductivity for pillared with respect to pristine stevensite clay mineral.

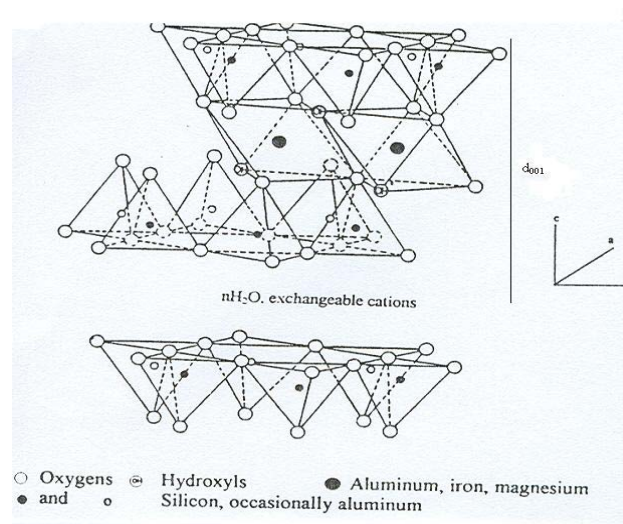
**Key-words:** stevensite, clay, pillaring, proton, conductivity,  $[\text{Al}_{13}]$ -Keggin polycation

### INTRODUCTION

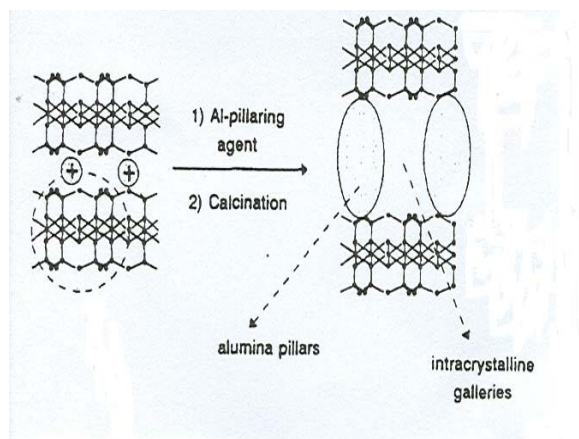
The clay mineral, of the smectite group constitute a 2:1 phyllosilicate family whose crystal structure is made up of two silica tetrahedral sheets with a central alumina or magnesia octahedral sheet (Fig 1). Common oxygen atoms bind these sheets. The layers are continuous in the a and b axis directions and are stacked one above the other in the c direction, in such a way to form a regular Van der Waals gap between them, called interlayer or interlamellar space or gallery (Fig 1). Isomorphic substitutions may occur within the layers, e.g.,  $\text{Al}^{3+}$  replaced by  $\text{Mg}^{2+}$  or by  $\text{Fe}^{2+}$ , or  $\text{Mg}^{2+}$  replaced by  $\text{Li}^+$ . These substitutions generate negative electrical charges, mainly located in the silicate octahedral layers, which are compensated for by hydrated alkali or alkaline earth cations situated in the gallery (Fig 1). The structural unit, consisted of both the tetrahedral and the octahedral sheets as well as the half of the gallery, represents the basal space  $d_{001}$  which is the main characteristic of the clay minerals. Thus for identifying their nature by XRD technique the basal reflexion should be maximized by achieving well-oriented samples preparation [1]. Several smectite variants (montmorillonite, beidellite, nontronite, stevensite, saponite and hectorite) exist according to the fact that substitutions occur in tetrahedral and/or octahedral layers [2].

