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BRIEF COMMUNICATIONS

Topotactic Dehydration of the Lamellar Oxide $HK_2Ti_5NbO_{14} \cdot H_2O$: The Oxide $K_4Ti_{10}Nb_2O_{27}$

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The lamellar oxide $HK_2Ti_5NbO_{14} \cdot H_2O$ can be topotactically dehydrated to $K_4Ti_{10}Nb_2O_{27}$. Electron diffraction and X-ray diffraction studies of this phase lead to a monoclinic cell with the parameters a = 17.005, b = 3.78, c = 9.01 Å and β = 92.14°. Diffusion streaks on the electron diffraction patterns indicate disorder whereas the existence of two sets of lattices on the same crystal give evidence of the topotactic character of the reaction. A structural model is proposed for $K_4Ti_{10}Nb_2O_{27}$, which corresponds to the intergrowth of $K_3Ti_5NbO_{14}$ layers with the $K_2Ti_6O_{13}$ tunnel structure. The possibility of formation of various intergrowths such as $(KTi_5NbO_{13})_n\,(HK_2Ti_5NbO_{14})'_n$ is suggested.

Introduction

The thermal decomposition of oxides prepared by ion-exchange reactions is an efficient method for preparation of new unstable oxides with empty or partially occupied tunnel structures. Several oxides such as $Ti_2Nb_2O_9$ (*1*), $TiO_2\beta$ (*2*), or $SiO_2 \cdot nH_2O$ (*3*) are prepared by such a "chimie douce" method; many protonic oxides with a layer structure may be considered as precursors for the synthesis of unusual structures. The study of the ion-exchange properties of the lamellar oxide $H_3Ti_5NbO_{14} \cdot H_2O$ (*4*) has shown that the maximum exchange ratio with alkaline salts was limited to the value $\tau = \frac{2}{3}$ in aqueous medium, independent of the nature of the ion A (A = Na, K, Rb, Cs).

The titanoniobates $HA_2Ti_5NbO_{14} \cdot nH_2O$ appear thus as particular compounds among the oxides $H_{3-x}A_xTi_5NbO_{14} \cdot nH_2O$. The present work deals with the study of the oxide $HK_2Ti_5NbO_{14} \cdot H_2O$ and its topotactical dehydration to the oxide $K_4Ti_{10}Nb_2O_{27}$.

Experimental Methods

The oxide $HK_2Ti_5NbO_{14} \cdot H_2O$ was prepared from the oxide $H_3Ti_5NbO_{14} \cdot H_2O$ by an ion-exchange reaction. The experimental procedure has been previously described for all oxides $HA_2Ti_5NbO_{14} \cdot H_2O$ (*4*).

The thermal decomposition of $HK_2Ti_5NbO_{14} \cdot H_2O$ was studied by thermogravimetric analysis (Setaram microbalance), by thermodifferential analysis (Setaram microdifferential analyzer), and by

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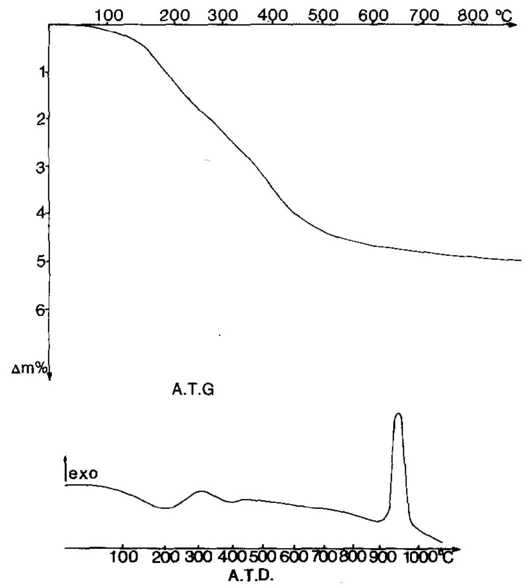

FIG. 1. The TG and DTA curves of $HK_2Ti_5NbO_{14} \cdot H_2O$.

X-ray diffraction (high-temperature Guinier–Lenné camera).

