

The Sodium Niobate NaNb_3O_8 : A Novel Lamellar Oxide Synthesized by Soft Chemistry

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The ion-exchange properties of the lamellar protonic niobate $\text{H Nb}_3\text{O}_8 \cdot \text{H}_2\text{O}$ allowed the hydrate $\text{NaNb}_3\text{O}_8 \cdot 2.5\text{H}_2\text{O}$ to be synthesized. The thermolysis of this latter hydrate allowed the oxides $\text{NaNb}_3\text{O}_8 \cdot \text{H}_2\text{O}$ and NaNb_3O_8 to be prepared. These three compounds are characterized by an orthorhombic cell whose parameters are closely related to those of KNb_3O_8 , in agreement with their lamellar character:

$$\begin{aligned} a &= 8.971(9) \text{ \AA}; b = 28.84(4) \text{ \AA}; c = 3.790(4) \text{ \AA} \text{ for } \text{NaNb}_3\text{O}_8 \cdot 2.5\text{H}_2\text{O} \\ a &= 9.072(10) \text{ \AA}; b = 22.34(3) \text{ \AA}; c = 3.792(3) \text{ \AA} \text{ for } \text{NaNb}_3\text{O}_8 \cdot \text{H}_2\text{O} \\ a &= 8.771(14) \text{ \AA}; b = 10.16(2) \text{ \AA}; c = 3.784(3) \text{ \AA} \text{ for } \text{NaNb}_3\text{O}_8 \end{aligned}$$

The structure of NaNb_3O_8 has been studied from X-ray powder data; a structural model has been established which shows that NaNb_3O_8 consists of octahedral layers similar to those observed in KNb_3O_8 ; the two structures differ from each other by the relative positions of the layers. The structure of NaNb_3O_8 can be deduced from that of KNb_3O_8 by a translation of an octahedral layer out of two of $c/2$. This behavior of potassium and sodium is different from that observed in other lamellar oxides $\text{Na}_2\text{Ti}_3\text{O}_7$, $\text{K}_x\text{Ti}_{2-x}\text{M}_x\text{O}_4$ and $\text{NaMnO}_2\text{-}\beta$. © 1987 Academic Press, Inc.

Introduction

The recent analysis of the structural relationships in lamellar oxides (1) has shown that it is possible to predict closely related structures built from identical layers but one differing from the other by the relative positions of those layers. This difference was shown to be due to the nature of the A cations located between the layers and which can take a different coordination according to their size. This is illustrated by the comparison of the three titanates and titanoniobates $\text{Na}_2\text{Ti}_3\text{O}_7$ (2), $\text{K}_3\text{Ti}_5\text{NbO}_{14}$ (3), and $\text{CsTi}_2\text{NbO}_7$ (4), which are all characterized by similar $[\text{M}_3\text{O}_7]$ layers of octa-

hedra and which are translated in different ways in the three structures. Moreover, sometimes a progressive transition from a layer structure to a close-packed structure can be observed as the size of the A ion decreases as shown for the cobalt oxides A_xCoO_2 (5, 6).

An interesting lamellar oxide KNb_3O_8 was recently described by Gasperin (7) and was found to exhibit ion-exchange properties leading to the protonic oxide $\text{H Nb}_3\text{O}_8 \cdot \text{H}_2\text{O}$ (8). The direct synthesis of NaNb_3O_8 by action of sodium carbonate and niobium oxide does not allow a lamellar oxide to be built: a tetragonal tungsten bronze structure is isolated by such a method (9). From the

previous analysis, it appears that a lamellar structure should be stabilized for NaNb_3O_8 by using soft chemistry. Thus, the present work deals with the study of the ion-exchange property of $\text{HfNb}_3\text{O}_8 \cdot \text{H}_2\text{O}$ in the presence of a soda solution, of the thermolysis of the exchanged products, and of the structure of the final niobate NaNb_3O_8 synthesized at low temperature.

Experimental Methods

The ion-exchange reaction was carried out by adding 2 g of the oxide $\text{HfNb}_3\text{O}_8 \cdot \text{H}_2\text{O}$ in 100 ml of an aqueous solution of NaOH(N) . The reaction was favored by stirring the mixture.

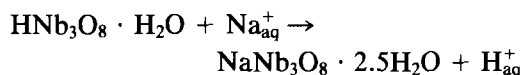
Thermolysis was controlled by using thermal differential analysis and thermogravimetry with a Setaram microbalance.

