N(4) and S(1) lying 0·55, 0·58 and 1·57 (1) Å respectively out of this plane. The four S—N bonds involving S(2) and S(4) are appreciably shorter than those at S(1) and S(3), indicating some localization of multiple-bond character [see Table 2; *cf.* S—N bond lengths 1·548–1·566 Å in $S_4N_3^+$ (Kruss & Ziegler, 1972)].

Fig. 2 shows a packing plot of the structure; the shortest intermolecular contacts are O(2)···N(3), 3·08, O(2)···S(4), 3·09, and O(2)···S(2), 3·10 (1) Å (second atoms at $x, \frac{1}{2}-y, -\frac{1}{2}+z$).

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Barium Strontium Niobate and Barium Strontium Tantalate, $Ba_3SrNb_2O_9$ and $Ba_3SrTa_2O_9$, a Rietveld Refinement of Neutron Powder Diffraction Data

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Abstract. $Ba_3SrNb_2O_9$: $M_r = 829{\cdot}45$, hexagonal, $P6_3/m$, $a = 6{\cdot}0704\,(1)$, $c = 15{\cdot}3758\,(5)$ Å, $V = 490{\cdot}68\,(3)$ Å^3, $Z = 2$, $D_x = 5{\cdot}61$ Mg m^{-3}. $Ba_3SrTa_2O_9$: $M_r = 1005{\cdot}53$, hexagonal, $P6_3/m$, $a = 6{\cdot}0776\,(1)$, $c = 15{\cdot}3360\,(5)$ Å, $V = 490{\cdot}58\,(3)$ Å^3, $Z = 2$, $D_x = 6{\cdot}81$ Mg m^{-3}. The structures have been refined by Rietveld analysis of powder neutron diffraction data at room temperature, $\lambda = 2{\cdot}5907\,(3)$ Å. $R_I = 2{\cdot}28$, 2·68%; $R_P = 4{\cdot}93$, 5·46%; $R_{wP} = 6{\cdot}12$, 6·49% respectively for 86 reflections. The structure of both compounds is of a modified hexagonal $BaTiO_3$ type.

Introduction. In a programme to investigate compounds with perovskite or related structures on their properties as a host lattice for nuclear waste we prepared $Ba_3SrNb_2O_9$ and $Ba_3SrTa_2O_9$. The latter compound is reported as an ordered 3*L* perovskite structure (Galasso, Barrante & Katz, 1961). Kemmler-Sack, Thumm & Hermann (1981), however, reported the hexagonal 6*L* $BaTiO_3$ structure (Burbank & Evans, 1948) for both compounds.

Experimental. The compounds were prepared by solid-state reaction of $BaCO_3$, $SrCO_3$ and Nb_2O_5 or Ta_2O_5. These AR materials were thoroughly mixed in an agate mortar in the appropriate ratios. The mixtures were heated in alumina crucibles at 1273 K for one day and 1573 K for a week, with repeated grindings. The compounds were annealed at 923 K for a week. X-ray powder-diffraction patterns were obtained with a Philips PW 1050 diffractometer and could be indexed with hexagonal cells. The symmetry and systematic absences indicated space group $P6_3/m$ or $P6_322$. Since no single crystals were available the Rietveld (1969) method for refinement of neutron powder diffraction data was used. Neutrons of wavelength 2·5907 (3) Å were obtained from the (111) planes of a copper crystal. Pyrolytic graphite with a total thickness of 12 cm was employed as a second-order filter. Soller slits with a horizontal divergence of 30′ were placed between the reactor and the monochromator and in front of each of the four ^{3}He counters. The sample holder (⌀ = 20 mm) consisted of a vanadium tube, closed with copper plugs fitted with O-rings. No precautions were taken against preferred orientations. The maximum absorption correction was 1·0%, $\mu R = 0{\cdot}191$ (Weber, 1967) for $Ba_3SrNb_2O_9$ and 2·5%, $\mu R = 0{\cdot}322$ for $Ba_3SrTa_2O_9$. The background was determined from parts of the diagrams, which did not contain any contribution from reflections, and linear extrapolation between these points. The statistically expected values of R_{wP} are 3·60 and 3·54% respectively.

