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Hexabarium Titanium(IV) Tetraniobate(V); a Rietveld Refinement of Neutron Powder Diffraction Data

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Abstract. $Ba_6TiNb_4O_{18}$, $M_r = 1531 \cdot 6$, rhombohedral, $R\bar{3}m$, $a = 5 \cdot 7852$ (1), $c = 42 \cdot 4886 \cdot (3)$ Å, $V = 1231 \cdot 52$ (2) Å^3, $Z = 3$, $D_x = 6 \cdot 195$ (1) Mg m^{-3}, room temperature. The structure has been refined by Rietveld analysis of powder neutron diffraction data ($\lambda = 1 \cdot 909$ Å, $R_{wp} = 7 \cdot 80\%$) for 216 reflections. The structure is of rhombohedral 18L type. BaO_3 layers are stacked $(hhcccc)_3$, resulting in a perovskite lattice with a shear plane every sixth layer. In the shear plane the octahedra are not filled. Ti and Nb ions have an octahedral coordination of oxygen atoms, and the octahedra share corners.

Introduction. The preparation, crystal structure determination and solubility test in water at elevated temperatures and pressures form part of a research program to investigate compounds with perovskite or related structures for their properties as a host lattice for nuclear waste. $Ba_6TiNb_4O_{18}$ was reported to adopt a rhombohedral 18L lattice (Schittenhelm & Kemmler-Sack, 1980), but the structure was not solved.

Experimental. AR starting materials $BaCO_3$, TiO_2 and Nb_2O_5 thoroughly mixed in an agate mortar in the appropriate ratio; mixture heated in Al_2O_3 crucible at 1270 K for 1 d and after grinding product was sealed in a platinum capsule and heated at 1570 K for one week.

X-ray powder diffraction pattern obtained with Philips PW 1050 diffractometer; all lines indexed with rhombohedral unit cell; in accordance with electron diffraction data (Siemens Elmiskop 102 electron microscope, double tilt, lift cartridge, 100 kV). Since no single crystals available, Rietveld's (1969) method used for refinement of neutron powder diffraction data; neutron powder profile recorded (293 K, atmospheric pressure) on D1A diffractometer of the Institut Laue–Langevin in Grenoble; $6 < 2\theta < 157 \cdot 9°$ in steps of 0.05°; sample (25 g) contained in thin-walled vanadium can ($\varnothing$ 18 mm); neutron wavelength 1.909 Å. No precautions to avoid preferred orientation. No absorption correction. Background determined by extrapolation between those parts in diagram containing no contribution or, for higher values of 2θ, only a small contribution from reflections. The stability in water and 10% NaCl solution at 573 K and 0.2 GPa for 1 week was tested: $Ba_6TiNb_4O_{18}$ was stable under these conditions. Trial model was deduced from known structure of $Ba_5\square Ta_4O_{15}$ ($hhccc$). This structure is built up from BaO_3 layers with Ta ions between them, but vacancies between the hh layers. In the trial model the $hhccc$ stacking of $Ba_5\square Ta_4O_{15}$ is combined with a sixth layer giving the rhombohedral $(hhcccc)_3$ structure, space group $R\bar{3}m$ (No. 166): Ba(1), Ba(2), Ba(3), Nb(1), Nb(2) on 6(c) sites; Ti on 3(b) site; O(1), O(2) and O(3) on 18(h) sites. 30 parameters in refinement: a scale factor, three halfwidth parameters defining Gaussian-like shape of reflections, counter zero error, preferred-orientation parameter (along [001]), unit-cell parameters, atomic positional parameters, isotropic thermal parameters, asymmetry parameter and three occupation numbers with a constraint forcing the formula to $Ba_3TiNb_4O_{18}$. In the final refinement it was necessary to introduce Ti and Nb on the octahedral positions. No significant occupation was found at the octahedral position at 0,0,0. Coherent scattering lengths: Ba 5·25, Ti −3·438, Nb 7·054, O 5·805 fm (Koester, Rauch, Herkens & Schroeder, 1981). The Rietveld (1969) program minimizes the function $\chi^2 = \sum_i w_i [y_i(\text{obs.}) - (1/c)y_i(\text{calc.})]^2$, where $y_i(\text{obs.})$ and $y_i(\text{calc.})$ are observed and calculated data points, w_i is statistical weight $[1/y_i(\text{obs.})]$ allotted to each data point and c is the scale factor; $R_{wp} = 100[\sum w_i | y_i(\text{obs.}) - (1/c)y_i(\text{calc.}) |^2 / \sum w_i | y_i(\text{obs.}) |^2]^{1/2} = 7 \cdot 80\%$, compared with 7·65% expected on purely statistical grounds.