The sodium content after the exchange reaction was determined by atomic absorption spectroscopy. The X-ray powder diffraction patterns were registered with a Philips goniometer with the $\text{CuK}\alpha$ radiation. The intensities of the different reflections were measured by planimetry.

The density of the products was determined by pycnometry at 25°C in carbon tetrachloride.

Results

The exchange of the proton by sodium ion is very fast; the reaction is completed after several minutes:



The reaction is reversible: by action of an acid solution on the sodium niobate, the oxide $\text{HfNb}_3\text{O}_8 \cdot \text{H}_2\text{O}$ is regenerated.

The thermodifferential and microthermogravimetric analyses of the hydrate $\text{NaNb}_3\text{O}_8 \cdot 2.5\text{H}_2\text{O}$ show its low stability: the two endothermic peaks whose maxima are ob-

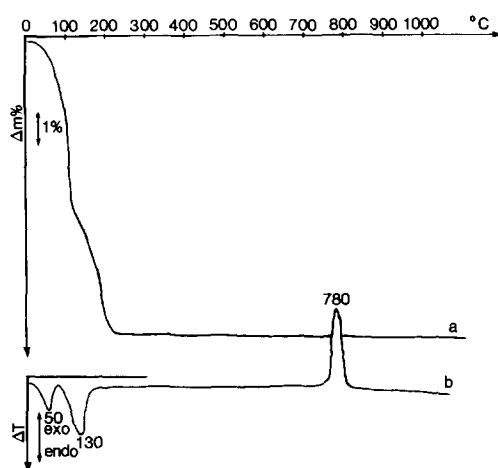
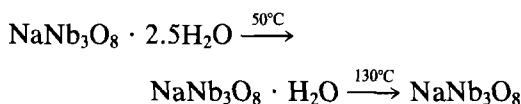


FIG. 1. The thermogravimetric and thermodifferential curves of $\text{NaNb}_3\text{O}_8 \cdot 2.5\text{H}_2\text{O}$.

served at 50 and 130°C (Fig. 1b) correspond to the loss of 1.5 and 2.5 mole of water, respectively (Fig. 1a), according to the equation:



Although the hydrate $\text{NaNb}_3\text{O}_8 \cdot \text{H}_2\text{O}$ is stable at room temperature, it exhibits a zeolithic character: it can be rehydrated in a wet atmosphere, reforming the hydrate $\text{NaNb}_3\text{O}_8 \cdot 2.5\text{H}_2\text{O}$. The rehydration of NaNb_3O_8 , however, has not been found to be possible. At higher temperature, 780°C , the thermodifferential curve (Fig. 1b) shows an exothermic peak, corresponding to an irreversible structural transition for NaNb_3O_8 , leading to the tetragonal tungsten bronze structure previously described (9).

The X-ray diffraction study of the dehydration process shows that the three compounds $\text{NaNb}_3\text{O}_8 \cdot 2.5\text{H}_2\text{O}$, $\text{NaNb}_3\text{O}_8 \cdot \text{H}_2\text{O}$, and NaNb_3O_8 are structurally closely related to $\text{HfNb}_3\text{O}_8 \cdot \text{H}_2\text{O}$; i.e., they exhibit a lamellar structure built-up from identical layers of octahedra. The spectrum obtained

TABLE I
CRYSTALLOGRAPHIC DATA

Compound	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	Space group	<i>d</i> _{calc}	<i>d</i> _{obs}
KNb ₃ O ₈	8.903(3)	21.16(2)	3.799(2)	<i>Amam</i>		
NaNb ₃ O ₈ · 2.5H ₂ O	8.971(9)	28.84(4)	3.790(4)	<i>Pncn</i>	3.22	3.34
NaNb ₃ O ₈ · H ₂ O	9.072(10)	22.34(3)	3.792(3)	<i>Pmnn</i> ; <i>P2nn</i>	3.87	3.89
NaNb ₃ O ₈	8.771(14)	10.16(2)	3.784(3)	<i>Pmnm</i> ; <i>Pmn2</i> ₁	4.23	4.17

with a Guinier–Lenne camera shows clearly that no intermediate hydrates are formed during the thermolysis.

