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A Layer Structure: The Titanoniobate $CsTi_2NbO_7$

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A new oxide, $CsTi_2NbO_7$, with a structure related to that of $KTiNbO_5$ has been prepared and described. This titanoniobate, with orthorhombic symmetry, has the unit-cell dimensions $a = 9.32_6$, $b = 18.41_2$, and $c = 3.79_8$ Å. From the electron diffraction results two space groups, $Pna2_1$ or $Pnam$, are possible. Its structure, which has been studied from powder data, is built up from units of 2 × 3 edge-sharing octahedra; these units share the corners of their octahedra, forming puckered layers. The layers are held together by cesium ions in distorted cubic sites, as in $KTiNbO_5$.

The layer structures of alkali titanates and titanoniobates or titanotantalates which are known at the present time can be considered, if referred to the unit cell, as built up from structural units of $2 \times n$ edge-sharing octahedra. Thus, this is the case in the oxides $A_{1-x}(Ti_{1-x}M_{1+x})O_5$ (*1, 2*), $Na_2Ti_3O_7$ (*3*), and $A_2Ti_4O_9$ (*4, 5*) which are characterized, respectively, by $n = 2$, 3, and 4.

The compounds $A_{1-x}(Ti_{1-x}M_{1+x})O_5$ are, however, quite different from the other titanates, in that the structural units of the two separate sheets are not parallel but are related by a glide plane, "*a*." We describe here a similar structure but one which is built up, like $Na_2Ti_3O_7$, from 2×3 edge-sharing octahedra structural units.

Synthesis and Crystallographic Data of $CsTi_2NbO_7$

$CsTi_2NbO_7$ was prepared from $CsNO_3$, TiO_2, and Nb_2O_5 in a molar ratio of 2 : 4 : 1. The mixture, first slowly heated from 400 to 750°C, was then fired at 950°C in a platinum crucible. Annealings at temperatures ranging from 1000 to 1200°C, for 1 to 24 hr, are necessary to obtain a good crystallization. All attempts to prepare isomorphous compounds $CsTi_2TaO_7$ and ATi_2MO_7 with $A = K$, Rb, Tl, Na and $M = Ta$, Nb were unsuccessful in these experimental conditions. The X-ray powder pattern of $CsTi_2NbO_7$, registered with a Philips goniometer for the Cu*kα* radiation, was indexed in an orthorhombic cell with the following parameters:

$$a = 9.32_6 \text{ Å}, \qquad b = 18.41_2 \text{ Å}, \qquad c = 3{,}79_8 \text{ Å}.$$

The electron diffraction study confirmed these results and showed the systematic absent reflections: $0kl$, $k + l = 2n + 1$ and $h0l$, $h = 2n + 1$. Two space groups are thus possible: $Pna2_1$ and $Pnam$.

The observed density, $d_o = 4.44$, measured by pycnometry in carbon tetrachloride, showed that $Z = 4$ ($d_{calc} = 4.42$).

A Structural Model for AM_3O_7 Oxides

From the comparison of the parameters of $CsTi_2NbO_7$ with those of $A_{1-x}(Ti_{1-x}M_{1+x})O_5$ (*1, 2*) and $Na_2Ti_3O_7$ (*3*),

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the following relationships can be obtained:

$$a_{CsTi_2NbO_7} \simeq a_{Na_2Ti_3O_7};$$

$$c_{CsTi_2NbO_7} \simeq b_{Na_2Ti_3O_7} \simeq b_{KTiNbO_5};$$

$$c_{CsTi_2NbO_7} \simeq c_{KTiNbO_5}.$$

In the two structures, $KTiNbO_5$ and $Na_2Ti_3O_7$, the edge- and corner-sharing octahedra form puckered layers parallel to (001) (Figs. 1a and b). The cells of these two oxides are, however, quite different: $KTiNbO_5$ is orthorhombic ($a = 6.45_9$, $b = 3.79_2$, and $c = 18.47_2$ Å) while $Na_2Ti_3O_7$[1] is monoclinic ($a = 9.13_5$ Å, $b = 3.80_4$ Å, $c = 8.57_1$ Å, $\beta = 101°57$). The stacking of the octahedra along b is the same for the two structures: along this direction the structural units of $2 \times n$ octahedra (Figs. 1c and d) form columns of edge-sharing octahedra (Figs. 1e and f), characterized by a width of n octahedra, and giving a b parameter close to the classical value of 3.8 Å which corresponds to the height of an octahedron. The value of the a parameter is determined by the length of the structural unit of $2 \times n$ octahedra, i.e., by the number n; the two a values are then closely related and can be obtained by the relationship $a_n \sim 2.9(n^2+1)^{1/2}$ Å, where 2.9 Å corresponds to the mean distance between two oxygen atoms. In return, there is no relationship between the c values of these structures. The cohesion of the structure in the c direction is ensured by the alkali cations which hold the sheets $[(TiNb)O_5]^-$ or $[Ti_3O_7]^{2-}$ together. The relative orientations of the latter sheets are quite different in the two structures: two successive $[(TiNb)O_5]^-$ sheets deduce one from the other by a glide plane "a" (Fig. 1a), while two adjacent $[Ti_3O_7]^{2-}$ sheets are related by a single translation, c. The result is a distorted cubic environment for potassium and two kinds of sites for sodium: a ninefold and a sevenfold coordination.

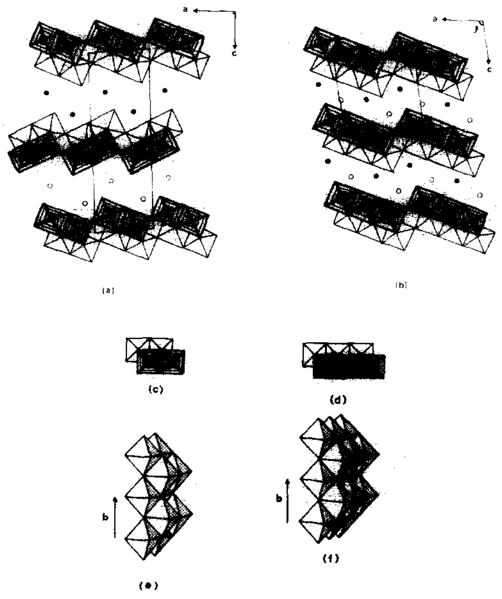

FIG. 1. Idealized drawing in projection of the structures of: (a) $KTiNbO_5$; (b) $Na_2Ti_3O_7$ and of the structural units of $2 \times n$ octahedra; (c) $n = 2$; (d) $n = 3$. These units form columns of edge-sharing octahedra characterized by a width of n octahedra. (e) $n = 2$; (f) $n = 3$.

From the above relationships observed for the parameters of $KTiNbO_5$, $Na_2Ti_3O_7$, and $CsTi_2NbO_7$ a structural model for the latter can be proposed (Fig. 2). The values of the a and c parameters, close to the a and b parameters of $Na_2Ti_3O_7$, indicate that the structure is built up from similar structural units of 2×3 edge-sharing octahedra; along c these units form columns, the width of which is determined by three edge-sharing octahedra (Fig. 1f); along a these units are linked by the corners of their octahedra. The b value, close to the c value of $KTiNbO_5$, and the two possible space groups obtained from electron diffraction indicate that two successive layers are related by a glide plane "a", as in $KTiNbO_5$. The pseudocubic sites between the layers show a geometry close to that of the potassium in $KTiNbO_5$; from the formula they would be fully occupied by the cesium ions.

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[1] The a and c parameters of $Na_2Ti_3O_7$ have been reversed with regard to Ref. (3) in order to allow a better comparison with $KTiNbO_5$.

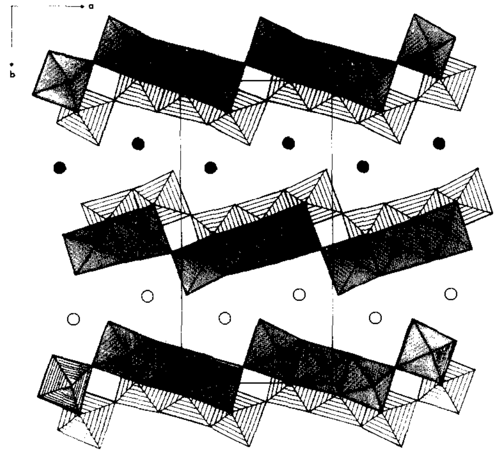

FIG. 2. Structure of $CsTi_2NbO_7$ projected onto (001). $[(Ti_2Nb)O_7]^-$ layers are held together by cesium ions (solid and open circles) in distorted cubic sites as in $KTiNbO_5$.