$\Delta/\sigma < 0.3$ in final cycle. E.s.d.'s calculated according to the original Rietveld formulation.*

Discussion. Atomic parameters are given in Table 1, atomic distances in Table 2. The agreement between the observed and calculated profile of the data is shown in Fig. 1. In Fig. 2(a) the structure of $Ba_6Ti\square Nb_4O_{18}$ is given. This can be explained as follows: when in a cubic perovskite, with layer stacking c, after every sixth BaO_3 layer a shear plane occurs in $(111)_c$ with a shear vector $1/3[101]_c$ the result is a layer stacking $(hhcccc)_3$. In the structure the octahedra in the shear plane are not filled.

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*The numbered intensity of each measured point on the profile has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42588 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The small Nb^{5+} and Ti^{4+} ions, radii 0.64 and 0.60 Å respectively (Shannon, 1976), are not statistically distributed over the other octahedra. Oct.(1), near the vacancy, is mainly occupied by Nb^{5+}, 94%, oct.(2) is occupied by 72% Nb^{5+} and oct.(3) by 69% Nb^{5+}. This corresponds to an almost equal distribution of Ti and Nb over oct.(1) and oct.(2).

The vacancy causes considerable distortion about O(3), the position of greatest valency imbalance. The deviations from the ideal close-packed model are: drastic shortening of the Nb(1)—O(3) distance and short Ba(2)—O(3) and Ba(3)—O(3) distances. The distortion of oct.(2) is also considerable as in most of the similar Nb^{5+} compounds.

Table 1. *Fractional atomic coordinates, isotropic thermal parameters (Å^2) and occupations for $Ba_6TiNb_4O_{18}$ at room temperature*

	$x (= -y)$	z	$B(\text{Å}^2)$	n (%)
Ba(1)	0	0.1391 (1)	0.60 (6)	100
Ba(2)	0	0.3134 (1)	0.72 (6)	100
Ba(3)	0	0.4144 (1)	0.74 (7)	100
Ti(1)	0	0.0512 (1)	0.36 (2)	6.3 (2)
Nb(1)	0	0.0512 (1)	0.36 (2)	93.7 (2)
Ti(2)	0	0.2235 (1)	0.36 (2)	28.2 (3)
Nb(2)	0	0.2235 (1)	0.36 (2)	71.8 (3)
Ti(3)	0	0.5	0.36 (2)	30.7 (5)
Nb(3)	0	0.5	0.36 (2)	69.3 (5)
O(1)	0.4994 (3)	0.13993 (4)	0.64 (3)	100
O(2)	0.5030 (2)	0.30201 (3)	0.80 (3)	100
O(3)	0.4968 (2)	0.41950 (4)	0.60 (3)	100

Table 2. *Atomic distances (Å) at room temperature and coordination numbers*

a indicates equilateral distances.

