JOURNAL OF SOLID STATE CHEMISTRY 77, 299–305 (1988)

Two Forms of Sodium Titanium(III) Diphosphate: α-$NaTiP_2O_7$ Closely Related to β-Cristobalite and β-$NaTiP_2O_7$ Isotypic with $NaFeP_2O_7$

A. LECLAIRE, A. BENMOUSSA, M. M. BOREL, A. GRANDIN, AND B. RAVEAU

Laboratoire de Cristallographie et Sciences des Matériaux, CRISMAT, ISMRa, Campus 2, Boulevard du Maréchal Juin, 14032 Caen Cedex, France

Received April 25, 1988; in revised form July 5, 1988

The structures of two new forms of a titanium(III) phosphate $NaTiP_2O_7$ have been determined. One of them, β-$NaTiP_2O_7$ [a = 7.394(1) Å, b = 7.936(3) Å, c = 9.726(3) Å, β = 111.85(2)° $P2_1/c$], is isotypic with $NaFeP_2O_7$ which has been previously described. The other form, α-$NaTiP_2O_7$ [a = 8.697(1) Å, b = 5.239(7) Å, c = 13.293(3) Å, β = 116.54(1)°, $P2_1/c$], is found to be closely related to the structure of β-cristobalite and of carnegieite and is described as a "pseudo-hexagonal" framework characterized by intersecting tunnels. © 1988 Academic Press, Inc.

Introduction

The association of a transition element with a covalent element such as phosphorus or silicon in oxides is an interesting direction of research which allows opened structures to be realized. In addition to the family of phosphate tungsten bronzes synthesized in Caen these last 10 years (*1*), several systems involving molybdenum have also been explored which lead to the formation of mixed frameworks built up from corner-sharing MoO_6 octahedra and PO_4 and/or SiO_4 tetrahedra (*2–11*). In the latter systems molybdenum takes various oxidation states, VI, V, IV, III. In this respect titanium should be an interesting candidate owing to its two current oxidation states IV, III. Moreover, this element participates in the famous nasicon structure $Na_xTi_2P_3O_{12}$, well known for its ion-exchange properties and for its ionic conductivity (*12–14*). Recently, it was shown that Ti(III) could replace Mo(III) in an interesting tunnel structure leading to the oxide $KMo_2TiP_6Si_2O_{25}$ (*4*). However, titanium does not seem to be involved in numerous mixed frameworks in spite of the ability of TiO_6 octahedra to distort. For this reason the system Ti–Na–P–O was explored. The present work deals with the crystal structure of two isomeric diphosphates α- and β-$NaTiP_2O_7$.

Synthesis

The preparations were performed in two steps. First, $(NH_4)_2HPO_4$, TiO_2, and Na_2CO_3 were mixed in an agate mortar in the molecular ratio to obtain the stoichiometry $NaTi_{0.75}P_2O_7$ and heated at 675 K to decompose the sodium carbonate and the ammonium phosphate. The resulting mixture was then added to the required amount of titanium (0.25) and heated in evacuated silica ampoules for a week at 1373 K. In the mix-

0022-4596/88 $3.00

TABLE I

ATOMIC AND THERMAL PARAMETERS OF α-$NaTiP_2O_7$

Atomic parameters[a]

Atom	x	y	z	B (Å^2)
Ti	0.26328(9)	0.2371(2)	0.02956(6)	0.52(1)
P1	0.1667(1)	0.7550(3)	0.14509(8)	0.54(2)
P2	0.6839(1)	0.2771(2)	0.11568(9)	0.60(2)
Na	0.4473(3)	0.2704(5)	0.3103(2)	1.58(5)
O1	0.0180(4)	0.257(1)	−0.0581(2)	1.00(6)
O2	0.5218(4)	0.2267(8)	0.1304(3)	0.90(6)
O3	0.2531(4)	0.0114(7)	0.1533(3)	0.86(7)
O4	0.2947(5)	−0.0954(7)	−0.0364(3)	1.09(8)
O5	0.3067(4)	0.4436(7)	−0.0878(3)	0.90(7)
O6	0.2729(4)	0.5395(6)	0.1335(3)	0.85(7)
O7	0.1610(4)	0.7180(7)	0.2634(3)	0.77(6)