The three compounds are characterized, like KNb₃O₈, by an orthorhombic cell (Table I) whose *a* and *c* parameters, which characterize the [Nb₃O₈] layers, are rather similar and close to those of KNb₃O₈. Nevertheless the *a* parameter of NaNb₃O₈ is smaller than those of the other oxides. The *b* parameter which corresponds to the direction perpendicular to the Nb₃O₈ layers increases with the water content. It is worth noting that the two niobates NaNb₃O₈ · 2.5H₂O and NaNb₃O₈ · H₂O which have *b* parameters of the same order of magnitude as that of KNb₃O₈ are characterized by different space groups. The anhydrous niobate NaNb₃O₈ is remarkable in that it exhibits a *b* parameter two times smaller; thus it is clear that *b* corresponds in this latter case to the interlayer spacing. From this simple observation it appears that two successive [Nb₃O₈] layers are at the same level along *b* in NaNb₃O₈, contrary to KNb₃O₈ where they are displaced of *c*/2. The structural study of NaNb₃O₈ was undertaken in order to understand this difference. The Guinier powder pattern is given in Table II.

Structural Study of NaNb₃O₈

No single crystal could be isolated for the determination of the structure. Thus the structure was studied from powder diffractogram on the 39 first reflections, i.e., 108

hkl. The reflection condition *hol*: *h* + *l* = 2*n* leads to two possible space groups *Pmnm* and *Pmn2*₁. The calculations were performed in the centrosymmetric group *Pmnm*. The positions of the oxygen and

TABLE II
GUINIER POWDER PATTERN NaNb₃O₈ CuKα₁
RADIATION

<i>h k l</i>	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>h k l</i>	<i>d</i> _{obs}	<i>d</i> _{calc}
0 1 0	10.077	10.165	0 5 1	1.794	1.791
1 1 0	6.612	6.640	1 5 1	1.760	1.757
0 2 0	5.073	5.082	2 1 2	1.712	{ 1.712 1.711
2 0 0	4.382	4.385	3 4 1		
2 1 0	4.013	4.027	1 6 0	1.660	{ 1.663 1.660 1.658
0 1 1	3.535	3.546	4 4 0		
0 3 0	3.388	3.388	5 2 0		
2 2 0	3.320	3.320	2 2 2	1.644	1.644
1 3 0	3.165	3.160	5 0 1	1.587	{ 1.591 1.580
0 2 1	3.021	3.035	2 6 0		
1 2 1	2.864	2.868	5 1 1	1.570	{ 1.572 1.569
3 1 0	2.800	2.809	3 1 2		
2 1 1	2.753	2.757	1 6 1	1.520	{ 1.523 1.520 1.519 1.517 1.466
2 3 0	2.685	2.681	4 4 1		
0 4 0	2.544	2.541	5 2 1		
0 3 1	2.526	2.524	0 4 2		
1 3 1	2.428	2.426	3 6 0		
3 0 1	2.313	2.313	6 0 0	1.462	{ 1.462 1.458
3 1 1	2.253	2.256	2 6 1	1.439	{ 1.440 1.438
3 3 0	2.217	2.213	5 3 1		
3 2 1	2.105	2.105	3 3 2		
0 5 0	2.038	2.033	0 7 1	1.360	1.356
4 2 0	2.012	2.013	5 1 2	1.276	1.276
1 5 0	1.986	1.980	0 1 3	1.252	{ 1.252 1.251 1.250 1.248 1.248
3 4 0	1.919	1.918	3 5 2		
0 0 2	1.892	1.892	1 6 2		
0 1 2	1.855	1.860	1 0 3		
1 1 2	1.812	1.819	4 4 2		

TABLE III
ATOMIC PARAMETERS ($\times 10^2$)
AND TEMPERATURE FACTORS
(\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Nb(1)	94	76	$\frac{1}{4}$	0.6
Nb(2)	$\frac{1}{4}$	48	$\frac{1}{4}$	0.6
Na	$\frac{1}{4}$	92	$\frac{3}{4}$	0.8
O(1)	44	28	1.4	1.
O(2)	03	90	$\frac{1}{4}$	1.
O(3)	09	58	$\frac{1}{4}$	1.
O(4)	$\frac{1}{4}$	41	$\frac{3}{4}$	1.
O(5)	$\frac{1}{4}$	14	$\frac{3}{4}$	1.

niobium atoms were proposed by comparison with KNb_3O_8 (7). We have supposed that both structures exhibit very similar layers of octahedra Nb_3O_8 : thus all atoms were located at the level $z = \frac{1}{4}$ and $\frac{3}{4}$. The refine-