The final compound $K_4Ti_{10}Nb_2O_{27}$ was investigated by X-ray diffraction with a Philips X-ray powder diffractometer and by electron microscopy with a JEOL 120 CX microscope (operated at 120 kV) using a side-entry concentric goniometer (±60°).

Results and Discussion

The thermogravimetric curve (Fig. 1) shows that $HK_2Ti_5NbO_{14} \cdot H_2O$ begins to lose water at 100°C; this dehydration is rather slow and is not complete below 600°C. A broadened endothermic peak observed at about 400°C (Fig. 1) is in agreement with this observation. The X-ray diffraction pattern of the dehydrated compound shows that a new phase has been generated according to the equation

$$2HK_2Ti_5NbO_{14} \cdot H_2O \rightarrow K_4Ti_{10}Nb_2O_{27} + 2H_2O.$$

The high exothermic peak at 900°C corresponds to the decomposition of $K_4Ti_{10}Nb_2O_{27}$ into a mixture of oxides. The X-ray diffraction indicates KTi_3NbO_9 and $K_2Ti_6O_{13}$ as the major phases. It must be pointed out that the oxide $HK_2Ti_5NbO_{14}$ could not be isolated, but the variation of the parameters of the monoclinic cell between 100° and 160°C (Fig. 2) suggests that

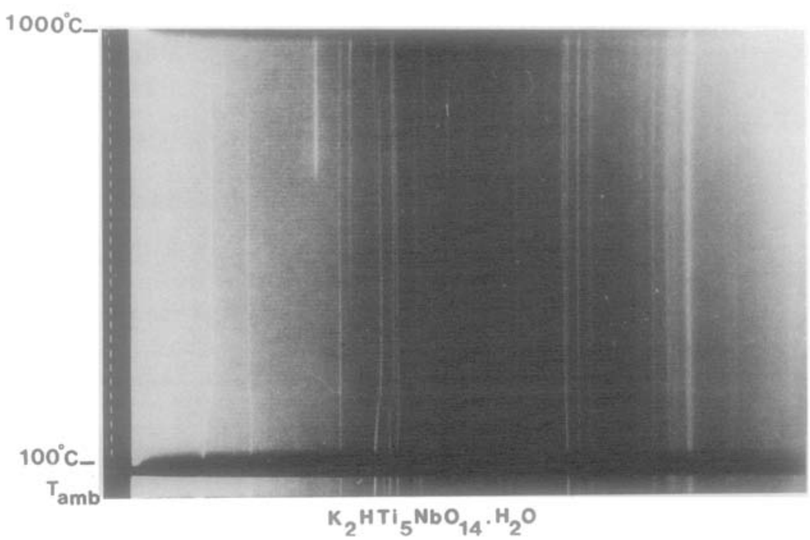

FIG. 2. X-ray diffraction pattern from room temperature to 1000°C (Guinier–Lenné camera).

TABLE I

CRYSTALLOGRAPHIC DATA OF $K_4Ti_{10}Nb_2O_{27}$ AND $HK_2Ti_5NbO_{14} \cdot H_2O$

	a (Å)	b (Å)	c (Å)	β (°)	S.G.
$K_4Ti_{10}Nb_2O_{27}$	17.005(13)	3.785(3)	9.013(8)	92.14(8)	$C2$, Cm, $C2/m$
$HK_2Ti_5NbO_{14} \cdot H_2O$	18.810(20)	3.771(3)	9.290(10)	98.20(10)	$C2$, Cm, $C2/m$

this oxide may exist as an intermediate and that it is rapidly decomposed into the phase $K_4Ti_{10}Nb_2O_{27}$.

The close analogy between the X-ray powder diffraction patterns reveals close relationships between the two structures of $HK_2Ti_5NbO_{14} \cdot H_2O$ and $K_4Ti_{10}Nb_2O_{27}$ (Fig. 2).

Preliminary parameters of a monoclinic cell of $K_4Ti_{10}Nb_2O_{27}$ were obtained from electronic diffraction study and were then refined by the X-ray data; refined parameters of the precursor and dehydrated compounds are given in Table I.