Thermal parameters[b]

Name	β (1,1)	β (2,2)	β (3,3)	β (1,2)	β (1,3)	β (2,3)
Ti	0.00225(7)	0.0048(2)	0.00092(3)	0.0001(3)	0.00139(7)	−0.0004(2)
P1	0.0023(1)	0.0051(3)	0.00093(4)	0.0013(5)	0.0014(1)	0.0003(3)
P2	0.0028(1)	0.0059(3)	0.00095(5)	−0.0001(4)	0.0017(1)	0.0002(3)
Na	0.0074(3)	0.0113(7)	0.0033(1)	−0.002(1)	0.0054(3)	−0.0011(7)
O1	0.0029(3)	0.012(1)	0.0015(2)	0.002(2)	0.0013(4)	−0.002(1)
O2	0.0027(3)	0.011(1)	0.0015(2)	0.001(1)	0.0020(4)	0.0007(8)
O3	0.0052(4)	0.0064(9)	0.0014(2)	−0.002(1)	0.0032(5)	−0.0011(7)
O4	0.0071(5)	0.009(1)	0.0015(2)	0.002(1)	0.0047(5)	−0.0022(8)
O5	0.0053(5)	0.0057(9)	0.0017(2)	−0.001(1)	0.0035(5)	0.0013(7)
O6	0.0046(4)	0.0051(9)	0.0017(2)	0.004(1)	0.0028(5)	−0.0002(7)
O7	0.0030(3)	0.010(1)	0.0012(1)	−0.000(1)	0.0025(4)	0.0008(7)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(\frac{4}{3}) * [a^2 * \beta(1,1) + b^2 * \beta(2,2) + c^2 * \beta(3,3) + ab(\cos\gamma) * \beta(1,2) + ac(\cos\beta) * \beta(1,3) + bc(\cos\alpha) * \beta(2,3)]$.

[b] The form of the anisotropic displacement parameter is: $\exp[-(\beta(1,1) * h^2 + \beta(2,2) * k^2 + \beta(3,3) * l^2 + \beta(1,2) * hk + \beta(1,3) * hl + \beta(2,3) * kl)]$.

ture two different forms of single crystals have been isolated. We called them respectively α and β forms.

Determination of the Structure

α-$NaTiP_2O_7$

A blue 0.072 × 0.072 × 0.048-mm single crystal was chosen for the X-ray study. The Laue patterns showed monoclinic symmetry ($2/m$). The cell parameters determined by diffractometric techniques at 294 K with a least-squares refinement based on 25 reflections are: $a = 8.697(1)$, $b = 5.2397(7)$, $c = 13.293(3)$ Å, $\beta = 116.54(1)°$, with $Z = 4$ formula units $NaTiP_2O_7$. The systematic absences led to the $P2_1/c$ space group. Data were collected on a CAD4 Enraf–Nonius diffractometer with Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å) isolated with a graphite monochromator. The intensities were measured up to $\theta = 45°$ with a $\omega - \frac{2}{3}\theta$ scan of $(1.20 + 0.35 \tan\theta)°$ and a counter slit aperture of

TABLE II

ATOMIC AND THERMAL PARAMETERS OF β-$NaTiP_2O_7$

Atomic parameters[a]