In the natural form, the application potentialities of smectite clay minerals are below

interesting possibilities that their versatile properties would really offer. For example, they suffer from thermal instability, resulting from sheets collapsing due to dehydration of compensating interlayer cations, once the temperature is over  $150^\circ\text{C}$  [3]. Moreover, for this reason, they have been replaced by zeolites as high temperature catalysts for oil cracking



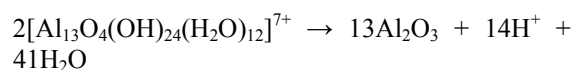
**FIGURE 1:** Crystalline structure of smectite clay minerals



**FIGURE 2:** Pillaring principle of smectite clay minerals [10].

industry [3]. So, there are recently continuing efforts devoted to the improvement of smectite clay minerals properties via pillaring operation [4-6]. In fact, due to the lower electrical charge of their layers (generally around 0.4) [1], Van der Waals interactions between sheets are so weak that the hydrated compensating interlayer cations can be easily exchanged by some cationic metal clusters which, after heat-treating, are converted at high temperature into the corresponding metal oxide clusters that act as pillars (Figure 2). Hence, these materials are called Pillared interlayer clays (PILCs). In PILCs, the pillars are so rigid that not only they prevent the interlayer space from collapsing but also they generate an increase in basal space  $d_{001}$ , high surface area and acidity as well as micropores larger than those of conventional zeolites [4]. These interesting physicochemical and textural properties make of PILCs a new class of microporous solids that have found a wide range of potential applications in catalytic, adsorption and separation processes [5-6]. Amongst the pillaring solutions, aluminium polyoxycations solutions are the most studied. In this context, it's assumed that the predominant Al-pillaring agent is the so-called "Al<sub>13</sub>" with  $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$  general formula, showing a Keggin-cage structure containing one central Al tetrahedron surrounded by twelve Al octahedral, whose size is about 9 Å and presenting an acid character[7].

During heat-treating, it's proposed that these oxhydroxy aluminium polycations species progressively transform into aluminium oxide pillars, according to a dehydration and dehydroxylation processes, whereby water and hydroxyl ions are lost. Thus, it's assumed that protons are generated during this pillar transformation according to the following reaction [8, 9]:



The released protons, with a positive charge and small volume, supposedly migrate into the silicate layers.

The structure and textural properties of PILCs have been extensively studied using various experimental techniques (XRD, BET... Nevertheless, little attention has been paid to proton conductivity of these materials. In this respect, the only study reported at our knowledge in the open literature, is that of Ruiz Hitzky et al [10]. These authors have studied, by applying electrochemical impedance technique, the behaviour of commercial montmorillonite clay mineral pillared by Al<sub>13</sub> polycation. The authors have carried out the conductivity measurements as a function of temperature according to a discontinuous mode; otherwise by measuring the material conductivity for a given temperature.

In a similar way, the aim of the present study is to use electrical measurements to study the protonic conductivity of another type of smectite clay mineral. This clay is the stevensite, which is extracted from a natural moroccan rhassoulite clay and pillared thereafter by Al<sub>13</sub> polycations. Unlike the device used by Ruiz Hitzky [10], the automated set up built in the laboratory allows to achieve continuous measurements of electrical magnitudes versus temperature. More recently, many studies have been devoted to the validation of this widespread natural matter in Morocco, particularly as adsorbent for retaining organic micropollutants from aqueous media [11,12]. In our case, due to the great thermal stability that PILCs generally exhibit, this study constitutes an attempt to validate this clay via figuring out the possibility to use it as high temperature proton conductor for fuel-cell applications.

## EXPERIMENTAL

Raw brown bulk "ghassoulite" clay samples were picked up from the east of middle Atlas in Moulouya valley. The clay was grinded, sieved at 50 μm and thereafter treated by dispersion four times in 200 ml of NaCl solution (2M). This cationic exchange operation yields as well as the homoionisation (Na<sup>+</sup>) of clay interlamellar space than the isolation by sedimentation of stevensite clay mineral fraction (< 2 μm) (designated by Na-stevensite). According to a more recent study [12], this Na-stevensite has shown to have the formula:  $Si_{3.78}Al_{0.22}Mg_{2.92}Fe_{0.09}Na_{0.08}K_{0.08}O_{10}(OH)_{12}.4H_2O$  and a cationic exchange capacity of about 76 meq/100g.