All electron diffraction patterns show an array of sharp intense spots with reflection conditions hkl, $h + k = 2n$. However, it must be pointed out that all crystals exhibit more or less pronounced diffusion streaks along a (Fig. 3). This phenomenon is correlated with variations of the periodicity along a and is confirmed by the low-resolution micrograph (Fig. 4, area 2). The examination of this micrograph (area 1) shows a great flexibility of the layers.

Several crystals show the presence of two sets of spots (Fig. 5a). One array corresponds to $a = 17$ Å, i.e., to the $K_4Ti_{10}Nb_2O_{27}$ lattice, whereas the second set, which is characterized by $a = 18.8$ Å, corresponds to the lattice of $HK_2Ti_5NbO_{14} \cdot H_2O$. Moreover, the diffusion streaks observed on this micrograph suggest that the two structures alternate in a pseudoperiodic way. The low-resolution image (Fig. 5b) confirms this model. Thus such crystals are not completely converted into $K_4Ti_{10}Nb_2O_{27}$. Moreover, observation of these two sets of lattices for the same crystal shows without any ambiguity that dehy-

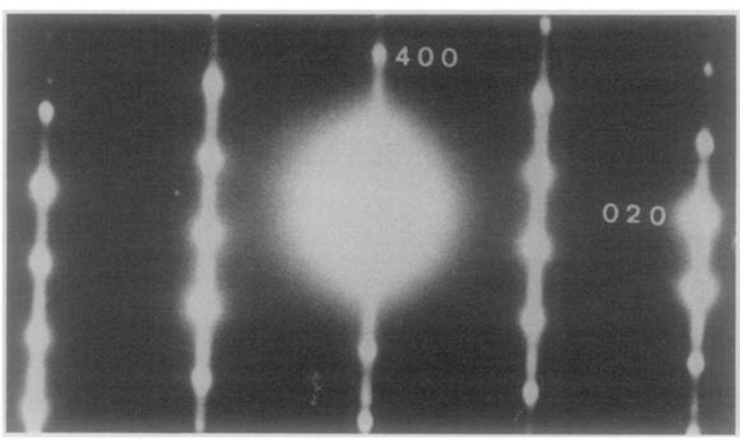

FIG. 3. Typical electron diffraction pattern of $K_4Ti_{10}Nb_2O_{27}$. The well-resolved spots indicate the parameters $a = 17$ and $b = 3.8$ Å (zone axis 001). Diffusion streaks along (100) are systematically observed.

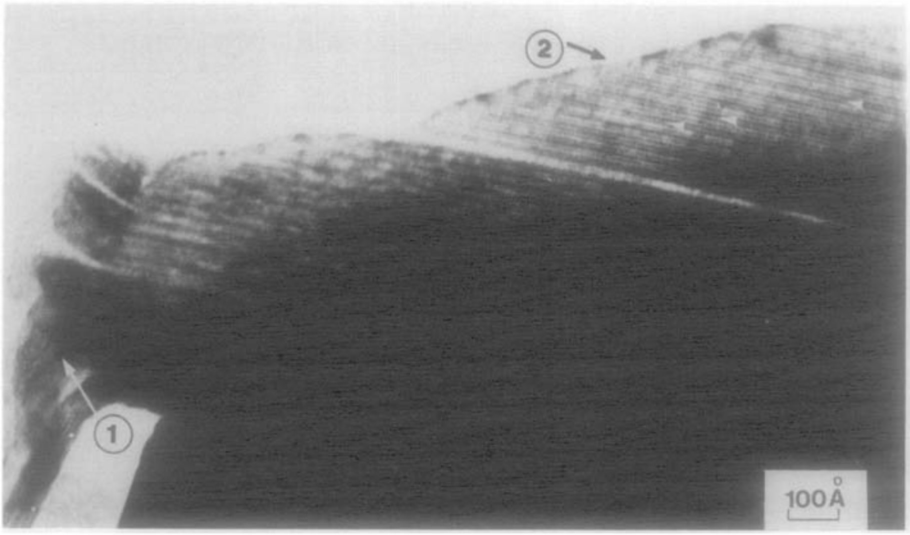

FIG. 4. Low-resolution image corresponding to the electron diffraction pattern shown in Fig. 3 (001).