Atom	x	y	z	B (Å^2)
Ti	0.26076(9)	0.00861(8)	0.24891(7)	0.391(9)
P1	0.0719(1)	0.2547(1)	0.4556(1)	0.39(1)
P2	−0.3269(1)	0.2127(1)	0.4547(1)	0.43(1)
Na	0.2841(3)	0.4788(3)	0.2918(3)	1.91(5)
O1	0.5355(4)	0.0863(4)	0.3529(3)	0.75(5)
O2	0.3063(4)	−0.2014(4)	0.3849(3)	0.78(5)
O3	0.1755(4)	0.1357(4)	0.3917(3)	0.94(5)
O4	−0.0130(4)	−0.0838(4)	0.1343(3)	0.69(5)
O5	0.1854(4)	0.2159(4)	0.1192(3)	0.86(5)
O6	0.3685(4)	−0.1084(4)	0.1024(3)	0.72(5)
O7	−0.1249(4)	0.1566(4)	0.4405(3)	0.69(5)

Thermal parameters[b]

Name	β (1,1)	β (2,2)	β (3,3)	β (1,2)	β (1,3)	β (2,3)
Ti	0.00220(8)	0.00199(7)	0.00086(4)	−0.0000(2)	0.00125(9)	−0.0000(1)
P1	0.0022(1)	0.0018(1)	0.00098(7)	0.0001(2)	0.0013(2)	−0.0002(2)
P2	0.0022(1)	0.0022(1)	0.00098(7)	−0.0005(2)	0.0012(2)	0.0002(2)
Na	0.0080(4)	0.0101(4)	0.0062(2)	0.0016(6)	0.0087(5)	0.0065(5)
O1	0.0032(4)	0.0035(4)	0.0021(3)	−0.0021(6)	0.0011(5)	−0.0024(5)
O2	0.0057(5)	0.0034(4)	0.0013(2)	−0.0002(7)	0.0022(5)	0.0007(5)
O3	0.0055(5)	0.0044(4)	0.0026(3)	0.0028(7)	0.0045(6)	−0.0009(5)
O4	0.0036(4)	0.0029(4)	0.0021(2)	−0.0008(6)	0.0019(5)	−0.0018(5)
O5	0.0053(5)	0.0034(4)	0.0016(2)	−0.0004(7)	0.0007(5)	0.0011(5)
O6	0.0039(4)	0.0032(4)	0.0020(3)	−0.0018(6)	0.0024(5)	−0.0028(5)
O7	0.0027(4)	0.0027(4)	0.0029(3)	0.0007(6)	0.0029(6)	0.0003(5)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(\frac{4}{3}) * [a^2 * \beta(1,1) + b^2 * \beta(2,2) + c^2 * \beta(3,3) + ab(\cos \gamma) * \beta(1,2) + ac(\cos \beta) * \beta(1,3) + bc(\cos \alpha) * \beta(2,3)]$.

[b] The form of the anisotropic displacement parameter is: $\exp[-(\beta(1,1) * h^2 + \beta(2,2) * k^2 + \beta(3,3) * l^2 + \beta(1,2) * hk + \beta(1,3) * hl + \beta(2,3) * kl)]$.

(1.20 + tan θ) mm, all determined after a study of some reflections in the $\omega - \theta$ plan. A periodic control of three reflections verified the stability of the sample. The 1085 reflections with $I \geq 3\sigma(I)$ were corrected for Lorentz and polarization effect; no absorption corrections were performed.

The atomic coordinates were determined by the heavy atom method. Scattering factors for Ti, P, Na, and O and their anomalous dispersion were taken from the "International Tables for X-Ray Crystallography" (*15*). Refinement of the atomic coordinates and their anisotropic thermal motion led to $R = 0.034$, $R_w = 0.038$, and to the atomic parameters of Table I.

β-$NaTiP_2O_7$

A blue 0.120 × 0.096 × 0.048-mm single crystal was chosen. The Laue patterns showed monoclinic symmetry ($2/m$). The cell parameters determined as above are

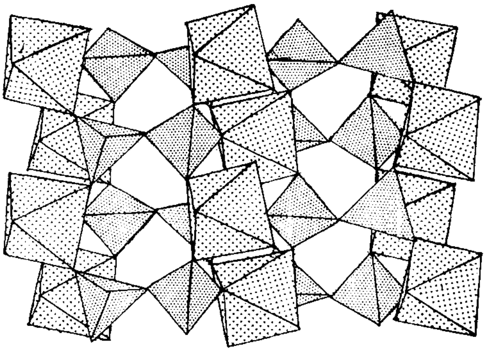

FIG. 1. Projection of the structure of α-$NaTiP_2O_7$ along **a**.