TABLE I

FRACTIONAL ATOMIC PARAMETERS FOR $CsTi_2NbO_7$[a]

Atom	x	y	z	Distribution
Cs	0.292_1	0.211_7	$\frac{3}{4}$	4 Cs
B_1	0.953_8	0.062_9	$\frac{1}{4}$	(3.2 Ti, 0.8 Nb)
B_2	0.260_0	0.020_9	$\frac{1}{4}$	(3.6 Ti, 0.4 Nb)
B_3	0.619_8	0.115_9	$\frac{1}{4}$	(1.2 Ti, 2.8 Nb)
O_1	0.536_1	0.211_8	$\frac{1}{4}$	4O
O_2	0.817_2	0.141_1	$\frac{1}{4}$	4O
O_3	0.148_0	0.098_2	$\frac{1}{4}$	4O
O_4	0.430_5	0.059_9	$\frac{1}{4}$	4O
O_5	0.228_7	0.498_3	$\frac{1}{4}$	4O
O_6	0.547_8	0.541_3	$\frac{1}{4}$	4O
O_7	0.840_1	0.600_0	$\frac{1}{4}$	4O

[a] Space group *Pnam* (No. 62); all atoms in 4(c); $x, y, \frac{1}{4}$; $\bar{x}, \bar{y}, \frac{3}{4}$; $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{4}$; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{4}$.

Structural Study

In order to confirm this model, the structure was studied from powder data. Sixty-eight observed reflections, i.e., 210 *hkl* registered with Cu$K\alpha$ radiation, were introduced in a structure factors calculation. All the atoms were located in the 4(c) sites of the space group *Pnam*, which is the most symmetrical: they are thus characterized by a special value $z = \pm\frac{1}{4}$. The isotropic thermal agitation parameters were fixed at $B = 1$ Å^2 for all the atoms. The niobium and titanium were first distributed at random over the three types of 4(c) sites. After refinement of the x, y coordinates of the oxygen and metallic atoms, the discrepancy factor R_I calculated on the intensities was lowered to 0.136. On account of the results obtained for the oxides $A_{1-x}(Ti_{1-x}M_{1+x})O_5$, the distribution of the titanium and niobium atoms over the three sorts of sites was then examined. A preferential occupancy of two of the 4(c) sites by the titanium atoms was found, which lowered R_I to 0.074. The final atomic parameters and the distribution of the metallic atoms over the sites respectively noted B_1, B_2, and B_3 are given in Table I. The calculated values of the intensities are in agreement with the experimental values (Table II). The interatomic distances Cs–O and B–O (Table III) are quite compatible with those usually obtained for these types of compounds (*1*, *6*, *7*). The distortion of the octahedra (Fig. 3) is similar to that observed in the compounds $A_{1-x}(Ti_{1-x}Nb_{1+x})O_5$. It is equally worth noting that the titanium atoms are preferentially distributed in the B_1 and B_2 octahedra which share, respectively, six and five edges with the adjacent octahedra, while the B_3 octahedra which share only three edges with their neighbors are preferentially occupied by the niobium atoms.

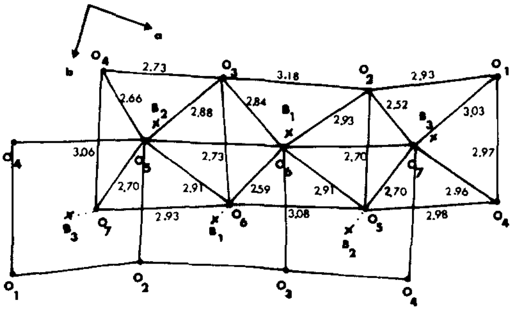

FIG. 3. Positions of oxygens and B atoms in $CsTi_2NbO_7$ showing octahedra distortion.

