

## Localization of Hydrogen in the Layer Oxide HTiNbO<sub>5</sub>

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The structure of HTiNbO<sub>5</sub> at 10 and 300 K and of DTiNbO<sub>5</sub> at 300 K has been investigated by neutron powder diffraction. The TiNbO<sub>5</sub> framework and the octahedral distortions previously found for the alkali titanates by X-ray diffraction are confirmed. The position of hydrogen (or deuterium) has been determined: very strong O-H . . . O hydrogen bonds with O . . . O distances ranging from 2.51 to 2.63 Å are observed. The similarity of these compounds with acids is shown, explaining their ion exchange properties. The absence of protonic conductivity can be explained from structural arguments. The open character of this structure, which can play a part in intercalation and deintercalation reactions is also discussed.

### Introduction

The ion exchange properties (1-2) of the layer titanates  $A_{1-x}Ti_{1-x}Nb_{1+x}O_5$  (3-4) have shown the great ability of this structure to intercalate ions of various size ranging from the proton to the alkyl ammonium ions and involving a drastic evolution of the *c* parameter, which characterizes the layer spacing. Most of these exchange reactions in aqueous media are similar to those observed for other layer structures: intercalation of cations with the same size or bigger than potassium does not involve insertion of solvent molecules, while intercalation of lithium or sodium, which are smaller than potassium, is accompanied by insertion of water. However, the protonic exchange of  $A_{1-x}(Ti_{1-x}Nb_{1+x})O_5$  compounds, in acidic solution is quite different from that of the other layer oxides: no hydration is observed during and after reaction, although

the resulting compounds,  $H_{1-x}(Ti_{1-x}Nb_{1+x})O_5$ , still exhibit ion exchange properties, indicating that they cannot be considered as simple hydroxides. The long-range mobility of the proton is, however, very low, since the conductivity of these phases is not measurable at room temperature. The present study deals with the neutron diffraction study of HTiNbO<sub>5</sub> and DTiNbO<sub>5</sub> in order to explain the particular behaviour of the proton in these compounds.

### Experimental

#### Synthesis of the Samples

HTiNbO<sub>5</sub> compound was prepared by action of an acidic solution on KTiNbO<sub>5</sub>, according to the ion exchange methods previously described (1, 2). The oxide DTiNbO<sub>5</sub> was prepared by deuteration of HTiNbO<sub>5</sub> in D<sub>2</sub>O. Previous experiments

with pyrochlore structure materials (5) had shown the exchange reaction  $D \rightleftharpoons H$  to be sometimes incomplete; hence, diffraction experiments were performed on both "natural" and deuterated samples.

### Neutron Diffraction

Powder neutron diffraction data were collected on the DIA high-resolution diffractometer (6) at the Institut Laue-Langevin using  $\lambda = 1.9094(2)$  Å. Sample materials were inserted in 15-mm-diameter vanadium containers, except DTiNbO<sub>5</sub>, which was sealed in a quartz ampoule. Data were collected from 8 to 160° in steps of 0.05°(2 $\theta$ ) taking about 20 hr for each measurement. The raw data from the 10 counters were subsequently reduced by using conventional ILL programs (7); integrated intensities were determined by fitting the Bragg peaks to a Gaussian function and the background to a first- or second-order polynomial (7). The cell parameters were obtained by least-squares refinement from the strongest reflections, the zero-point correction of the instrument being included in the refinement. The structure refinements are based on a conventional least-squares fitting in the integrated intensities (8) allowing for the refinement of a preferred orientation parameter  $G$ ; This empirical correction is defined by

$$I_{\text{corr}} = I_{\text{obs}} \cdot \exp(-G\alpha^2),$$

where  $\alpha$  is the acute angle between the scattering vector and the normal to the crystal-lites (9). With this simple correction, a striking improvement of the fits was observed (Table II). The scattering amplitudes  $b(\text{H}) = -3.74$ ,  $b(\text{D}) = 6.67$ ,  $b(\text{Ti}) = -3.4$ ,  $b(\text{Nb}) = 7.1$  and  $b(\text{O}) = 5.8$  fm were used.