$a = 7.394(1)$, $b = 7.936(3)$, $c = 9.726(3)$ Å, $\beta = 111.85(2)°$, with $Z = 4$ formula units $NaTiP_2O_7$. The systematic absences led to the $P2_1/c$ space group. The data collection was performed as above but with a $\omega - \frac{3}{4}\theta$ scan of $(1.09 + 0.35 \tan \theta)°$ and a counter slit aperture of $(1 + \tan \theta)$ mm. Refinement of the atomic coordinates and their anisotropic thermal motion with 1756 reflections with $I \geq 3\sigma(I)$, led to $R = 0.044$ and $R_w = 0.054$, and to the atomic parameters of Table II.

Description of Structures and Discussion

Both structures are built up of TiO_6 octahedra sharing their corners with diphosphate P_2O_7 groups (Figs. 1 and 2), forming an alternated stacking of octahedral layers and phosphate layers parallel to (001).

In both phosphates, the PO_4 tetrahedra present the usual features observed in several diphosphate compounds: one observes one long P–O distance corresponding to the bridging oxygen of the P_2O_7 group and three shorter P–O bonds corresponding to the oxygen atoms which are shared with the TiO_6 octahedron (Tables III and IV). The configuration of the P_2O_7 group is different in the two structures: it is almost eclipsed in β-$NaTiP_2O_7$, whereas it is really staggered in α-$NaTiP_2O_7$. The TiO_6 octahedron is slightly distorted in both oxides, with a greater distortion in the α form than in the β one (Tables V and VI). The sums of the bond strengths calculated with Zachariasen's curve (*16*) lead to titanium valencies of 3.19 and 3.09 for α- and β-$NaTiP_2O_7$, respectively. These calculations are quite in agreement with the oxidation state III of titanium in this oxide. In those oxides the sodium ions are located in cages, with Na–O distances ranging from 2.42 to 3.09 (Table VII and VIII).

TABLE III

DISTANCES (Å) AND ANGLES (°) IN THE PO_4 TETRAHEDRA OF α-$NaTiP_2O_7$

P1	$O1^i$	$O3^{ii}$	O6	O7
$O1^i$	1.503(3)	2.545(5)	2.504(5)	2.467(4)
$O3^{ii}$	114.7(2)	1.519(4)	2.501(5)	2.488(6)
O6	112.4(2)	111.3(2)	1.510(4)	2.510(6)
O7	105.0(2)	105.5(2)	107.3(2)	1.606(4)
P2	O2	$O4^{iii}$	$O5^{iv}$	$O7^v$
O2	1.531(4)	2.522(6)	2.507(6)	2.479(4)
$O4^{iii}$	113.1(2)	1.492(5)	2.525(5)	2.465(5)
$O5^{iv}$	110.5(2)	113.9(2)	1.521(4)	2.534(5)
$O7^v$	104.5(2)	105.7(2)	108.5(2)	1.600(3)

Note. See Table VIII for symmetry code.

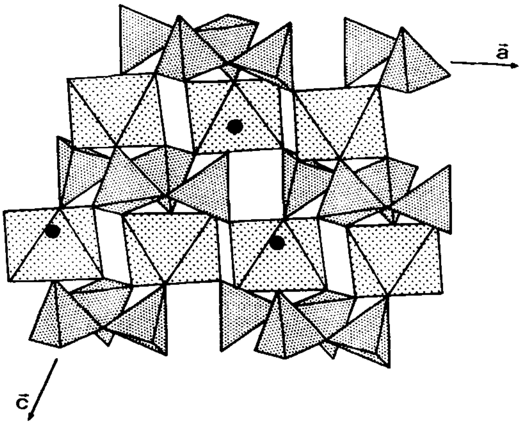

FIG. 2. Projection of the structure of β-$NaTiP_2O_7$ along **b**.