For achieving the preparation of the Aluminium Pillared Interlayer stevensite Clay (noted Al-pillared stevensite), a solution (90 ml) of

dilute Al-pillaring solution, priorly prepared, was added drop-wise, under vigorous stirring, to a 2% w/w aqueous suspension of 1g of Na-stevensite, so

that the  $\frac{Al}{clay}$  ratio was fixed at 9 mmol/g. The

synthesis of Al-pillaring solution was accomplished by slow titration, under stirring, of 0.3M solution of  $AlCl_3 \cdot 6H_2O$  (30ml) by 0.3M solution of NaOH

(60ml). Thus, the  $\frac{OH}{Al}$  ratio, defining the

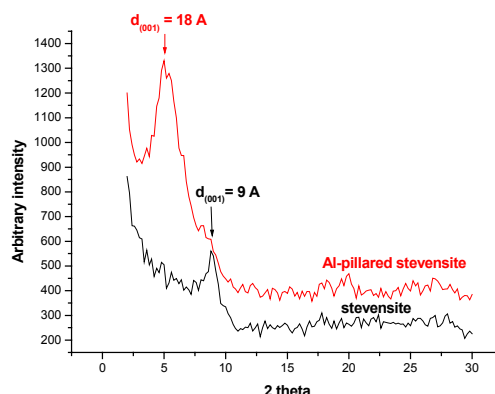
hydrolysis conditions of  $Al^{3+}$  ( $[Al(H_2O)_6]^{3+} + hOH^- \leftrightarrow [Al(OH)_h(H_2O)_{6-h}]^{(3-h)+}$ ), was fixed at 2. These conditions actually led to the predominant formation of  $Al_{13}$  polycations species as it was checked out by typical well-known  $^{27}Al$ -RMN spectra [4] obtained from the Al-pillaring solution prepared and aged for 1 month.

The Al-pillared stevensite slurry obtained was washed by centrifugation (at 2500 t/mn for 3 mn) several times till it's quiet free from chlorures (confirmed by  $AgNO_3$  test). Thereafter, it was air-dried.

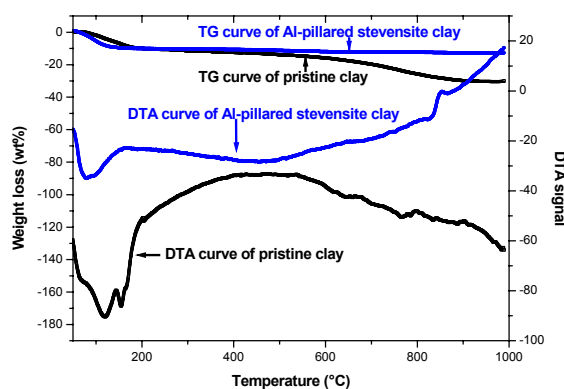
The clay samples were characterized using XRD, TG-ATD, SEM equipped with EDX. For XRD analysis in particular, the sample preparation requires careful handling. Indeed, the wet clay powders were spread on a sample carrier into glass grooved at the middle and pressed several times in the same direction in order to favour the lamellar orientation and hence intensify the basal  $d_{001}$  reflexion [1]. Electrical measurements were performed, using a HP 4284A capacimeter, in the frequency range [20 Hz-100 kHz] and for temperature varying from ambient to 600 °C with a ramp of 4°C/mn. For this purpose, cylindrical pellet samples (8 mm of diameter) were made by pressing clay powders (150 kg/m<sup>2</sup>). A pair of platinum wires has been applied on pellet surface using silver glue to assure electrical contact and to permit measurements of electrical resistance.

## RESULTS AND DISCUSSION

The powder X ray diffractograms of the annealed raw clay, for which interlayer compensating cations are anhydrous, and Al-pillared stevensite are reported in figure 3. These patterns clearly show that the basal reflexion  $d_{001}$  increases, after pillaring operation, from 9 Å to 18 Å. This actually corresponds to an interlayer spacing of 9 Å which is consistent with the size of  $[Al_{13}]$ -Keggin polycation.



**FIGURE 3 :** X-ray diffraction of stevensite clay mineral heat treated at 490 °C for 2 h and that pillared by  $Al_{13}$  polycation.