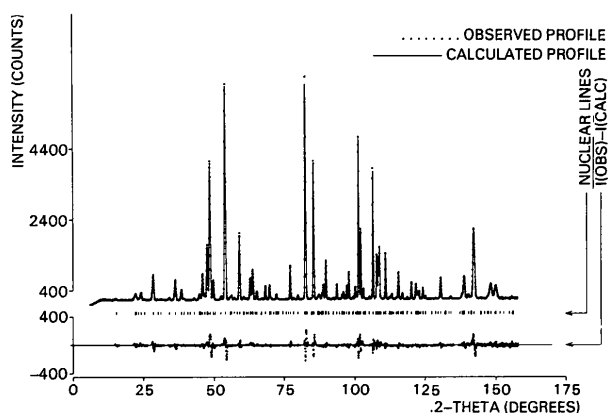| $Ba_6TiNb_4O_{18}$ (this work)			$Ba_5Ta_4\square O_{15}$ (Shannon & Katz, 1970)		
Ba(1)—O(1)a	2.893 (4)		Ba(1)—O(1)a	2.8880 (5)	6×
—O(1)	2.851 (4)		—O(2)	2.829 (26)	3×
—O(2)	2.821 (3)		—O(2)	2.829 (26)	3×
Ba(2)—O(2)a	2.901 (5)		Ba(2)—O(2)a	2.903 (3)	6×
—O(1)	3.004 (3)		—O(1)	3.052 (45)	3×
—O(3)	2.714 (3)		—O(3)	2.643 (25)	3×
Ba(3)—O(3)a	2.933 (8)		Ba(3)—O(3)a	2.928 (49)	6×
—O(3)	2.762 (3)		—O(3)	2.765 (26)	3×
—O(2)	3.256 (4)		—O(2)	3.241 (29)	3×
Oct(1)—O(3)	1.846 (2)		Ta(1)—O(3)	1.856 (22)	3×
—O(2)	2.261 (3)		—O(2)	2.219 (28)	3×
Oct(2)—O(1)	2.104 (4)		Ta(2)—O(1)	2.065 (21)	3×
—O(2)	1.920 (3)		—O(2)	1.943 (27)	3×
Oct(3)—O(1)	2.017 (2)				6×
O(1)—O(11)a	2.897 (4)		O(1)—O(1)a	2.8880 (5)	2×
—O(1)a	2.888 (4)		—O(1)a	2.8880 (5)	2×
—O(1)	2.818 (3)		—O(2)	2.804 (27)	2×
—O(2)	2.820 (2)		—O(2)	2.804 (27)	2×
O(2)—O(2)a	2.954 (3)		O(2)—O(2)a	2.839 (40)	2×
—O(2)a	2.832 (3)		—O(2)a	2.937 (40)	2×
—O(3)	2.869 (2)		—O(3)	2.851 (36)	2×
O(3)—O(3)a	2.944 (2)		O(3)—O(3)a	2.312 (49)	2×
—O(3)a	2.841 (2)		—O(3)a	2.947 (33)	2×
—O(3)	3.127 (2)		—O(3)	2.829 (33)	2×

Fig. 1. Observed (dots) and calculated (full line) neutron diffraction profile of $Ba_6TiNb_4O_{18}$ at room temperature; a difference (observed—calculated) curve appears at the bottom of the figure. Tick marks below the profile indicate the positions of the Bragg reflections included in the calculation.
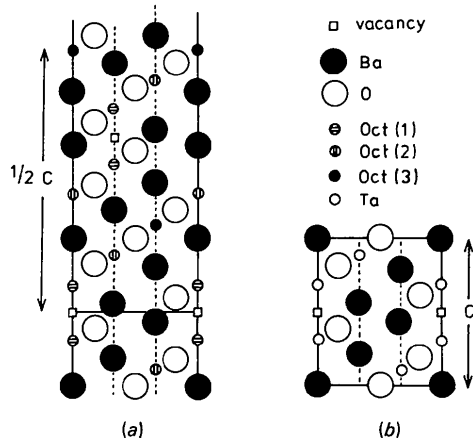

Fig. 2. (a) The (110) plane of $18L$-$Ba_6TiNb_4O_9$. (b) The (110) plane of $5L$-$Ba_5Ta_4O_{15}$.

The structure of $Ba_5Ta_4\square O_{15}$ (Shannon & Katz, 1970), Fig. 2(b), is related to the described one. Here the stacking of the BaO_3 layers is (hhccc). This results in a perovskite lattice with a shear plane every fifth layer with vacancies in the shear plane. The structure is, around the empty layers, in detail the same as the structure of $Ba_6TiNb_4O_{18}$ (radii for Nb^{5+} and Ta^{5+} are the same).

Empty layers in perovskite-like compounds occur also in $Ba_4Re_2M\square O_{12}$, M=Mg, Ca, Co, Zn or Cd, (Longo, Katz & Ward, 1965) and in $Ba_4M_2W\square O_{12}$, M=Nb, Ta (Rother, Kemmler-Sack, Treiber & Cyris, 1980) with $(hhcc)_3$ layers. In this latter structure, there is a shear plane after every fourth layer, with the vacancy in the shear plane.