TABLE IV
OBSERVED AND CALCULATED INTENSITIES FOR
 NaNb_3O_8

<i>hkl</i>	<i>I</i> _{obs}	<i>I</i> _{calc}	<i>hkl</i>	<i>I</i> _{obs}	<i>I</i> _{calc}
0 1 0	71.31	70.09	3 5 0	20.45	2.42
1 1 0	40.65	38.22	1 6 0		0.96
0 2 0	18.95	17.48	4 4 0	12.97	0.44
1 2 0	7.00	3.03	5 2 0		0.32
2 0 0		2.71	2 5 1	13.11	
2 1 0	8.50	9.61	4 3 1	11.97	0.71
0 1 1	33.17	34.09	0 3 2		1.20
1 0 1		0.02	2 2 2	12.59	
0 3 0	100.00	11.05	5 0 1	6.73	0.58
2 2 0		57.90	2 6 0		6.73
1 1 1	8.00	25.28	5 1 1	20.70	2.13
1 3 0		5.24	3 1 2		3.91
1 2 1	22.50	23.42	5 3 0	4.50	3.51
3 1 0	10.72	11.20	0 6 1		1.52
2 1 1	18.71	20.19	3 5 1	7.48	0.10
2 3 0	5.24	4.98	1 6 1		4.93
0 4 0	26.44	20.45	4 4 1	4.50	0.24
3 2 0		1.18	5 2 1		9.58
0 3 1	7.48	7.99	0 4 2	3.74	4.18
2 2 1		0.78	3 2 2		0.42
1 4 0	3.74	3.28	3 6 0	3.16	0.77
1 3 1		3.40	6 0 0		2.70
3 0 1	3.74	4.34	2 6 1	3.16	0.14

TABLE IV—Continued

<i>hkl</i>	<i>I</i> _{obs}	<i>I</i> _{calc}	<i>hkl</i>	<i>I</i> _{obs}	<i>I</i> _{calc}
3 1 1	4.23	4.19	0 7 0	11.47	0.35
3 3 0	29.00	23.27	6 1 0		0.70
2 4 0		2.44	5 4 0	0.57	
4 0 0		3.63	5 3 1	0.38	
2 3 1	3.49	1.12	3 3 2	3.74	8.71
0 4 1		0.62	2 4 2		0.83
3 2 1	2.24	3.55	1 7 0	12.72	0.03
1 4 1		1.31	4 0 2		1.60
0 5 0	1.50	1.98	1 5 2	3.74	1.32
4 2 0	1.50	1.53	3 6 1		0.10
1 5 0	2.74	3.45	0 7 1	3.16	7.41
3 4 0	6.23	1.96	6 1 1		0.86
3 3 1		4.18	5 4 1	0.59	
2 4 1	14.22	0.61	3 4 2	3.74	0.77
0 0 2		14.08	6 3 0		0.44
4 1 1	3.49	0.11	4 6 0	3.16	0.03
0 1 2		0.88	1 7 1		0.10
2 5 0	1.50	1.44	5 1 2	3.74	3.35
4 3 0		1.79	1 8 0		0.29
1 1 2	1.50	2.08	5 5 1	3.16	1.33
0 5 1	1.50	2.47	0 1 3		1.27
4 2 1	3.49	0.39	3 5 2	3.16	1.42
0 2 2		0.93	1 6 2		0.41
1 5 1	3.49	2.11	1 0 3	3.16	0.01
1 2 2		0.33	4 4 2		0.36
2 0 2	35.67	0.32	5 2 2	5.24	0.18
5 1 0		4.98	2 8 0		0.46
2 1 2	35.67	1.68	5 6 0	5.24	0.09
3 4 1		23.75	7 2 0		0.01
0 6 0	35.67	5.99	2 6 2	5.24	3.83
			1 2 3		1.46
			4 7 0		0.34

ment of the structure was carried out with the program Maryse (10) which takes the orientation phenomena into account. Only the atomic positions were refined.

The reliability factor calculated on the intensities was lowered to $R = 0.07$ for the atomic positions given in Table III. In Table IV the observed and calculated intensities are given.