The hexagonal $BaTiO_3$ structure (Burbank & Evans, 1948) was used as the trial model, modified for space group $P6_3/m$: Ba(1) in 2(*a*) $(0,0,\frac{1}{4})$; Ba(2) in 4(*f*) $(\frac{1}{3}, \frac{2}{3}, z)$; Sr in 2(*b*) (0,0,0); Nb in 4(*f*); O(1) in 6(*h*) $(x,y,\frac{1}{4})$ and O(2) in 12(*i*) (*x*,*y*,*z*). The parameters in the refinement were: a scale factor, three half-width

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parameters defining the Gaussian line shape, the counter zero error, the unit-cell parameters, the atomic positional parameters, isotropic temperature factors, a preferred-orientation parameter and an asymmetry parameter below $2\theta = 37°$. The coherent scattering lengths assumed were: Ba 5·2, Sr 6·9, Nb 7·1, Ta 7·0 and O 5·8 fm (Bacon, 1972). The Rietveld program minimizes the function $X^2 = \sum_i w_i[y_i(\text{obs.}) - (1/c) \times y_i(\text{calc.})]^2$, where y_i(obs.) and y_i(calc.) are the observed and calculated profile data points, w_i is the statistical weight $[1/y_i(\text{obs.})]$ allotted to each data point and c is the scale factor. The following R factors were calculated:

$$R_I = 100 \sum |I_i(\text{obs.}) - (1/c)I_i(\text{calc.})| / \sum I_i(\text{obs.}),$$
$$R_p = 100 \sum |y_i(\text{obs.}) - (1/c)y_i(\text{calc.})| / \sum y_i(\text{obs.}),$$
$$R_{wP} = 100[\sum w_i|y_i(\text{obs.}) - (1/c)y_i(\text{calc.})|^2 / \sum w_i|y_i(\text{obs.})|^2]^{1/2},$$

where I_i (obs.) and I_i (calc.) are the observed and calculated integrated intensities of each reflection. The shifts in the parameters during the final cycles were smaller than 0·03 times their e.s.d. The trial model with space group $P6_322$ did not refine to reasonable R values.

Discussion. Atomic parameters* are given in Table 1, the agreement between observed and calculated profiles is shown in Figs. 1 and 2. The present refinements confirm the conclusion of Kemmler-Sack, Thumm & Hermann (1981) that the structure is of the 6L type. However, $Ba_3SrNb_2O_9$ and $Ba_3SrTa_2O_9$ adopt a modified hexagonal $BaTiO_3$ structure.

Table 1. *Fractional atomic coordinates and thermal parameters*

	x	y	z	B(Å^2)
$Ba_3SrNb_2O_9$ (this work)				
Ba(1)	0	0	0·25	0·36 (8)
Ba(2)	0·33333	0·66667	0·1185 (2)	1·04 (7)
Sr	0	0	0	0·82 (8)
Nb	0·33333	0·66667	0·8465 (1)	0·28 (5)
O(1)	0·5645 (4)	0·0424 (4)	0·25	0·60 (5)
O(2)	0·7661 (3)	0·6446 (4)	0·0977 (1)	1·30 (4)
$Ba_3SrTa_2O_9$ (this work)				
Ba(1)	0	0	0·25	0·39 (9)
Ba(2)	0·33333	0·66667	0·1162 (2)	1·15 (8)
Sr	0	0	0	1·12 (9)
Ta	0·33333	0·66667	0·8462 (1)	0·27 (6)
O(1)	0·5673 (5)	0·0450 (4)	0·25	0·61 (5)
O(2)	0·7624 (3)	0·6433 (4)	0·0968 (1)	1·35 (5)
$BaTiO_3$ (Burbank & Evans, 1948)				
Ba(1)	0	0	0·25	
Ba(2)	0·33333	0·66667	0·097 (1)	
Ti(1)	0	0	0	
Ti(2)	0·33333	0·66667	0·845 (2)	
O(1)	0·522 (10)	0·044 (20)	0·25	
O(2)	0·836 (5)	0·672 (10)	0·76 (2)	

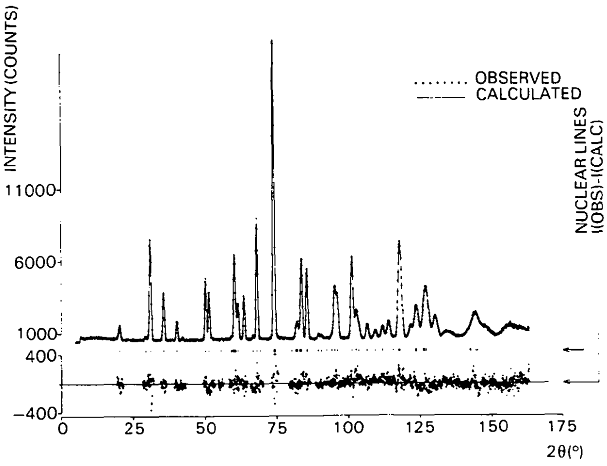

Fig. 1. Observed (dots) and calculated (full line) neutron diffraction profile of $Ba_3SrNb_2O_9$ at room temperature, a difference (observed–calculated) curve appears at the bottom of the figure. Tick marks below the profile indicate the positions of the Bragg reflections included in the calculation.