**FIGURE 4 :** TG-ATD thermograms of stevensite before and after pillaring by  $Al_{13}$  polycation.

endothermic effect in [100-200°C] range is observed and is associated to a quite similar weight loss of about 10.8 % for pristine clay and 11.13 % for Al-pillared stevensite, respectively. This is due to the loss of adsorbed water from interlayer regions. On the other hand, it seems that the size, shape and temperature of this peak depend on the saturating cations present between layers. Actually, the peak appears split into two peaks for raw clay with respect to Al-pillared stevensite. This denotes that the gallery of raw clay contains various compensating cations [13], whereas the interlamellar space of Al-pillared stevensite relatively appears homogeneous and occupied by the same type of compensating cations ( $[Al_{13}]$ -Keggin polycation). Another endothermic effect, very clear for raw clay with respect to Al-stevensite, is observed in [600 °C-800°C]. The corresponding weight loss is about 19.2 % and 2.4 % for raw clay and Al-pillared stevensite respectively. It's associated in both cases to weight

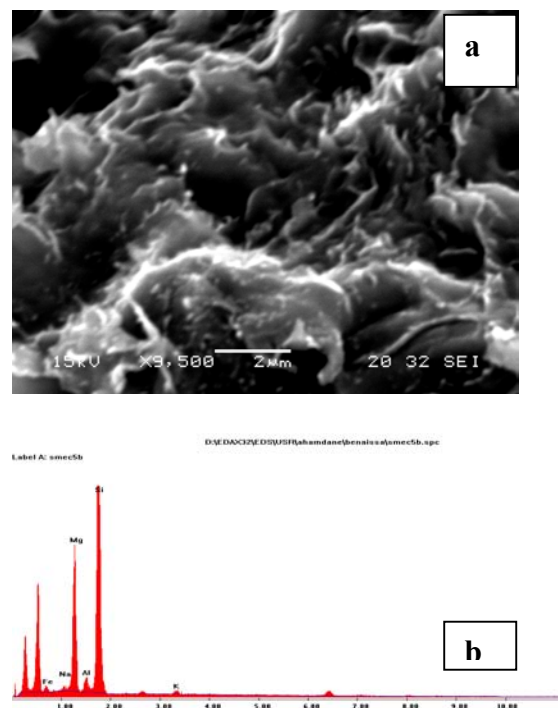
loss of constitution water by dehydroxylation. Nevertheless, the high weight loss value registered for pristine clay may be due besides to carbonate decomposition.

SEM micrographs as well as EDX analysis results, for Na-stevensite before and after pillaring operation, are reported in Figures 5 and 6 respectively. They exhibit a petal-like structure which is known to be the main microstructural feature characterizing smectite clay minerals. It should be emphasized that EDX spectra (Figures 5 and 6) reveal an increase in Al amount for Al-pillared stevensite (%Al (wt%)= 8.2 or %Al<sub>2</sub>O<sub>3</sub> (wt%)= 13.93) compared to pristine clay (%Al (wt%)= 2.34 or %Al<sub>2</sub>O<sub>3</sub> (wt%)= 3.38). This once more denotes that Na-stevensite actually has been successfully pillared.