### Structure Determination

The cell parameters observed for these compounds (Table I) are quite close to

TABLE I  
CELL PARAMETERS ( $\lambda = 1.9094(2)$  BASED ON  
 $a_{\text{Ni}} = 3.5238$  Å)

Compound	$T$ (K)	$a$ (Å)	$b$ (Å)	$c$ (Å)
HTiNbO <sub>5</sub>	10	6.521(2)	3.773(1)	16.656(4)
HTiNbO <sub>5</sub>	300	6.534(3)	3.777(1)	16.675(9)
DTiNbO <sub>5</sub>	300	6.534(4)	3.776(2)	16.677(11)

Note. The  $SD_e$ s are given in parentheses and refer to the last digit.

those obtained from X-ray diffraction spectra (1). All the calculations were made in the space group  $Pnma$  and are based on 37 (DTiNbO<sub>5</sub>) and 50 (HTiNbO<sub>5</sub>) observed intensities, i.e., on 144 and 176  $hkl$ . In a first set of refinements, the atoms of the [TiNbO<sub>5</sub>] framework were placed in the 4c positions previously observed for KTiNbO<sub>5</sub> (4). The positions of titanium, niobium, and oxygen atoms were first refined, the isotropic thermal parameters being fixed at 1 Å<sup>2</sup>. After three cycles the discrepancy indexes ( $R_1 = \sum |I_o - I_c| / \sum I_o$ ) leveled at values in the range 0.22–0.25. The hydrogen or deuterium atoms were then localized on Fourier difference maps. In the case of the hydrogen compound, several negative peaks appeared: most of them were located very close to the  $M$  positions ( $M = \text{Ti}, \text{Nb}$ ), and could be identified as residual peaks due to the presence of titanium which has a negative scattering factor. Only one series of peaks corresponding to the equivalent position 4c ( $x \approx 0.4$  and  $z \approx 0.2$ ) and with a much higher intensity could be assigned to the hydrogen atoms. Three series of refinements were made corresponding respectively to the coordinates ( $x, \frac{1}{4}, z$ ) of the hydrogen, its isotropic Debye-Waller factor  $B$  and finally all three parameters simultaneously. Refinement of the occupancy factor of the proton site did not modify it, confirming that only this 4c site is occupied by the hydrogen atoms. At this stage of the determination the possibility of preferred

orientation was considered: this hypothesis was supported by a preliminary X-ray study on HTiNbO<sub>5</sub> oxide, which showed a drastic preferred orientation of the flat samples, owing to the layer structure of this compound. Refinement of the empirical preferred orientation parameter  $G$  (plates perpendicular to  $c$ ) did not affect significantly the positional parameters but led to a drastic decrease of the  $R$  factors (Table II). DTiNbO<sub>5</sub> diffraction data were analyzed in a similar way; however, the lower background led to better resolved Bragg peaks and Fourier difference maps showed only one set of peaks, very close to the one observed for the proton in HTiNbO<sub>5</sub>. Further refinements of the atomic coordinates, temperature factors and preferred orientation parameter  $G$  led to the results given in Table III.

It is worth noting that for all three structures the distribution of titanium and niobium atoms over the octahedral sites was refined step by step in order to avoid correlation effects. The observed distributions are very close to those obtained by X-ray diffraction for the starting material KTiNbO<sub>5</sub> (4). The three sets of atomic coordinates and thermal parameters given in Table III are not significantly different; moreover they are quite similar to the results obtained for the [TiNbO<sub>5</sub>]<sup>-</sup> layers of KTiNbO<sub>5</sub>. Thus, it can be stated that neither the temperature nor the nature of the

TABLE II  
DISCREPANCY FACTORS CALCULATED ON  
INTENSITIES

Compound	$T$ (K)	Without preferred orientation correction		With preferred orientation correction		$G$
		$R$	$R_w$	$R$	$R_w$	
HTiNbO <sub>5</sub>	10	0.079	0.069	0.061	0.055	0.13(3)
	300	0.094	0.092	0.061	0.056	0.17(2)
DTiNbO <sub>5</sub>	300	0.119	0.096	0.053	0.048	0.18(3)