Recently, the crystal structure of the perovskite-like $Ba_3SrNb_2O_9$ (Zandbergen & IJdo, 1983) was determined. This compound, with all octahedra filled, adopts the hexagonal $BaTiO_3$ structure with face-sharing

$Nb_2O_9^{8-}$ groups, in contrast to the title compound, where the octahedra share corners.

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Structure du Bis(cyclo-triphosphate) de Nickel(II) et de Tetrasodium Hexahydraté

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Abstract. $Na_4Ni(P_3O_9)_2.6H_2O$, $M_r = 732.6$, triclinic, $P\bar{1}$, $a = 9.186$ (2), $b = 8.020$ (2), $c = 6.838$ (1) Å, $\alpha = 89.17$ (1), $\beta = 102.89$ (1), $\gamma = 98.03$ (1)°, $V = 486.2$ Å^3, $Z = 1$, $D_m = 2.438$ (5), $D_x = 2.441$ Mg m^{-3}, $\lambda(Mo\,K\alpha) = 0.7107$ Å, $\mu = 1.649$ mm^{-1}, $F(000) = 366$, $T = 293$ K, final $R = 0.036$ for 1783 independent reflexions. The nickel atom is octahedrally surrounded by six water molecules. The $P_3O_9^{3-}$ ring anions are linked by a three-dimensional network of sodium polyhedra. Edge-sharing NaO_6 sodium polyhedra link so as to form linear chains running parallel to the $a + c$ direction. Sodium polyhedra are connected to nickel octahedra $[Ni(H_2O)_6]^{2+}$ via $O(W1)$ water molecules.

Introduction. Les cyclo-triphosphates hydratés du nickel associés aux monovalents sont très peu connus; on ne peut guère citer que $K_4Ni(P_3O_9)_2.7H_2O$ (Seethanen, Tordjman & Averbuch-Pouchot, 1978). Leur étude systématique a mis en évidence l'existence des deux nouveaux cyclo-triphosphates isotypes $Na_4Ni(P_3O_9)_2.6H_2O$ et $Ag_4Ni(P_3O_9)_2.6H_2O$. La présente étude a été réalisée à l'aide du sel de nickel–sodium, $Na_4Ni(P_3O_9)_2.6H_2O$, dont la préparation, l'analyse chimique et les caractéristiques cristallographiques ont été décrites (Jouini & Dabbabi, 1985).

Partie expérimentale. Cristal prismatique à section carrée $(0,14 \times 0,14 \times 0,16)$ mm; appareillage: Philips PW 1100; monochromateur: graphite; domaine de mesure 3 à 35° (θ); type de balayage: ω; domaine de balayage: $1,2°$ (θ); vitesse de balayage: $0,03°s^{-1}$; réflexions de référence: $31\bar{1}$, 221, 410, variation négligeable; temps total de mesure du fond continu: 10s; nombre de réflexions mesurées: 2731 $(\pm h, \pm k, l)$, $h_{max} = 15$, $k_{max} = 13$, $l_{max} = 11$; 1783 réflexions indépendantes telles que $F_o > 4\delta_F$, correction de Lorentz–polarisation; aucune correction d'absorption. Structure déterminée par des méthodes classiques: exploitation de la fonction de Patterson et synthèses de Fourier successives; $\sum \Delta^{F2}$ minimisée; schéma de pondération unitaire utilisé pour tous les affinements par moindres carrés à matrice complète; atomes d'hydrogène non localisés; coordonnées atomiques, coefficients de température anisotropes et facteur d'échelle affinés: $\Delta/\sigma = 0,43$; $R = 0,036$; $wR = 0,049$; $S = 1,014$; $\Delta\rho_{max} = 0,4$ e Å^{-3}; $(\Delta/\sigma)_{max} = 0,00$ au dernier cycle d'affinement; facteurs de diffusion atomique des atomes neutres (International Tables for X-ray Crystallography, 1974); les programmes SDP (Enraf–Nonius, 1980) ont été utilisés; D_m(pycnométrie): liquide = bromobenzène.