Description of the Structure of NaNb_3O_8 and Discussion

The rather small number of data versus the rather great number of variable parame-

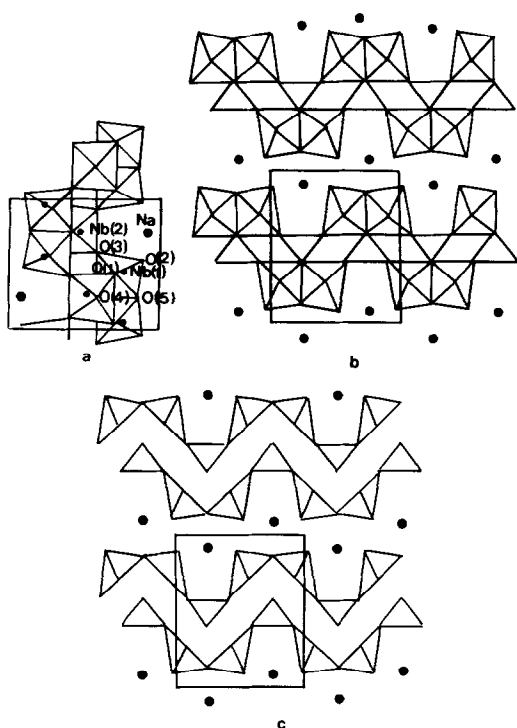


FIG. 2. Projection of the structure on (001) (a) in terms of edge-sharing octahedra, (b) in terms of edge-sharing octahedra sharing their corners with tetrahedra, (c) in terms of ribbons of corner-sharing pyramids and tetrahedra.

ters does not allow an accurate determination of the atomic positions. It is clear that the results obtained here must be considered as a structural model rather than an accurate structure. Nevertheless, the drastic distortion of the NbO_6 octahedra (Table V), (Fig. 2a) can be considered significant, in agreement with the results previously observed for KNb_3O_8 on a single crystal (7). The two abnormally long $\text{Nb}(2)\text{-O}(1)$ distances (2.57 Å) are to be compared to the one observed for $\text{Nb}(1)$ in KNb_3O_8 (2.42 Å); consequently it is clear that $\text{Nb}(2)$ tends to take a tetrahedral coordination in NaNb_3O_8 . Although less distorted, the $\text{Nb}(1)\text{O}_6$ octahedron is characterized by one long $\text{Nb}(1)\text{-O}(4)$ distance (2.35 Å) which can be

compared to that observed for $\text{Nb}(2)$ in KNb_3O_8 (2.29 Å).

From these results it appears that the layers of NaNb_3O_8 can also be described in terms of edge-sharing $\text{Nb}(1)\text{O}_6$ octahedra sharing their corners with $\text{Nb}(2)\text{O}_4$ tetrahedra (Fig. 2b) or in terms of ribbons of corner-sharing $\text{Nb}(1)\text{O}_5$ pyramids and $\text{Nb}(2)\text{O}_4$ tetrahedra (Fig. 2c). In this respect those structures can be compared to those of vanadium bronzes $A_{1+x}\text{V}_3\text{O}_8$ (11, 12) whose layers are generally described in terms of 2×2 edge-sharing octahedra linked through VO_5 pyramids but which can also be described as only edge-sharing VO_6 octahedra (1). Moreover those oxides exhibit a similarity with the vanadium phosphates such as $(\text{VO})_2\text{P}_2\text{O}_7$ (13) and VOPO_4 (14) whose three-dimensional framework is built-up from PO_4 tetrahedra and VO_6 octahedra.

The projection of this structure on (001) (Fig. 3a) shows that its layers of octahedra are similar to those observed for KNb_3O_8 (Fig. 3b). In both structures each $[\text{Nb}_3\text{O}_8]$ layer is formed of infinite ribbons of corner- and edge-sharing octahedra running along a (Figs. 3c and 3d). These ribbons share the corners of their octahedra along c and are associated through their edges along b . The main difference between the two structures deals with the relative positions of two successive layers: the structure of NaNb_3O_8 can indeed be deduced from that of KNb_3O_8 by displacing one layer out of two of $c/2$. This difference between sodium and potassium is very similar to the one observed by

TABLE V
COORDINATION OF THE CATIONS

$\text{Nb}(1)\text{-O}(2)$	1.70 Å	$\text{Nb}(2)\text{-O}(3)$	1.77 (×2) Å
$\text{Nb}(1)\text{-O}(1)$	1.93 (×2)	$\text{Nb}(2)\text{-O}(4)$	2.03 (×2)
$\text{Nb}(1)\text{-O}(5)$	2.01	$\text{Nb}(2)\text{-O}(1)$	2.57 (×2)
$\text{Nb}(1)\text{-O}(3)$	2.16		
$\text{Nb}(1)\text{-O}(4)$	2.35	$\text{Na-O}(2)$	2.69 (×4) Å
		$\text{Na-O}(5)$	2.23