TABLE IV

DISTANCES (Å) AND ANGLES (°) IN THE PO_4 TETRAHEDRA OF β-$NaTiP_2O_7$

P1	O3	O4^{ix}	O5^{x}	O7
O3	1.490(4)	2.498(4)	2.484(4)	2.444(5)
O4^{ix}	112.1(2)	1.521(3)	2.542(4)	2.523(4)
O5^{x}	115.5(2)	113.7(2)	1.516(3)	2.518(3)
O7	104.1(2)	107.4(1)	107.4(2)	1.609(3)
P2	**O1^{xi}**	**O2^{xii}**	**O6^{xiii}**	**O7**
O1^{xi}	1.508(3)	2.547(4)	2.517(4)	2.392(4)
O2^{xii}	114.9(2)	1.513(3)	2.498(4)	2.551(5)
O6^{xiii}	112.8(1)	111.3(2)	1.514(3)	2.518(4)
O7	100.4(2)	109.3(2)	107.2(2)	1.613(3)

Note. See Table VIII for symmetry code.

TABLE VI

DISTANCES (Å) AND ANGLES (°) IN THE TiO_6 OCTAHEDRON OF β-$NaTiP_2O_7$

Ti	O1	O2	O3	O4	O5	O6
O1	2.000(3)	2.928(4)	2.851(5)	4.047(3)	2.923(3)	2.758(4)
O2	91.8(1)	2.076(3)	2.854(4)	2.846(3)	4.089(4)	3.040(4)
O3	91.0(1)	88.9(1)	1.998(4)	2.941(4)	2.752(5)	4.085(5)
O4	175.7(1)	87.3(1)	93.2(1)	2.049(3)	2.827(4)	2.957(4)
O5	93.3(1)	173.2(1)	86.4(1)	88.0(1)	2.021(3)	2.941(4)
O6	84.7(1)	93.7(1)	175.0(1)	91.2(1)	91.3(1)	2.091(3)

Although they are built from the same units and they have the same composition the two forms are very different and do not exhibit very close relationships. The P . . . P bonds of each P_2O_7 group are indeed perpendicular to the (001) octahedral or tetrahedral layers in the α form (Fig. 1), whereas they are parallel to this plane in the β form (Fig. 2). This difference comes from the fact that a diphosphate group shares two corners with the same octahedron in β-$NaTiP_2O_7$ forming $[TiP_2O_{11}]$ units (Fig. 3), whereas a P_2O_7 group shares only one corner with the same octahedron in the α form.

It results that an octahedron is linked to five P_2O_7 groups in the β form, against six P_2O_7 groups in the α form. The structure of β-$NaTiP_2O_7$ is very similar to those described for $NaFeP_2O_7$ (*17*) and $NaMoP_2O_7$ (*9*). The frameworks are approximately the same, except that the TiO_6 octahedra seem to be slightly more distorted than the MoO_6 and FeO_6 octahedra. Thus this structure, which is also related to the $KMoP_2O_7$ (*21*) structure, will not be described further here.