TABLE III  
ATOMIC PARAMETERS, THERMAL PARAMETERS AND  
OCCUPANCY FACTORS FOR HTiNbO<sub>5</sub> AND DTiNbO<sub>5</sub>

Compound		HTiNbO <sub>5</sub> (10 K)	HTiNbO <sub>5</sub> (300 K)	DTiNbO <sub>5</sub> (300 K)
H or D	$x$	0.393(15)	0.404(7)	0.401(8)
	$z$	0.197(6)	0.192(3)	0.193(4)
	$B$ (Å <sup>2</sup> )	3.8(20)	3.7(9)	4.2(18)
$M_1$	$x$	0.301(16)	0.291(16)	0.291(16)
	$z$	0.023(7)	0.024(7)	0.024(7)
	$\tau_1^a$	0.77	0.77	0.77
$M_2$	$x$	0.792(9)	0.794(4)	0.784(12)
	$z$	0.125(3)	0.122(2)	0.119(4)
	$\tau_2^a$	0.23	0.23	0.23
$O_1$	$x$	0.072(6)	0.069(3)	0.064(9)
	$z$	0.074(3)	0.077(2)	0.077(4)
	$B$ (Å <sup>2</sup> )	1.9(9)	0.8(5)	1.9(12)
$O_2$	$x$	0.644(7)	0.641(3)	0.650(8)
	$z$	-0.006(3)	-0.008(2)	-0.009(4)
	$B$ (Å <sup>2</sup> )	1.5(13)	1.0(5)	0.8(10)
$O_3$	$x$	0.467(6)	0.469(3)	0.475(7)
	$z$	0.132(3)	0.131(2)	0.140(3)
	$B$ (Å <sup>2</sup> )	0.7(14)	2.0(6)	1.0(13)
$O_4$	$x$	0.836(7)	0.833(4)	0.834(8)
	$z$	0.226(3)	0.224(1)	0.221(3)
	$B$ (Å <sup>2</sup> )	0.2(9)	1.3(6)	1.3(11)
$O_5$	$x$	0.228(10)	0.231(3)	0.244(11)
	$z$	0.913(3)	0.909(2)	0.913(4)
	$B$ (Å <sup>2</sup> )	0.8(9)	1.3(4)	0.9(9)

<sup>a</sup>  $\tau_1$  and  $\tau_2$  give the occupancy factors of  $B_1$  and  $B_2$  sites by titanium atoms. Isotropic Debye-Waller factors  $B$  (Å<sup>2</sup>) are corrected for absorption when necessary (10). All atoms are in (4c) position of  $Pnma$ .

<sup>b</sup> Owing to the weak contribution of  $B_1$  atoms (Ti + Nb) the  $B$  values have been fixed.

A<sup>+</sup> cation really modify the structure of the [TiNbO<sub>5</sub>]<sup>-</sup> sheets. This is further confirmed by neutron powder diffraction data on H<sub>0.85</sub>Ti<sub>0.85</sub>Nb<sub>1.15</sub>O<sub>5</sub>, which led to very similar results; however, the crystallinity of this material was rather poor and the refined parameters showed standard deviations about twice as large as the  $SD_e$ s of HTiNbO<sub>5</sub>; the detailed results on this material will not be given here.

One can notice that the parameters of the first cationic site  $M_1$  are poorly defined for all three sets of results; this comes from the distribution of titanium and niobium atoms over this site which leads fortuitously to an

almost zero-scattering amplitude for this position.

### Discussion

This study confirms the results previously observed by X-ray diffraction for the octahedral framework of the oxides  $A_{1-x}Ti_{1-x}Nb_{1+x}O_5$  (4): the structure is built up from units of  $2 \times 2$  edge-sharing octahedra forming sheets perpendicular to the  $c$  axis as shown in Fig. 1.

The distortion of the  $MO_6$  octahedra (Table IV, Fig. 1) is very similar to that observed in the corresponding alkali niobates. It is, however, difficult to compare both results, owing to the fact that the oxygen positions obtained from X-ray diffraction study for the potassium and rubidium compounds are not so accurate as those obtained here. In return, the contrary is observed for metal atoms of the  $M$  sites, whose positions as obtained by neutron diffraction are less accurate owing to the opposite signs of scattering factors of niobium and titanium, involving for these atoms a smaller contribution to the structure factors than that observed by X-ray diffraction. Nevertheless, it can be stated that the ion exchange reactions do not modify drasti-

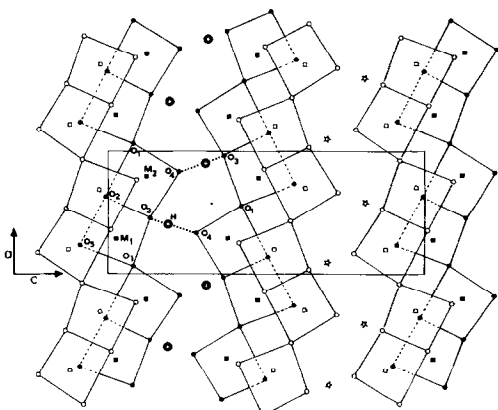


FIG. 1.  $HTiNbO_5$ : Projection of the structure onto the (0 1 0) plane.