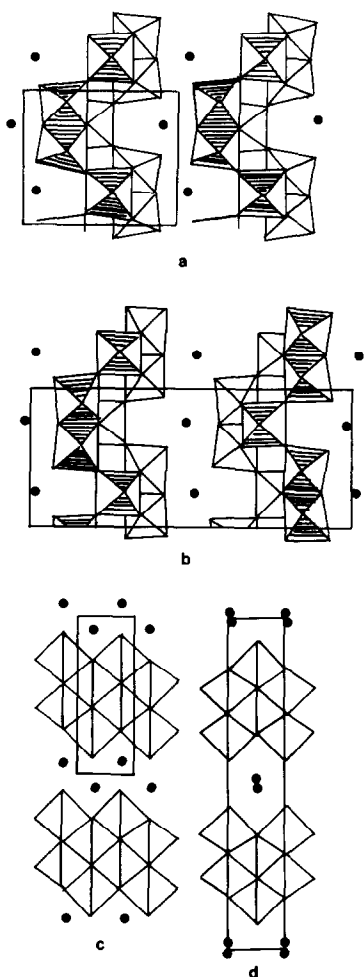


FIG. 3. Projection on (001) of (a) NaNb_3O_8 and (b) KNb_3O_8 . Projection on (100) of (c) NaNb_3O_8 and (d) KNb_3O_8 .

comparison of the lamellar oxides $\text{K}_x\text{Ti}_{2-x}\text{M}_x\text{O}_4$ (15) and $\text{NaMnO}_2\text{-}\beta$ (16). Both oxides exhibit similar layers of edge-sharing octahedra (Fig. 4) and differ by the relative positions of their layers: the structure of $\text{NaMnO}_2\text{-}\beta$ (Fig. 4b) is deduced from that of $\text{K}_x\text{Ti}_{2-x}\text{M}_x\text{O}_4$ (Fig. 4a) by a translation of one layer out two of $a/2$ in the orthorhombic cell. These two examples clearly show that the positions of the layers are mainly dictated by the coordination of

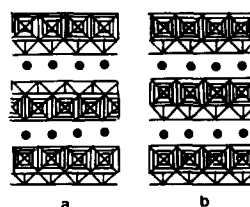


FIG. 4. Structure of (a) $\text{K}_x\text{M}_2\text{O}_4$ and (b) $\text{NaMnO}_2\text{-}\beta$.

the A cation located between the layers: the great ability of K^+ to take the trigonal prismatic coordination makes that the octahedral layers adopt similar positions in KNb_3O_8 (Fig. 3b) and $\text{K}_x\text{Ti}_{2-x}\text{M}_x\text{O}_4$ (Fig. 4a) respectively; on the contrary, the introduction of Na^+ leads to a translation of one layer out of two involving fivefold coordination of Na^+ in NaNb_3O_8 (Fig. 3a) and an octahedral coordination in $\text{NaMnO}_2\text{-}\beta$ (Fig. 4b). This ability of sodium to displace the octahedral layer of a lamellar structure with respect to potassium can also be observed by comparing the structures of $\text{K}_3\text{Ti}_5\text{NbO}_{14}$ (Fig. 5a) and $\text{Na}_2\text{Ti}_3\text{O}_7$ (Fig. 5b) which differ one from the other by a translation of $b/2$ of one layer out of two alternately. However, in these latter compounds the K^+ ions adopt a pseudocubic coordination whereas the Na^+ ions exhibit a ninefold and a sevenfold coordination with rather dispersed Na-O distances ranging from 2.23 to 2.93 Å.

In conclusion, the synthesis of the niobate NaNb_3O_8 with an original structure

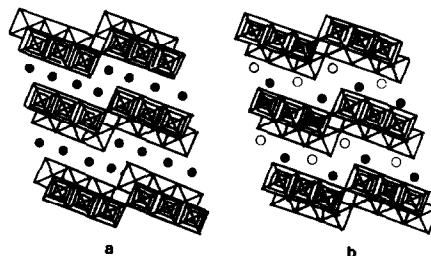


FIG. 5. Structure of (a) $\text{K}_3\text{Ti}_5\text{NbO}_{14}$ and (b) $\text{Na}_2\text{Ti}_3\text{O}_7$.

by soft chemistry methods suggests that other niobates, ANb_3O_8 with univalent cations (Ag^+ , Rb^+ , Cs^+ , Tl^+) or with divalent cations (Sr^{2+} , Ba^{2+} , Pb^{2+}) with related structures should be synthesized by such methods.

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