TABLE V

DISTANCES (Å) AND ANGLES (°) IN THE TiO_6 OCTAHEDRON OF α-$NaTiP_2O_7$

Ti	O1	O2	O3	O4	O5	O6
O1	1.923(3)	3.961(4)	2.932(4)	2.945(6)	2.881(6)	2.922(5)
O2	176.5(2)	2.039(3)	2.731(6)	2.783(5)	2.890(4)	2.730(5)
O3	94.8(2)	83.6(2)	2.059(4)	2.760(6)	4.116(6)	2.792(5)
O4	96.5(2)	86.5(2)	85.1(2)	2.023(4)	2.918(5)	4.072(6)
O5	92.4(2)	89.4(2)	172.2(2)	91.0(2)	2.067(4)	3.124(6)
O6	93.7(2)	83.0(2)	84.9(2)	166.2(1)	97.8(2)	2.079(4)

To the contrary, α-$NaTiP_2O_7$ presents an original and very simple framework. This host lattice is in fact closely related to the tetrahedral frameworks of β-cristobalite (*18, 22*) and of carnegieite $NaAlSiO_4$ (*19*). The projection of a double layer of octahedra and diphosphate groups onto the (001) plane (Fig. 4a) shows the pseudo-hexagonal character of this structure similar to that observed for the projection onto the (111) plane of the pure tetrahedral structure of β-cristobalite (Fig. 4b). This pseudo-hexagonal character is also shown by the fact that the view of the structure of α-$NaTiP_2O_7$ is very similar along the three directions [010], [110], and [$\bar{1}$10]. The pseudo-hexagonal character results from the fact that the

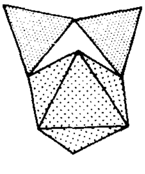

FIG. 3. TiP_2O_{11} units in β-$NaTiP_2O_7$.

TABLE VII

DISTANCES (Å) Na–O IN THE NaO_9 POLYHEDRON OF α-$NaTiP_2O_7$

Na–O2 = 2.752(5)
–O2^{vi} = 2.936(5)
–O2^{vii} = 2.494(5)
–O3 = 2.429(4)
–O3^{v} = 2.737(5)
–O4^{v} = 2.921(4)
–O5^{viii} = 2.463(5)
–O6 = 2.574(4)
–O6^{vi} = 2.514(4)

Note. See Table VIII for symmetry code.

TABLE VIII

DISTANCES (Å) NaO_8 POLYHEDRON OF β-$NaTiP_2O_7$

Na–O1^{v} = 2.426(4)
–O2^{ii} = 2.680(4)
–O3 = 3.096(4)
–O4^{ix} = 2.420(4)
–O5 = 2.606(4)
–O6^{v} = 2.484(3)
–O6^{x} = 3.028(4)
–O7^{ix} = 2.550(3)

Note: Symmetry code: *i*, $-x, 1-y, -z$; ii, $x, 1+y, z$; iii, $1-x, -y, -z$; iv, $1-x, 1-y, -z$; v, $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; vi, $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; vii, $1-x, 1-y, 1-z$; viii, $x, \frac{1}{2}-y, z-\frac{1}{2}$; ix, $-x, \frac{1}{2}+y, \frac{1}{2}-z$; x, $x, \frac{1}{2}-y, \frac{1}{2}+z$; xi, $1-x, y, z$; xii, $-x, -y, 1-z$; xiii, $-x, y-\frac{1}{2}, \frac{1}{2}-z$.

P–O–P angle is less than 180° in diphosphate groups whereas the Si–O–Si equals 180°. One indeed observed hexagonal tunnels running along these three directions and which are formed of hexagonal rings built up of two diphosphate groups and two TiO_6 octahedra (Fig. 5a). In the same way β-cristobalite and carnegieite exhibit a structure with intersecting hexagonal tunnels as shown, for instance, from the $[1\bar{1}0]$ direction of β-cristobalite (Fig. 5b). Thus β-cristoballite can be described as built of identical $[Si_2O_4]_\infty$ layers of tetrahedra joined together by corner sharing. In α-$NaTiP_2O_7$, the rings which form the hexagonal tunnels are formed of $[P_2O_4]_\infty$ infinite layers (Figs. 5a and 1) parallel to (001), similar to the $[Si_2O_4]_\infty$ infinite layers parallel to (111) shown in Fig. 5b for β-cristobalite. The α-$NaTiP_2O_7$ structure is related to that of β-cristobalite in the following way. Every

