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Research paper

Crystallographic, vibrational, thermal and electrochemical properties of nacrite-NH₄Cl nanohybrid

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ABSTRACT

Si₂Al₂O₅(OH)₄·(1-χ)NH₄Cl·(1-χ)H₂O nanohybrid was prepared by indirect intercalation of ammonium chloride into the interlamellar space of nacrite. The number and position of intercalated ions and water molecules, the layer thicknesses, the stacking mode along the normal to the layer plane (z) were determined by modelling X-ray diffraction patterns. Infrared spectroscopy was carried out to observe the interactions between the silicate “network” and the ammonium chloride salt. Thermogravimetric analysis was achieved to study the phase transition of the nanohybrid when the system temperature is increased. Finally, the electrochemical identification of the new nanohybrid material was performed with both parameters: frequency and temperature. Indeed, the prepared compound has a fairly high ionic conductivity at higher temperatures and can be classified as a superionic conductor.

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1. Introduction

Clays and clay minerals are interesting materials not only because of their low cost but also because they are ubiquitous and environment friendly (Bergaya and Lagaly, 2006; Zhou and Keeling, 2013). Moreover, clay minerals are at the epicenter of nanohybrid lamellar materials research (Fernandes et al., 2014).

It is well-documented that the surface and the interlayer space of clay minerals can be modified. Furthermore, the interlayer space of clay minerals can also act as a confined nanoreactor for in situ interlayer reaction and a nanoscale ‘container’ for confined nucleation, growth, or clustering of nanoparticles and nanoaggregate (Zhou et al., 2016). Intercalation is probably the most often used method for modifying clay minerals (Zhu et al., 2014). Intercalated clay minerals, have found wide applications in environmental remediation, e.g., as adsorbents for inorganic and organic contaminants, and catalysts for the degradation of organic contaminants. Intercalated clay minerals have also been used as a carrier for drugs, pesticides, and biochemicals for various application purposes (Zhu et al., 2014). The capability of tuning materials' performances, not only in terms of tailoring their physico-chemical properties to answer prerequisites of a given application, but also regarding the elaboration of novel concepts, opened a door to a radical new world in materials science (Fernandes et al., 2014).

Kaolin is one of the naturally occurring abundant clays in the earth's crust. The kaolin group consists of dioctahedral 1:1 layer structures with the idealized formulae Si₂Al₂O₅(OH)₄. Dehydrated kaolin minerals shows different polytypes: kaolinite, dickite and nacrite and halloysite-(0.7 nm) (Brigatti et al., 2013). These clay minerals are characterized by certain properties, including a layer structure with one dimension in the nanometer range, the thickness of this 1:1 layer is about 0.7 nm (Bergaya and Lagaly, 2006). One side of the layer is gibbsite-like with aluminum atoms octahedrally coordinated to corner oxygen atoms and hydroxyl groups. The other side of the layer constitutes a silica-like structure in which the silicon atoms are tetrahedrally coordinated to oxygen atoms. The adjacent layers are linked via hydrogen bonds (O—H···O) involving aluminol (Al—OH) and siloxane (Si—O) groups (Wypych and Satyanarayana, 2004).

From the initial pioneering works to nowadays, a great number of contributions have been published dealing with the intercalation of organic and/or inorganic guest species between the layers of kaolinite forming nanohybrid materials (Brunet et al., 2015).

In the same line, the extensive study of Tunisian nacrite (Table 1), as mentioned in the bibliometric data (Ben Haj Amara et al., 1998, 2000; Naamen et al., 2004; Jaafar et al., 2014, 2015, 2016), illustrates that this layered clay mineral has high chemical stability and well-packed structure which constitute a suitable host matrix for the incorporation of inorganic salts (LiCl (Jaafar et al., 2016), CsCl (Naamen et al., 2004), KCl (Naamen et al., 2004), and MgCl₂·6H₂O (Jaafar et al., 2014)) or organic compounds such as (DMSO, NMA) (Ben Haj Amara et al., 2000). The intercalation of organic and/or inorganic guest species in the

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Table 1
Crystallographic data of a well-crystallized Tunisian nacrite (Ben Haj Amara et al., 1998).

| | |
|------------------|---|
| Chemical formula | $\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4$ |
| Crystal system | Monoclinic |
| Space group | Cc |
| Stacking mode | 2 M |
| Cell parameters | $a = 0.8906 \text{ nm}$ $b = 0.5146 \text{ nm}$ $c = 1.5669 \text{ nm}$ $\beta = 113.58^\circ$ |
| Basal spacing | $d_{002} = c \sin\beta/2 = 0.72 \text{ nm}$ |

interlayer space of nacrite has shown the importance of preparing new nanohybrid materials with both structural and functional properties.

In order to throw some additional light on the role of cation (nature, charge and location) on the expansion of Tunisian nacrite, this research was broadened to prepare a new nanohybrid material via intercalation of nacrite with a polyatomic cation: NH_4^+ . Noteworthy, the intercalation of NH_4Cl into the interlayer space of kaolinite failed in the major previous experiments. However, ammonium chloride was smoothly adsorbed (Wada, 1959) or directly sandwiched (Garrett and Walker, 1959) within the interlayer region of halloysite.

An innovative and inexpensive experimental hybridization process has been adopted to ensure the synthesis of nacrite- NH_4Cl nanohybrid material. The elaborated nanohybrid exhibited significantly improved crystallographic, vibrational and electrical characteristics compared to that of unmodified nacrite. Furthermore, the in-situ heat treatment of the nanohybrid, the phase transition and its influence on the conduction has been comprehensively undertaken in the present work. The ultimate goal of this paper was to reflect upon all these characterizations, how this new nanohybrid with improved functionality could be integrated from a technologic point of view.