TABLE IV  
 $HTiNbO_5$  AND  $DTiNbO_5$ : INTERATOMIC DISTANCES

Distance	$HTiNbO_5$ (300 K)	$HTiNbO_5$ (10 K)	$DTiNbO_5$ (300 K)
$O_3-O_4$	2.58(4)	2.53(7)	2.50(7)
$O_4-O_4$	3.38(3)	3.36(7)	3.41(7)
$H-O_3$	1.10(6)	1.19(12)	1.01(9)
$H \dots O_4$	1.48(5)	1.35(11)	1.51(9)
$H-O_1$	2.91(5)	2.93(11)	2.92(9)
Octahedron I			
$M_1-O_1$	1.70(11)	1.73(12)	1.72(13)
$M_1-O_3$	2.13(12)	2.12(13)	2.27(13)
$M_1-O_2$	2.35(11)	2.28(12)	2.41(12)
$M_1-O_5$	1.95(13)	1.89(13)	1.88(14)
$M_1-O_2 (\times 2)$	1.96(3)	1.94(3)	1.94(3)
$O_1-O_3$	2.76(3)	2.75(6)	2.88(8)
$O_3-O_2$	2.57(4)	2.57(7)	2.73(8)
$O_2-O_5$	3.01(3)	3.03(8)	2.96(9)
$O_5-O_1$	2.99(4)	2.87(7)	2.98(10)
$O_1-O_2$	2.91(2)	2.89(5)	2.89(6)
$O_3-O_2$	2.88(3)	2.92(5)	3.00(6)
$O_2-O_2$	2.65(2)	2.67(5)	2.74(5)
$O_5-O_2$	2.64(3)	2.58(5)	2.57(6)
Octahedron II			
$M_2-O_3$	2.13(3)	2.12(7)	2.05(9)
$M_2-O_4$	1.72(4)	1.70(7)	1.73(8)
$M_2-O_1$	1.94(3)	2.02(7)	1.96(10)
$M_2-O_2$	2.38(4)	2.39(7)	2.31(9)
$M_2-O_5 (\times 2)$	1.96(1)	2.00(2)	1.97(3)
$O_2-O_3$	2.57(4)	2.57(7)	2.73(8)
$O_3-O_4$	2.84(3)	2.87(6)	2.71(7)
$O_4-O_1$	2.88(3)	2.96(6)	2.83(8)
$O_1-O_2$	3.14(3)	3.09(6)	3.06(8)
$O_2-O_5$	2.64(3)	2.58(5)	2.57(6)
$O_3-O_5$	2.81(2)	2.85(6)	2.78(6)
$O_4-O_5$	2.95(3)	3.02(5)	2.97(7)
$O_1-O_5$	2.73(2)	2.73(5)	2.77(7)

cally the octahedral framework  $TiNbO_5^-$ , except that the niobium and titanium atoms are displaced inside their octahedra in a significant way. This displacement is probably correlated with the formation of O-H bonds as will be explained below.

The main changes with regard to the alkali compounds concern the relative positions of the  $TiNbO_5^-$  layers which have been brought closer together. The  $O_3-O_4$  distances, ranging from 2.50 to 2.58 Å are

indeed considerably shorter than those observed for the alalititanoniobates (4) (3.21 to 3.73 Å). Moreover, this translation of the octahedral layers along the  $\langle 001 \rangle$  direction involves shorter O<sub>4</sub>-O<sub>4</sub> distances ranging from 3.36 to 3.41 Å in the hydrogen compounds as compared to 3.57 to 3.77 Å in the alkali compounds. This proximity of the TiNbO<sub>5</sub> layers, which corresponds to the minimum oxygen distances usually observed in oxides, is in fact due to the formation of very strong hydrogen bonds. Hydrogen is indeed located between O<sub>3</sub> and O<sub>4</sub> (Fig. 1); it forms with the atom O<sub>3</sub> a strong bond characterized by a distance ranging from 1.01 to 1.19 Å, thus close to the distances observed in hydroxides and water. The other oxygen atom O<sub>4</sub> is situated at a rather short distance from the hydrogen atom, ranging from 1.51 to 1.35 Å. These results are similar to those observed in a lot of acids and acidic salts (11-14).

Moreover the O<sub>3</sub>-H . . . O<sub>4</sub> bond angle is equal to 180°, in agreement with the observation made by Brown (13) about the strong hydrogen bonds, confirming the structural results obtained here for the hydrogen and oxygen positions. It must also be outlined that the M<sub>1</sub>-O<sub>3</sub> and M<sub>2</sub>-O<sub>3</sub> distances will be more affected than the M<sub>2</sub>-O<sub>4</sub> since the O<sub>3</sub>-H bond is stronger than the O<sub>4</sub> . . . H bond; this assumption is in agreement with the experimental results: the M<sub>1</sub>-O<sub>3</sub> and M<sub>2</sub>-O<sub>3</sub> distances are much greater than the M<sub>2</sub>-O<sub>4</sub> distance. Hence it is the substitution of the alkali cation by H<sup>+</sup>, which is responsible for the displacement of Ti and Nb in their octahedra.