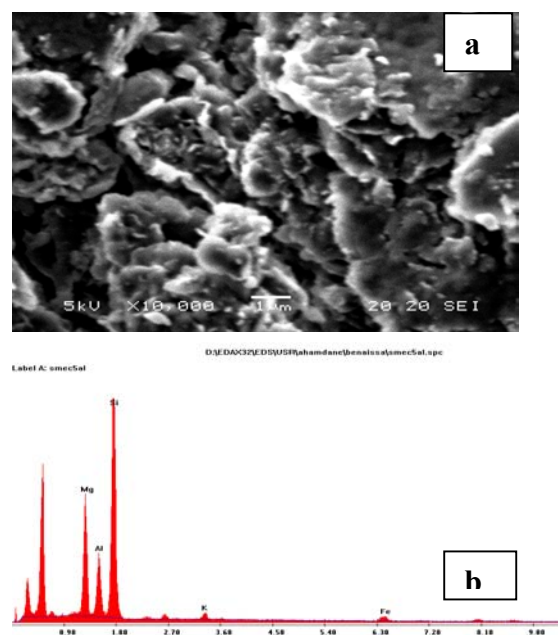
Electrical measurements, performed on pristine clay and Al-pillared stevensite, show for a frequency range [20Hz - 100 kHz], similar behaviour for both samples. For low frequencies ( $\leq 1$  kHz), a typical curve, depicting the real component of the complex impedance (R) versus temperature at 1 kHz, is reported in figure 7. It should be remarked that, in both cases, the resistance decreasing occurs, for this frequency for example, starting from a temperature of about 300°C. So, the ionic conductivity can't be activated, for the both materials, before this temperature. This result is in a good agreement with that of Ruiz-Hitzky et al [10] for enhancement of ionic conductivity of Al-pillared stevensite clay with respect to pristine clay. In both cases, the ionic conductivity observed may be ascribed to protons species [10,14]. Indeed, Calvet and Mamy [14] has suggested that the major charge carriers in Na-montmorillonite are protons species, possibly due to the Brønsted acidity of the clay mineral surface. For Al-pillared stevensite, this proton mobility may be due in addition to the acid intracrystalline environment generated during the pillar formation [10].

### CONCLUDING REMARKS

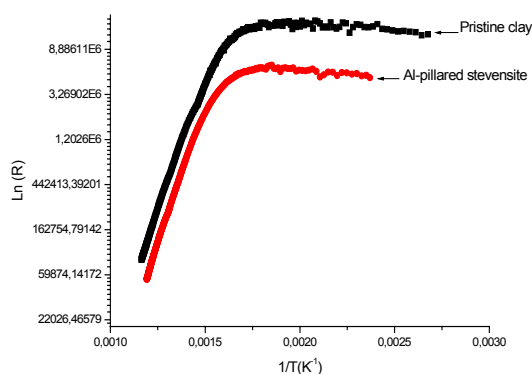
This preliminary study has shown the possibility to achieve pillaring of stevensite clay mineral extracted from moroccan natural ghassoulite clay by Al<sub>13</sub>Keggin polycation species. In fact, all Physico-chemical characterizations used were concordant and prove the pillaring of stevensite clay mineral. Besides, it has shown the usefulness of the electrical impedance technique for studying the protons conductivity of clay minerals and their pillared derivatives. Furthermore, it has revealed the enhancement of ionic conductivity of pillared clay with respect to pristine clay. For much improving the proton conductivity of pillared clays, this study would be carried on, particularly by using materials (pillaring agents, clay mineral) with stronger acidity, such as Ti or Zr-pillars and beidellitic clays.



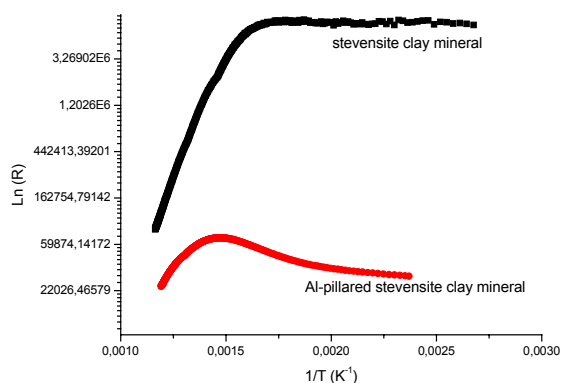
**FIGURE 5:** microstructure (a) and EDX (b) analysis of stevensite mineral clay



**FIGURE 6:** microstructure (a) and EDX (b) analysis of Al-pillared stevensite clay mineral Al-montmorillonite pillared organoderivatives (PILCs- (oxyethylene or PEO) composite materials obtained by treatment of PILCs with polyethylene oxide (PEO)) but not for PILCs. Above 300 °C, the curve shows a trend of the Arrhenius type. Likewise, Al-pillared stevensite exhibits resistance values lower than those observed for pristine clay. This resistance values decreasing becomes tremendous at high frequency (Fig 8). This proves an



**FIGURE 7:** variation of resistance versus temperature at 1 KHz



**FIGURE 8:** Variation of resistance versus temperature at 10 KHz

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