2. Materials and methods

2.1. Materials

The raw nacrite used was collected from North Tunisia (Ben Haj Amara et al., 1998, 2000) (mine of Jbel Slata, Kef). This starting clay material shows large particles with minor impurities. Potassium acetate (CH_3COOK) and ammonium chloride (NH_4Cl) were purchased from Prolabo. The purities of all chemicals were >99%.

2.2. Nanohybrid preparation

The intercalation of ammonium chloride salt into the interlayer space of nacrite was carried out indirectly by means of an entraining agent, i.e., potassium acetate. Potassium acetate "KAc" was the best precursor selected for the expansion of nacrite. In fact, KAc was widely used as a small and highly polar molecule for the intercalation of guest species that could not directly intercalate kaolin materials (Ben Haj Amara et al., 2000).

It was then possible to prepare nacrite- NH_4Cl nanohybrid material in two steps: The first step, has been already detailed and published in the previous research papers (Ben Haj Amara, 1997; Ben Haj Amara et al., 1998) where the raw nacrite ($d_{002} = 0.72 \text{ nm}$) was converted into nacrite-KAc complex ($d_{002} = 1.40 \text{ nm}$) (Fig. 1). The CH_3COOK was then successfully eliminated by repeated washing of the nacrite-KAc intercalate with deionized water and air-drying until the elaboration of a homogeneous hydrate ($d_{002} = 0.84 \text{ nm}$) (Fig. 1). Removal of the intercalated CH_3COOK was proofed by referring to the vibrational characterization of hydrated nacrite (Ben Haj Amara, 1997; Jaafar et al., 2015). Analysis of the features and assignment of infrared (IR) bands provide the significant differences and the obvious structural change between the nacrite-KAc complex and the hydrate (Jaafar et al., 2015). The

disappearance of $\text{C}=\text{O}$ antisymmetric stretching vibration around 1572 cm^{-1} ; $\text{O}-\text{C}-\text{O}$ symmetric stretching vibration around 1423 cm^{-1} and the symmetric deformation band of the CH_3 group around 1351 cm^{-1} (Jaafar et al., 2015), and, meanwhile the perturbations in both the position and the intensity of the hydroxyl vibration modes in the IR spectrum of the hydrate gave evidence of the removal of acetate and potassium ions (Jaafar et al., 2015; Zhang et al., 2011).

In the second step, 4.81 g of NH_4Cl dissolved in water (Normality = 3 N) was added to the hydrate. The mixture was then heated at 50°C under a magnetic stirring for 7 days. The resulting complex was kept at ambient atmosphere for three hours. The use of water as solvent favor the expansion of the clay mineral and the intercalation of the ammonium chloride within the nacrite layers leading to the resulting nacrite- NH_4Cl nanohybrid ($d_{002} = 1.03 \text{ nm}$) (see Fig. 1).

2.3. Characterization techniques

X-ray diffraction (XRD) pattern of nacrite- NH_4Cl nanohybrid was performed at ambient temperature using a reflection setting on a Bruker D8 installation monitored by the EVA-version Diffrac plus software (Bruker AXS GmbH, Karlsruhe, Germany) and $\text{CuK}\alpha_1$ radiation. Usual scanning parameters were $0.02^\circ 2\theta$ as step size and 6 s as counting time per step over the angular range $5-120^\circ 2\theta$.

IR spectra were recorded at ambient temperature using a thermo scientific Nicolet IR 200 FT-IR with ATR Spectrometer, equipped with a diamond crystal and operating in the medium IR [$4000-400 \text{ cm}^{-1}$] spectral region. IR spectroscopy was used as a reliable tool for the characterization of intercalation nanohybrids in order to examine the interactions between functional surface groups of the nacrite layers and the ammonium chloride.

Thermogravimetric analysis (TGA) of nacrite- NH_4Cl nanohybrid was carried out using a 92 SETARAM equipment in flowing air, in a temperature ranging from ambient temperature to 800°C along with a heating rate of $5^\circ\text{C}/\text{min}$. This technique was very powerful to monitor the structural modification of clay minerals when heated at different temperatures.

Electrochemical Impedance Spectra (EIS) were performed using a frequency response analyzer (Hewlett-Packard 4192). Complex impedance measurements were performed in an open circuit using two electrode configurations with signal amplitude of 50 mV and a frequency band ranging from 10 Hz to 13 MHz at different temperatures. The examined sample was pressed into pellet using a hydraulic press. To ensure good electrical contact between the sample and the electrical junctions, the pellet was sandwiched between two platinum electrodes to form a symmetrical cell. The cell was eventually placed into a programmable oven coupled with a temperature controller. The collected data were fitted using the equivalent circuit of the Zview software.

3. Results and discussion

3.1. Diffraction data collection and refinement

3.1.1. Qualitative XRD analysis

Examining the experimental 00l reflections of the stable nacrite- NH_4Cl nanohybrid, (Fig. 2), a main 00l reflection at $2\theta_{002} = 8.570^\circ$ and $d_{002} = 1.03 \pm 0.002 \text{ nm}$ basal spacing value can be observed. This means that an expansion of the interlayer space of nacrite by $\sim 0.31 \text{ nm}$ along the c^* axis has occurred. This result is probably due to the insertion of ammonium chloride salt with one water sheet into the nacrite matrix. Additional reflections are attributed to excess of salt and are identified by ($^\circ$) symbol.

Data in Table 2 reveals that the number of layers per particle, \bar{M} , deduced from the classic Debye-Scherrer formula (Eq. (1)) decreases from " $\bar{M} = 70 \pm 1$ " for raw nacrite (Ben Haj Amara et al., 1998) to " $\bar{M} = 17 \pm$

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