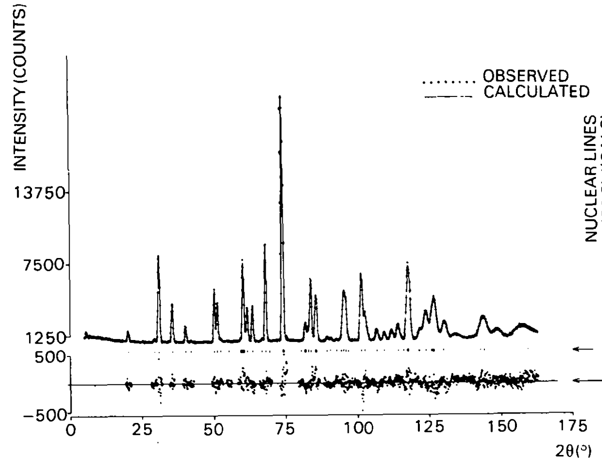

Fig. 2. Observed (dots) and calculated (full line) neutron diffraction profile of $Ba_3SrTa_2O_9$ at room temperature, a difference (observed–calculated) curve appears at the bottom of the figure. Tick marks below the profile indicate the positions of the Bragg reflections included in the calculation.

As in the hexagonal $BaTiO_3$ structure BaO_3 layers are stacked $(hcc)_2$ resulting in pairs of face-sharing octahedra which share corners with single octahedra. The Sr atoms are located in the single octahedra and the Nb(Ta) atoms in the face-sharing octahedra.

Unlike the octahedra in hexagonal $BaTiO_3$ all the octahedra are tilted around their threefold axis, leading to the lower space group $P6_3/m$. The tilt angles for the SrO_6 octahedra are 10·35 (6)° for $Ba_3SrNb_2O_9$ and 10·86 (6)° for $Ba_3SrTa_2O_9$. A projection of the structure on (001) is given in Fig.3; the atomic distances are given in Table 2.

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* The numerical intensity of each measured point, as a function of the angle, and the final parameters, which are not given in this paper, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38474 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Atomic distances* (Å) *and angles* (°)

a (about) equilateral distances.

	$Ba_3SrNb_2O_9$	$Ba_3SrTa_2O_9$
Ba(1)–O(1) *a*	2·781 (3)	2·777 (3)
a	3·306 (3)	3·320 (3)
O(2)	3·015 (2)	3·029 (2)
Ba(2)–O(1)	2·839 (3)	2·872 (3)
O(2) *a*	2·716 (2)	2·698 (2)
a	3·393 (2)	3·414 (2)
	3·721 (3)	3·669 (3)
SrO_6 octahedron		
Sr–O(2)	2·422 (2)	2·420 (2)
O(2)–O(2) *a*	3·290 (3)	3·311 (3)
	3·554 (3)	3·531 (3)
O(2)–Sr–O(2)	85·57 (6)	86·31 (6)
$M_2'O_9$ group		
M'–O(1)	2·147 (2)	2·134 (2)
O(2)	1·879 (2)	1·886 (2)
M'–M'	2·968 (3)	2·951 (3)
O(1)–O(1) *a*	2·688 (4)	2·671 (4)
O(2)	2·817 (2)	2·817 (2)
	2·873 (2)	2·880 (2)
O(2)–O(2) *a*	2·895 (4)	2·894 (4)
O(1)–M'–O(1)	77·50 (8)	77·47 (8)
O(1)–M'–O(2)	163·38 (10)	163·78 (10)
	88·54 (8)	88·78 (8)
	90·80 (8)	91·30 (9)

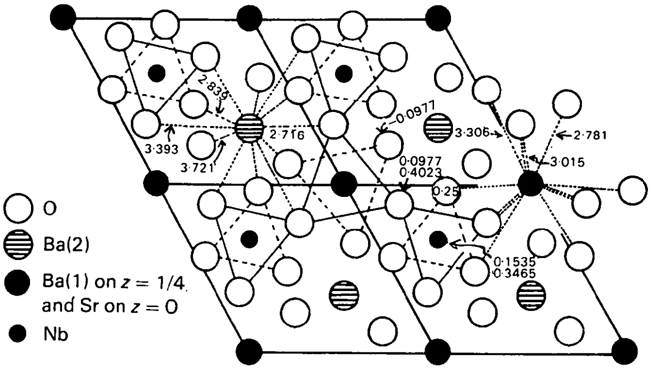

Fig. 3. $Ba_3SrNb_2O_9$. Projection on (001) showing the tilt of the octahedra and the coordination of Ba. Only the atoms between $z = -0{\cdot}1$ and $z = 0{\cdot}49$ are given.

