

Reinvestigation of proton-exchanged layered hexaniobate phase

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Introduction

The hexaniobate $K_4Nb_6O_{17}$ is formed by the organized stacking of negative charged layers, comprising distorted $[NbO_6]$ octahedron units that share adjacent edges and corners in infinite chains. The interlayer region is occupied by potassium ions which maintain the charge neutrality. There are two types of interlayer region, denoted by I and II. The interstratified material of formula $H_xK_{4-x}Nb_6O_{17}$ is formed by exchanging ions K^+ for H^+ . The proton-exchanged hexaniobate is important to produce nanoscrolls and nanosheets by exfoliation reactions enabling the development of new materials with high surface area, applied in heterogeneous acid catalysis, proton conductors and sensors [1,2].

This work aims revisit the hexaniobate proton-exchange process and the $H_xK_{4-x}Nb_6O_{17}$ isolated phases by X ray diffraction (XRD), thermal analysis, Raman spectroscopy, and potassium analysis by ICP - AES (Inductively Coupled Plasma - Atomic Emission Spectrometry).

Results and Discussions

The acid phase was obtained suspending $K_4Nb_6O_{17}$ in 6 mol L⁻¹ of HCl solution for 6, 12, 18 and 24 h at 60 °C under stirring. The XRD patterns of the $H_xK_{4-x}Nb_6O_{17}$ samples show two (040) peaks related to the hexaniobate basal spacing. Most intense peaks are attributed to the acid phase (d_{040} equal to 7.9 Å) while the less intense matches with $K_4Nb_6O_{17} \cdot 3H_2O$ phase (d_{040} equal to 9.3 Å) [1].

Currently it is considered that just region I can be hydrated and filled with H^+ ions and that the proton-exchanged percentage has a maximum value of about 50 % [1,2]. The literature points out that at about 315 °C occurs the dehydroxylation process, and the lamellar structure collapse. Hence the -OH groups (formed by the interlayer protons interacting with the Nb=O terminal groups) condense releasing water molecules [1,2].

Thermogravimetric (TG), derived thermogravimetric (DTG) and mass spectroscopy (MS) curves for $H_xK_{4-x}Nb_6O_{17}$ show four events related to the water release ($m/z = 18$), as displayed in Figure 1. The first and second events of water weight loss, occurring in 25 - 130 °C and 130 - 230 °C temperature ranges, are assigned to the adsorbed water molecules in the material. The third and fourth steps observed in 230 - 310 °C and 310 - 600 °C ranges are attributed to the dehydroxylation process. Raman spectra and XRD patterns of $H_xK_{4-x}Nb_6O_{17}$ heated at 250, 300,

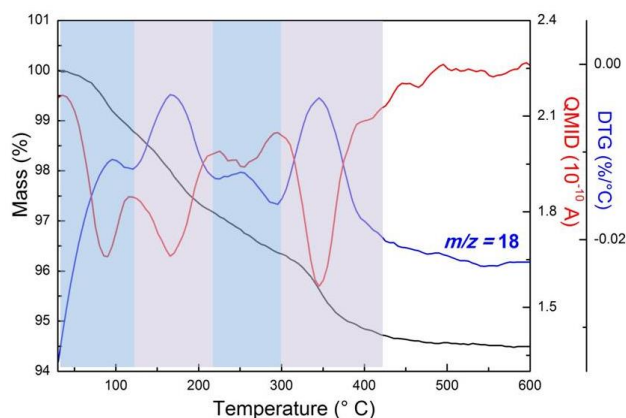


Figure 1. TG (black line), DTG (red line) and MS (blue line) curves of $H_xK_{4-x}Nb_6O_{17}$ sample prepared in 24 h.

350 and 400 °C suggest that the onset temperature of dehydroxylation reaction is 250 °C.

The proton-exchange percentages were calculated by thermal analysis (considering T_{onset} for dehydroxylation equal to 250°C) and also by the amount of K^+ ions released during the ion-exchange reaction (Table 1).

Table 1. Proton-exchange percentages determined by thermogravimetric analysis and potassium ions released.

Reaction time (h)	Proton-exchange percentage by K^+ analysis (%)	Proton-exchange percentage by TG (%)
6	72.4	75.9
12	76.5	76.0
18	79.1	76.5
24	77.4	77.2

The values obtained of proton-exchange for the four reaction times analyzed were higher than 70 %.

Conclusions

The hexaniobate proton-exchange process was optimized by the reaction method used in this work, once all materials exhibited up to 70 % of exchange degree. It can be proposed that both interlayers regions, I and II, can be hydrated and consequently undergo proton-exchange reactions.

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