TABLE II

$CsTi_2NbO_7$: COMPARISON OF OBSERVED AND CALCULATED INTENSITIES

h k l	I_o	I_c	*h k l*	I_o	I_c	*h k l*	I_o	I_c	*h k l*	I_o	I_c
0 2 0	7.22	6.56	2 7 1	0.33	0.31	2 10 1	3.21	3.67	4 12 0	8.60	0.00
1 2 0	3.00	1.27	1 8 1	2.75	0.25	3 9 1		0.13	4 11 1		0.95
1 3 0	24.08	23.14	4 2 1		1.50	6 0 0		0.80	7 4 0		0.34
2 0 0	17.43	17.12	0 0 2	20.12	20.11	6 1 0	3.78	4.44	5 4 2		0.17
0 4 0	2.58	1.63	3 6 1		4.48	4 9 0		0.02	2 13 1		4.38
2 2 0	27.06	10.17	4 3 1		0.03	0 12 0	3.11	1.91	2 10 2		1.98
1 4 0		17.04	0 2 2	3.13	0.11	6 2 0		0.56	3 9 2		0.82
0 1 1	12.03	0.29	4 6 0		1.00	0 11 1		0.17	2 14 0		0.23
2 3 0		10.85	5 1 0		0.03	3 4 2		0.01	7 5 0	5.05	1.48
1 1 1	2.29	1.72	1 1 2		0.01	1 12 0	4.13	0.03	1 1 3		0.08
1 5 0		0.47	3 8 0		0.99	1 11 1		1.56	5 5 2		3.62
1 2 1		0.08	0 10 0		1.70	6 3 0		0.47	5 11 0		0.02
2 4 0	9.25	9.14	2 8 1	6.42	2.32	4 8 1		2.40	7 2 1		0.61
0 3 1	60.36	59.62	1 10 0		1.17	6 4 0	2.29	0.34	1 11 2		0.00
0 6 0	56.42	1.96	0 9 1		2.23	4 0 2		0.26	1 2 3		0.01
3 1 0		10.05	5 3 0	11.34	0.09	5 6 1		0.31	4 8 2	3.44	0.70
1 3 1		44.08	1 3 2		2.23	4 1 2		1.64	0 3 3		2.36
3 2 0	25.30	16.05	3 7 1		3.03	0 8 2		0.01	5 10 1		1.15
2 0 1		9.11	1 9 1		5.51	3 10 1	2.98	0.39	6 9 0		0.08
1 6 0	74.70	37.17	2 0 2	4.70	1.97	2 7 2		2.94	1 14 1	2.07	0.03
2 1 1		28.93	0 4 2		0.18	2 12 0		0.38	7 3 1		0.20
2 5 0		8.16	2 1 2		0.08	2 11 1		0.02	1 3 3		1.95
2 2 1	8.49	8.82	4 5 1		1.39	4 2 2		0.00	2 3 1	3.44	1.31
1 4 1		0.02	4 7 0		0.01	6 1 1	5.85	0.04	1 15 0		0.02
2 3 1	6.77	6.60	5 4 0	3.21	0.26	3 6 2		1.78	3 10 2		1.67
0 5 1		0.07	2 2 2		1.64	6 5 0		0.45	4 12 1		0.40
2 6 0	3.50	3.83	1 4 2		2.76	4 3 2		3.72	7 4 1		0.90
1 5 1	4.98	5.41	2 10 0	3.75	3.37	4 9 1		0.31	2 11 2		0.42
1 7 0		0.05	3 9 0	1.42	1.27	6 2 1	3.55	4.56	2 3 3	2.53	0.32
3 1 1	3.56	3.53	2 3 1	2.98	2.28	5 7 1	2.07	2.66	0 5 3		0.00
3 5 0		0.61	2 9 1	6.77	6.97	1 12 1	0.82	0.93	4 9 2		0.02
4 1 0	19.15	4.22	4 6 1	8.53	1.10	4 4 2	4.57	5.18	0 12 2		1.41
1 6 1		3.11	5 1 1		0.08	6 3 1	10.89	0.31	6 10 0	2.70	0.00
0 8 0		0.01	5 5 0		5.66	1 13 0		0.34	1 5 3		0.18
2 5 1		3.18	3 8 1		2.19	2 8 2		0.65	5 7 2		1.33
2 7 0		8.36	1 5 2		0.05	3 7 2		1.18	2 15 0		0.55
4 2 0		0.01	1 11 0	7.08	0.00	5 9 0		0.38	5 12 0		0.46
3 3 1	3.90	2.26	5 2 1		5.23	1 9 2		2.76	1 12 2	0.41	0.00
1 8 0		1.32	2 4 2		2.41	3 11 1		0.07	5 11 1		0.01
3 6 0	15.94	4.51	4 8 0		1.02	6 4 1		3.63	2 4 3		0.07
4 3 0		9.93	5 3 1	3.21	0.25	2 12 1	10.08	2.05	6 3 2		0.30
0 7 1		0.74	0 6 2		0.44	4 11 0		1.82	4 2 3	3.90	0.22
3 4 1	7.90	8.19	3 1 2		2.61	2 13 0		0.88	4 11 2		1.65
2 6 1		0.13	3 2 2	18.35	4.64	5 8 1		2.74	7 8 1		1.12
1 7 1	7.34	6.81	5 6 0		0.22	4 10 1		0.24	2 13 2		0.74
4 4 0	12.84	12.18	1 6 2		9.94	4 6 2	2.47	0.46	1 8 3		0.02
3 5 1	16.17	6.55	2 5 2		2.25	5 1 2		0.02	4 14 1	2.78	1.43
3 7 0		2.35	4 7 1		2.97	0 13 1		0.50	8 3 1		0.00
1 9 0		5.74	3 1 0		2.46	3 8 2		0.56	3 6 3		0.59
4 0 1	4.36	3.51	2 11 0	2.98	0.66	0 10 2		0.91	4 3 3		0.01
4 1 1	5.40	4.55	5 4 1		1.37	7 2 0		0.01	6 7 2		0.03
4 5 0		0.55	3 3 2		0.30				1 16 1		0.28
									3 15 1		0.05
									6 12 0		0.00
									6 11 1		0.14