dration is topotactic with a bidimensional accord between the two structures along the (100) plane. Consequently, the correlation of these close relationships between the two structures and of the parameters allows a structural model to be proposed (Fig. 6b). The structure of $K_4Ti_{10}Nb_2O_{27}$ results from the structure of $HK_2TiNbO_{14} \cdot H_2O$ (Fig. 6a) by elimination of H_2O molecules between two adjacent $[Ti_5NbO_{14}]^{3-}$ layers which then form rectangular tunnels similar to those of $K_2Ti_6O_{13}$ (*5*) by sharing the corners of their octahedra. This phenomenon appears in one interlayer space out of two as if such spaces were occupied by "$1K^+ + 2H^+$" and "$3K^+$" alternately in

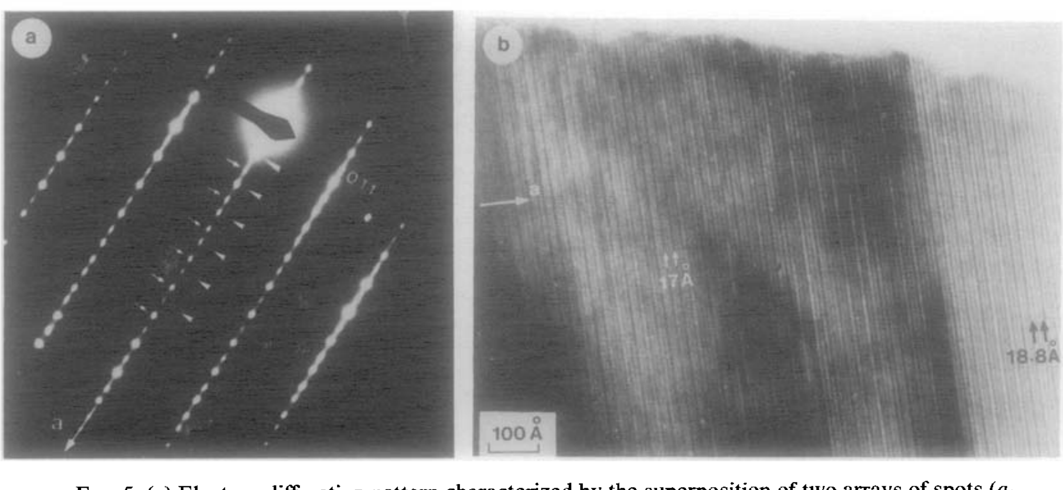

FIG. 5. (a) Electron diffraction pattern characterized by the superposition of two arrays of spots (a_1 = 17 and a_2 = 18.8 Å (smaller arrows)). (b) Corresponding image showing the variations in the fringe spacing.

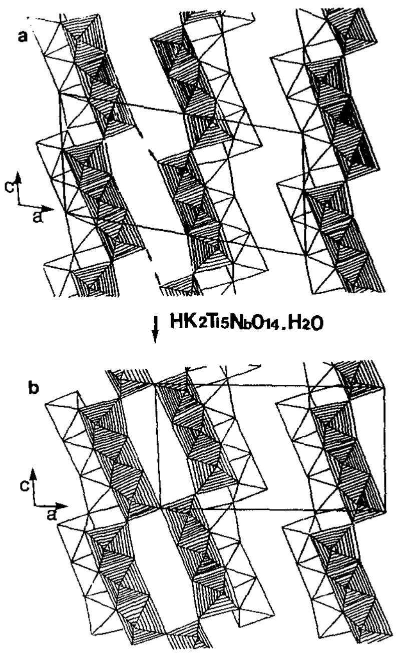

FIG. 6. Relationships between the structure of (a) $HK_2Ti_5NbO_{14} \cdot H_2O$ and the proposed structure (b) $K_4Ti_{10}Nb_2O_{27}$.

