

## Synthesis and characterization of nanoscale interstratified particles composed by layered hexaniobate intercalated with hexadecyltrimethylammonium cations

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**Abstract** – Layered hexaniobate intercalated with hexadecyltrimethylammonium cations (CTA<sup>+</sup>) with different ratios between CTA<sup>+</sup> and interlayer exchangeable K<sup>+</sup> were synthesized in water. X ray diffraction (XRD) data and FTIR spectroscopy suggest formation of a phase with a perpendicular monolayer of *trans* conformation intercalated CTA<sup>+</sup> ions. Thermal and elemental analysis reveal high K<sup>+</sup> exchange degree by CTA<sup>+</sup> in all cases and quantitative CTA<sup>+</sup> substitution when CTA<sup>+</sup> amount below hexaniobate surface saturation was used, considering hexaniobate layer charge density and the CTA<sup>+</sup> dimensions. TG-DSC-MS data show that intercalation leads rather to oxidation of CTA<sup>+</sup> along heating while pure CTA<sup>+</sup> decomposes through Hofmann elimination mechanism.

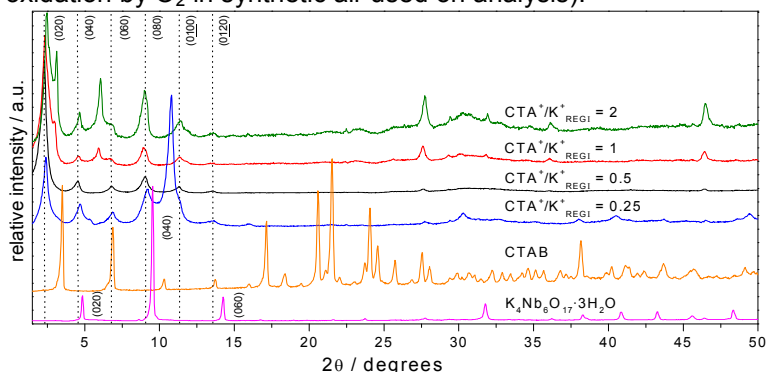
The main goal of this work was to modify the physical-chemical properties of the layered potassium hexaniobate, K<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>, through the increase of the basal spacing and the organophilicity of the layers surfaces. Hexaniobate presents high negative layer charge density and quite different intercalation and cationic exchange behaviors between the two interlayer regions (interlayer named I exhibits higher reactivity than region II) [1]. In order to achieve the goal, intercalation reactions via cationic exchange of intercalated K<sup>+</sup> by CTA<sup>+</sup> cations were performed, leading to hybrid organic-inorganic nanoscale interstratified hexaniobate particles. The obtained organophilic interlayered materials can be used to prepare advanced nanostructured composites with polymers of low polarity through different methods such as extrusion or polymer synthesis by “*in-situ*” polymerization [2].

K<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>·3H<sub>2</sub>O precursor was synthesized by ceramic method based on previous report [3]. Cationic exchange reactions were carried out using CTA<sup>+</sup>/K<sup>+</sup><sub>REGI</sub> molar ratios 0.25, 0.5, 1 and 2, using hexaniobate dispersed in hexadecyltrimethylammonium bromide (CTAB) aqueous solutions. The mixtures were kept under heating and stirring for about two weeks. Materials were isolated by centrifugation and washed with deionized water.

FTIR spectra of the hybrid materials are similar to the CTAB spectrum: the narrow bands assigned to —CH<sub>2</sub>— stretching ( $\nu_s = 2849 \text{ cm}^{-1}$ ,  $\nu_{\text{ass}} = 2918 \text{ cm}^{-1}$ ) and the bands splitting related to —CH<sub>2</sub>— scissoring ( $\delta_s = 1473, 1462 \text{ cm}^{-1}$ ) and rocking ( $\rho = 731, 719 \text{ cm}^{-1}$ ) modes suggest high *trans/gauche* ratio for conformation of intercalated CTA<sup>+</sup> methylenic chains. Consequently, a high intermolecular interaction and ordered packing array among adjacent hexadecyl groups. XRD patterns for all materials (Figure 1) exhibit a series of (0k0) peaks (even k indexes from 2 to 12), corresponding to a basal spacing increase from 3.7 nm (pristine) to about 7.8 nm in intercalated materials. Considering the CTA<sup>+</sup> length (about 2.5 nm) and the FTIR analysis, it can be concluded a pure phase formation with a perpendicular monolayer of highly organized CTA<sup>+</sup> in *trans* conformation intercalated only into interlayer I for the product obtained using CTA<sup>+</sup>/K<sup>+</sup><sub>REGI</sub> = 0.5. Besides the monolayer phase, the other products present other phases. Elemental and TG-DSC-MS analysis suggest the compositions CTA<sub>0.50</sub>K<sub>3.50</sub>Nb<sub>6</sub>O<sub>17</sub>·1.1H<sub>2</sub>O, CTA<sub>0.92</sub>K<sub>3.08</sub>Nb<sub>6</sub>O<sub>17</sub>·2H<sub>2</sub>O, CTA<sub>1.49</sub>K<sub>2.51</sub>Nb<sub>6</sub>O<sub>17</sub>·1.5H<sub>2</sub>O and CTA<sub>1.43</sub>K<sub>2.57</sub>Nb<sub>6</sub>O<sub>17</sub>·1.5H<sub>2</sub>O for products with reactional CTA<sup>+</sup>/K<sup>+</sup><sub>REGI</sub> ratios 0.25, 0.5, 1 and 2, respectively. TG-DTG curves showed reduction of about 50 °C on initial temperature for thermal decomposition of the organic intercalated species compared to CTAB. TG-MS-EGA data revealed significant changes in the degradation mechanism (from Hofmann elimination to a major degree of CTA<sup>+</sup> oxidation when in presence of hexaniobate). DSC curves also exhibit a change in general thermal decomposition process from endothermic to exothermic. These observations suggest that [Nb<sub>6</sub>O<sub>17</sub>]<sup>4-</sup> layers have stronger Brønsted basic character than Br<sup>-</sup> anions. Thus, the first can react more easily with hexadecyl β-hydrogens, leading Hofmann elimination at lower temperatures. The decomposition through Hofmann elimination is readily followed by oxidation of produced hexadecene by interlayered Nb=O units (maybe enabled by Nb(V) reduction and subsequent oxidation by O<sub>2</sub> in synthetic air used on analysis).

### References

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**Figure 1:** XRD patterns of K<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>·3H<sub>2</sub>O, CTAB and products obtained with CTA<sup>+</sup>/K<sup>+</sup><sub>REGI</sub> molar ratios 0.25, 0.5, 1 and 2.