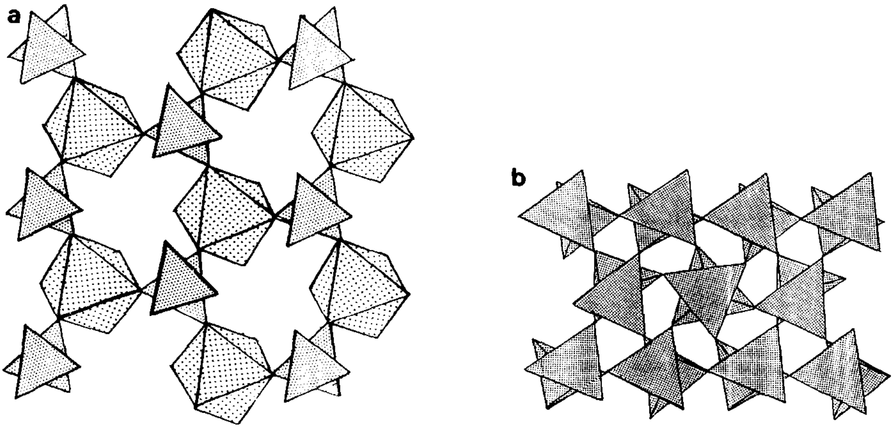

FIG. 4. (a) Projection of a double layer of TiO_6 and P_2O_7 onto (001) in α-$NaTiP_2O_7$. (b) Projection of the β-cristoballite structure onto (111).

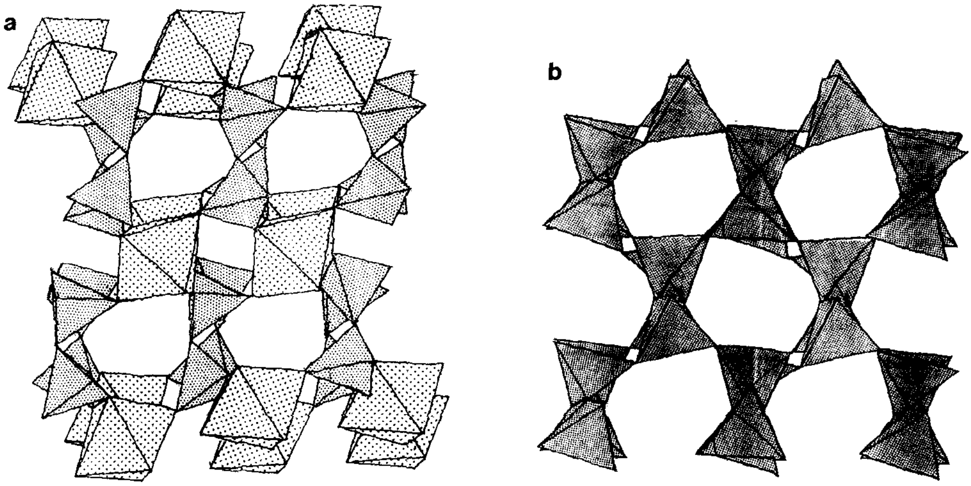

FIG. 5. (a) Projection of the structure of α-$NaTiP_2O_7$ along $[\bar{1}10]$. (b) Projection of the β-cristoballite structure along $[1\bar{1}0]$.

other layer of tetrahedra in β-cristobalite is replaced by a layer of $[TiO_3]_\infty$ octahedra.

The resulting host structure can then be described as a stacking of $[P_2O_4]_\infty$ layers of tetrahedra of cristobalite type and $[TiO_3]_\infty$ layers of octahedra. It must be pointed out that such a description shows that there is a bidimensional accord between the (001) plane of α-$NaTiP_2O_7$ and the (111) plane of β-cristobalite so that intergrowths between both structures similar to those observed between $A_3M_8O_{21}$ and $Ba_8Nb_6Si_9O_{26}$ should be possible (*20*).

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