The similarity of the hydrogen bonds with those observed in many acids suggests to us consideration of this phase as a titanoniobic acid, which explains its ability to ion exchange and to fix bases like amines (2). The thermal stability of this material, which decomposes at temperatures higher than 330°C, is another indication of the strength of the hydrogen bonds.

This compound is not hydrated, contrary to most of the exchanged protonic materials. The explanation is to be found in the layer feature of the structure: in three-dimensional framework structures like the pyrochlores HTaWO<sub>6</sub> or H<sub>2</sub>Ta<sub>2</sub>O<sub>8</sub> (5), there are one or two protons linked to only one oxygen atom of the framework and then available for bonding to a water molecule; moreover, the tunnels of the pyrochlore are big enough to accommodate one molecule of water. This is no longer true for the HTiNbO<sub>5</sub> structure because of its two-dimensional character: the protons, through the O<sub>3</sub>-H . . . O<sub>4</sub> bonds are responsible for the cohesion of the solid along the *c* direction and they are not available for bonding to a water molecule; furthermore, the shortness of the interlayer distance (O<sub>3</sub>-H . . . O<sub>4</sub> bond) does not leave much room to accommodate extra molecules of solvent in the interlayer gap (compare for instance, the formula unit volume of the pyrochlore HTaWO<sub>6</sub> ( $V = 142.4 \text{ \AA}^3$ ) and HTiNbO<sub>5</sub> ( $V = 102.8 \text{ \AA}^3$ )). The structure of HTiNbO<sub>5</sub> can thus be described either as a layer structure or, alternatively, as a three-dimensional lattice with pentagonal tunnels "O<sub>3</sub>-O<sub>4</sub>-O<sub>3</sub>-O<sub>1</sub>-O<sub>4</sub>" (Fig. 1).

The poor proton conductivity of these materials ( $\sigma < 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$  at room temperature) can also be accounted for by the structure: the proton motion is restricted to the (*a*, *b*) plane but the shortest proton-proton distances in this plane are larger than 3.8 Å; the best direction for proton motion would be along *a*, but the oxygen atom which could allow a hopping mechanism in this direction is too far away, the H-O<sub>1</sub> distance being about 2.9 Å.

## Conclusion

The structural study of the layer oxide HTiNbO<sub>5</sub> has shown the particular behavior of this compound which can be considered as an acid. The poor protonic conduc-

tivity of this phase despite its good ion exchange properties has been explained. The open framework of this compound allows consideration of the possibility of electrochemical intercalation of small cations like lithium and sodium. Finally, it must also be remembered that the oxides  $H_{1-x}Ti_{1-x}Nb_{1+x}O_5$  represent a step in the deintercalation of alkali titanoniobates  $A_{1-x}Ti_{1-x}Nb_{1+x}O_5$  leading to the empty tunnel structure  $Ti_2Nb_2O_9$  (1).

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### References

1. H. REBBAH, G. DESGARDIN, AND B. RAVEAU, *Mater. Res. Bull.* **14**, 1125 (1979).
2. H. REBBAH, M. M. BOREL, AND B. RAVEAU, *Mater. Res. Bull.* **15**, 317 (1980).
3. A. D. WADSLEY, *Acta Crystallogr.* **17**, 623 (1964).
4. H. REBBAH, G. DESGARDIN, AND B. RAVEAU, *J. Solid State Chem.* **31**, 321 (1980).
5. D. GROULT, J. PANNETIER, AND B. RAVEAU, to be published.
6. A. W. HEWAT AND I. BAILEY, *Nucl. Instrum. Methods* **137**, 463 (1976).
7. P. WOLFERS, Programs for treatment of powder profiles (1975). Private communication.
8. H. L'HELGOUALCH, G. FONTENEAU, AND J. PANNETIER, unpublished computer program (1975).
9. H. M. RIETVELD, *J. Appl. Cryst.* **2**, 65 (1969).
10. A. W. HEWAT, *Acta Crystallogr. Sect. A* **35**, 248 (1979). Note that the correction  $\Delta B$  given in this paper has to be divided by 2.
11. W. C. HAMILTON AND J. A. IBERS, "Hydrogen Bonding in Solids," Benjamin, New York (1968).
12. G. E. BACON, "Neutron Diffraction." Oxford Univ. (Clarendon), Oxford (1975).
13. I. D. BROWN, *Acta Crystallogr. Sect. A* **32**, 24 (1976).
14. I. D. BROWN, *Acta Crystallogr. Sect. A* **32**, 786 (1976).