$HK_2Ti_5NbO_{14}$. Determination of the structure of $K_4Ti_{10}Nb_2O_{27}$ could not be carried out from the X-ray powder data owing to the preferential orientation phenomena resulting from the layer structure of this compound. The ion-exchange properties of $K_4Ti_{10}Nb_2O_{27}$ confirm that this oxide remains lamellar: the action of an acid solution at room temperature allows more than half of the potassium ions to be exchanged in a reversible way. The morphology of the crystals is shown in Fig. 7: the splitting of the platelets can also be considered as a proof of the almost fibrous character of $K_4Ti_{10}Nb_2O_{27}$.

Thus $K_4Ti_{10}Nb_2O_{27}$ can be considered as an intergrowth of a tunnel structure of the $K_2Ti_6O_{13}$ type with a layer oxide of type $K_3Ti_5NbO_{14}$. In some crystals (Fig. 8) regions corresponding to a regular spacing of 26.4 Å along *a* (labelled A) surrounded by regions of $K_2Ti_6O_{13}$ (labelled B) and of $HK_2Ti_5NbO_{14}$ (labelled C) were observed.

Regions A may easily be interpreted as intergrowths of double layers of $HK_2Ti_5NbO_{14}$ with single layers of $K_2Ti_6O_{13}$ according to the formulation $[KTi_5NbO_{13}][HK_2Ti_5NbO_{14}]_2$. This suggests that other types of intergrowths such as $[KTi_5NbO_{13}]_n[HK_2Ti_5NbO_{14}]_n$ may exist.

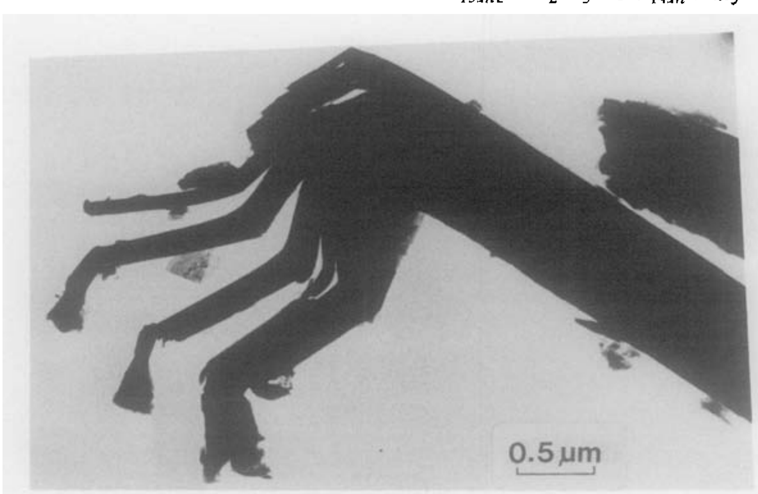

FIG. 7. Low-resolution image showing the morphology of the $K_4Ti_{10}Nb_2O_{27}$ microcrystals.

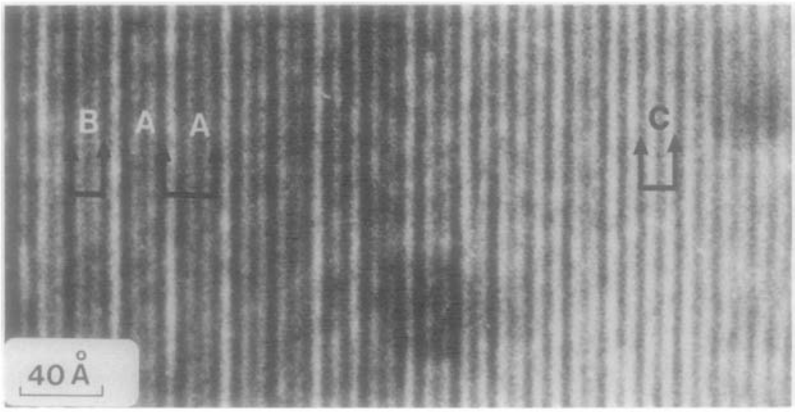

FIG. 8. Image (001) of a crystal showing layers with three different spacings.

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