TABLE III

INTERATOMIC DISTANCES IN $CsTi_2NbO_7$[a]

	Length (Å)		Length (Å)		Length (Å)
$Cs–O_1$	2.97	$B_2–O_7$	2.35	$O_3–O_4$	2.73
$Cs–O_1$	3.36	$B_3–O_1$	1.93	$O_3–O_5$	2.88
$Cs–O_2$	3.32	$B_3–O_2$	1.90	$O_3–O_6$	2.73
$Cs–O_3$	3.13	$B_3–O_4$	2.05	$O_3–O_6$	2.84
$B_1–O_2$	1.92	$B_3–O_5$	2.33	$O_4–O_4$	3.18
$B_1–O_3$	1.94	$B_2–O_7$	1.96	$O_4–O_5$	2.98
$B_1–O_5$	2.34	$O_1–O_2$	2.93	$O_4–O_5$	2.66
$B_1–O_6$	2.11	$O_1–O_4$	2.97	$O_4–O_7$	2.96
$B_1–O_6$	1.94	$O_1–O_7$	3.03	$O_4–O_7$	3.06
$B_2–O_3$	1.77	$O_2–O_3$	3.18	$O_5–O_6$	3.08
$B_2–O_4$	1.74	$O_2–O_5$	2.70	$O_5–O_6$	2.91
$B_2–O_5$	1.95	$O_2–O_6$	2.93	$O_5–O_7$	2.70
$B_2–O_6$	2.28	$O_2–O_7$	2.52	$O_6–O_6$	2.59
				$O_6–O_7$	2.93

[a] Ti, Nb distributions over B_1, B_2, and B_3 sites are given in Table I.

This partial order, which has already been found in the $A_{1-x}(Ti_{1-x}M_{1+x})O_5$, probably results from the repulsion between metallic atoms: B_1 and B_2 octahedra, more rigid, have their metallic atoms submitted to a greater repulsion due to their more numerous neighbors. They should preferentially accommodate atoms of smaller size, which can be repulsed toward the outside of the sheets without distorting the oxygen framework.

Conclusion

A new oxide has been obtained, which presents analogies with the two layer structures $Na_2Ti_3O_7$ and $KTiNbO_5$. There is the possibility of intergrowth of $Na_2Ti_3O_7$ and $CsTi_2NbO_7$, corresponding to successive layers of "Ti_3O_7" and "Ti_2NbO_7" held together by Na^+ planes or Cs^+ planes. On the other hand, regarding the similar disposition of the layers for $KTiNbO_5$ and $CsTi_2NbO_7$, let us think that $CsTi_2NbO_7$ could be considered as the member $n = 2$ of a series ATi_nNbO_{2n+3} where $KTiNbO_5$ is $n = 1$. The synthesis of the members $n \geq 3$ is, however, not very likely, due to the decrease among A^+ with regard to the octahedral layers, involving a decrease of the cohesion of the structure; the term $n = 3$, ATi_3NbO_9 has not been obtained. This composition is generally characterized by a tunnel structure (*1–8*). However, the existence of $A_{1+x}M_{n+1}O_{2n+3}$ oxides with greater amounts of A^+ can be considered. The relation with the tunnel structure $A_2Ti_6O_{13}$ (*6*), which is built up from the same structural units as $CsTi_2NbO_7$, must be noted. The possibility of the existence of more complex frameworks related to these structures should be considered.

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