The deviations from the hexagonal $BaTiO_3$ structure can be explained as follows. In the parent structure the octahedra have about the same size, all occupied by Ti^{4+} ions (radius 0·61 Å). In the investigated compounds the radius of Sr^{2+} (1·18 Å) differs very much from the radii of Nb^{5+} and Ta^{5+} [0·64 Å, all radii for six coordination (Shannon, 1976)]. Consequently, octahedra of different size are expected and indeed found to occur (Table 2). Stacking of SrO_6 and NbO_6 (TaO_6) octahedra of different size results in too much space for Ba. This space is decreased by a tilt of the octahedra around their threefold axis resulting in three shorter and three longer equilateral Ba—O distances.

The coordination of $Ba(2)^{2+}$ ions is also reduced by the large Sr^{2+} ion. The $Ba(2)^{2+}$ ions are surrounded by three $O(1)^{2-}$ ions in an adjacent layer, by two groups of three $O(2)^{2-}$ ions in the same layer and by three $O(2)^{2-}$ ions in the other adjacent layer. However, this last Ba—O(2) distance is much increased by the interjacent Sr^{2+} ion.

Table 3. *Lattice parameters* (Å) *and axial ratio of compounds with* (*modified*) *hexagonal* $BaTiO_3$ *structure*

	a	*c*	*c/a*	Reference
$BaTiO_3$	5·735	14·05	2·45	Burbank & Evans (1948)
$Ba_3FeRu_2O_9$	5·726	14·06	2·455	Treiber, Kemmler-Sack, Ehmann, Schaller, Dürrschmidt, Thumm & Bader (1981).
$Ba_3YbRu_2O_9$	5·862	14·435	2·462	
$Ba_3TmRu_2O_9$	5·867	14·445	2·462	
$Ba_3DyRu_2O_9$	5·888	14·53	2·468	
$Ba_3EuRu_2O_9$	5·913	14·63	2·474	
$Ba_3NdRu_2O_9$	5·934	14·765	2·488	
Ba_3LaRu_2O9	5·957	15·04	2·524	
$Ba_3NiRu_2O_9$	5·745	14·095	2·453	Treiber, Kemmler-Sack & Ehmann (1982)
$Ba_3CoRu_2O_9$	5·756	14·13	2·455	
$Ba_3MgRu_2O_9$	5·762	14·155	2·457	
$Ba_3CaRu_2O_9$	5·876	14·49	2·466	
$Ba_3CaRu_2O_9$	5·900	14·570	2·469	Darriet, Drillon, Villeneuve & Hagenmuller (1976)
$Ba_3NiSb_2O_9$	5·834	14·395	2·467	Treiber & Kemmler-Sack (1982)
$Ba_3MgSb_2O_9$	5·848	14·425	2·467	
$Ba_3CoSb_2O_9$	5·858	14·465	2·470	
$Ba_3MnSb_2O_9$	5·903	14·600	2·473	
$Ba_3SrNb_2O_9$*	6·0704 (1)	15·3758 (5)	2·533	This work
$Ba_3SrTa_2O_9$*	6·0776 (1)	15·3360 (5)	2·523	

* E.s.d.'s in the lattice parameters do not include errors in the neutron wavelength.

Regarding these results it should be noted that a similar modification of the hexagonal $BaTiO_3$ structure type is to be expected for all $Ba_3MM_2'O_9$ compounds which are reported to have the $BaTiO_3$ structure and have a relatively large *M* ion.

In Table 3 some compounds from the literature are listed together with their axial ratio *c/a*. For the undeformed packing with ideal octahedra $c/a = \sqrt{6} \simeq 2{\cdot}45$. A tilt around threefold axes decreases the lattice parameter *a* and thus increases *c/a*. For compounds $Ba_3MM_2'O_9$ with small *M* the *c/a* value is close to the expected value, indicating the tilt is near or equal to zero. With increasing radius of the *M* ion in a series *c/a* increases indicating that the tilt as described above might be present. The tilt in this modified hexagonal $BaTiO_3$ is analogous to the tilt around threefold axes in perovskites of the type $LaAlO_3$ (Megaw, 1973). The relation between coordination of the *A* ion and tilt angle around triad and tetrad axes for perovskites ABX_3 is reported by Lelieveld & IJdo (1980).

It will be difficult to establish a deviation from the hexagonal $BaTiO_3$ structure by means of X-ray powder diffraction since the tilt of the octahedra is only revealed by diffraction of the O^{2-} ions which have the smallest scattering factor (Table 1). Neutron diffraction has the advantage of a relatively high scattering length for O.

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