Soft chemical synthesis of lepidocrocite alkaline titanates.

Marina M. Leite[1] (PG), Flavio M. Vichi*[1] (PQ)

[1] Instituto de Química – Universidade de São Paulo

fmvichi@iq.usp.br

Palavras Chave: *lepidrocrocite titanate, caesium titanate, soft chemistry*

Introdução

Alkaline titanates having the layered lepidocrocite structure are of great interest for their ion exchange properties. Moreover, it has been suggested that Na^+ and H^+ ion-exchanged lepidrocrocite titanates (LT) have the same crystal structure as the TiO_2-derived nanotubes produced by the hydrothermal method, a topic that remains under debate.[1]

LTs are nonstoichiometric oxides composed of layers of TiO_6 octahedra, Vacancies or low valence metals substitute Ti^{4+} generating a negative charge, compensated by alkali metal cations in the interlayer region. One of the first LTs studied, $Cs_2Ti_6O_{13}$, was found to actually have the $Cs_xTi_{(2-x/4)}\square_{x/4}O_4$ formula, $0.61<x<0.65$.[2]

LTs are usually produced by the solid state method, which requires 20h – 40h of reaction at 800 °C. Here, we report the synthesis of $K_{0.8}Ti_{1.73}Li_{0.27}O_4$ (K-Li-LT) and $Cs_{0.7}Ti_{1.825}\square_{0.175}O_4$ (Cs-LT) by a modified sol-gel method with reduced reaction time.

In a typical procedure, aqueous solutions of the alkaline metal carbonates are added dropwise to a mixture of titanium n-butoxide in n-butanol. All the reagents are mixed in the desired stoichiometric proportions. After stirring for 1h at 25 ºC, the resulting suspensions are dried in air at 80 °C, and then fired at 800 °C for 2h. The products were characterized by x-ray diffraction (XRD).

Resultados e Discussão

Figures 1 and 2 show the XRD pattern of the Cs-LT and K-Li-LT products, respectively, in comparison to JCPDS standards for the lepidocrocite compounds.

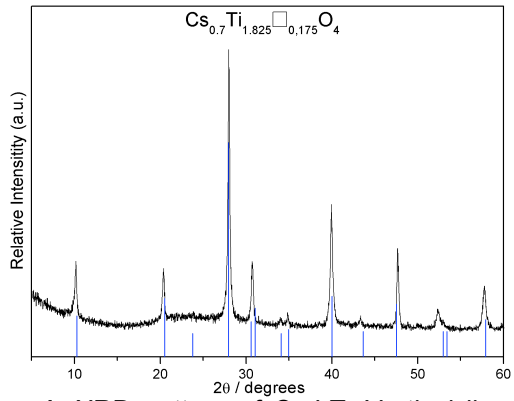

Figure 1. XRD pattern of Cs-LT. Vertical lines are the JCPDS standard for $Cs_2Ti_6O_{13}$

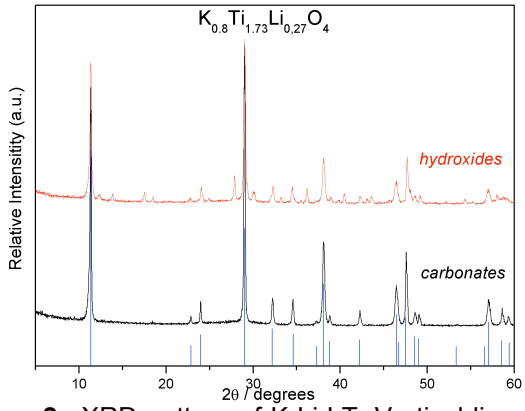

Figure 2.. XRD pattern of K-Li-LT. Vertical lines are the JCPDS pattern for $K_{0.8}Ti_{1.73}Li_{0.27}O_4$.

Both materials were obtained with no crystalline impurities. An atempt to prepare LT from the hydroxides produced a crystalline material, but peaks due to imputities can be observed. Traditional solid state synthesis was performed for comparison (20h at 800 ºC), and the crystallite size of the samples was determined by the Scherrer formula (Table 1). The products of the soft chemical method presented smaller crystallite sizes than the solid state products, probably due to the shorter period under high temperature.

Table 1. Scherrer crystallite sizes

	Solid state	Sol-gel
Cs-LT	78 nm	64 nm
K-Li-LT	91 nm	86 nm

Conclusões

The lepidocrocite titanates $Cs_{0.7}Ti_{1.825}\square_{0.175}O_4$ and $K_{0.8}Ti_{1.73}Li_{0.27}O_4$ were successfully prepared by a modified sol-gel method. This route decreased the reaction time from 20h to 2h, forming materials with smaller crystallite sizes.

Agradecimentos

The authors thank CNPq and Fapesp (11/19941-4) for the financial support.

[1] Gao, T.; Fjellvåg, H.; Norby, P.*Inorg. Chem.* **2009**, *48*, 1423.
[2] Grey, I. E; Madsen, I. C.;Watts, J. A.; Bursoll, L. A. *J. Solid State Chem.* **1987**, *66*, 7.