Within the precision of our measurement the PSe_4^{3-} (AsS_4^{3-}) groups depart slightly from an idealized tetrahedral arrangement, as indicated by the data in Table 2. The average P—Se bond length is 2·207 Å (As—S 2·167 Å). Individual bond angles are also distorted from perfect tetrahedral geometry, with an average Se—P—Se deviation of 1·5° (S—As—S 1·8°).

Although small geometric distortions exist in the tetrahedral PSe_4^{3-}(AsS_4^{3-}) groups and an unusually large anisotropic thermal parameter exists in these materials, no specific conclusions concerning the observed lattice softening can be drawn at this time. Further structural studies are being conducted on these chalcogenides, including single-crystal neutron structure determinations at 15 K and a high-pressure single crystal neutron structure determination on Tl₃PSe₄ at 1·5 GPa. With room-temperature structure parameters now defined, clearer understanding of the role of structure *versus* solid-state properties (as a function of temperature and pressure) will be possible.

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The Structures of Onoratoite, Sb₈O₁₁Cl₂ and Sb₈O₁₁Cl₂.6H₂O

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Abstract. Sb₈O₁₁Cl₂ (I): $M_r = 1220·9$, monoclinic, $C2/m$, $a = 19·047$ (35), $b = 4·0530$ (3), $c = 10·318$ (3) Å, $\beta = 110·25$ (4)°, $V = 747$ (1) Å³, $Z = 2$, $D_x = 5·425$ Mg m⁻³, Mo $K\bar{\alpha}$, $\lambda = 0·7107$ Å, $\mu = 14·99$ mm⁻¹, $F(000) = 1060$, room temperature, $R = 0·054$ for 828 observed reflections. All the examined crystals are twinned, with (001) as twin plane. Sb₈O₁₁Cl₂.6H₂O (II): $M_r = 1329·0$, orthorhombic, $Immm$, $a = 9·618$ (3), $b = 13·148$ (6), $c = 4·078$ (1) Å, $V = 515·7$ (3) Å³, $Z = 1$, $D_x = 4·279$ Mg m⁻³, Mo $K\bar{\alpha}$, $\lambda = 0·7107$ Å, $\mu = 10·75$ mm⁻¹, $F(000) = 590$, room temperature, $R = 0·038$ for 346 observed reflections. Crystals grown from a cold solution. The structures of (I) and (II) exhibit similar features. Both have Sb—O

trigonal bipyramids linked together in chains along the needle axis and joined to form 'tubes' parallel to [010] in (I) and sheets parallel to (010) in (II). The structures are held together by interactions of Cl with the nearest atoms. In both structures some oxygens show partial occupancy.

Introduction. During field work in Southern Tuscany, Italy, onoratoite was collected and identified in material from Le Cetine (Siena). Onoratoite is the only antimony chloride oxide occurring as a mineral; previous studies are not in full agreement as regards the chemical formula and the crystal structure (Edstrand, 1955b; Sgarlata, 1970; Belluomini, Fornaseri & Nicoletti, 1967). The fairly good quality of the onoratoite found suggested a review of its characteristics in order to clarify problems still open.

Because of the scarcity of the natural material, syntheses were undertaken for analytical purposes. A compound with all the characteristics of onoratoite was recovered from boiling solution. From cold mother liquor a second compound crystallizes; the tiny crystals obtained, up to 5 mm long, were identified by Weissenberg photographs and powder pattern as Edstrand's (1955a) γ phase. Its IR spectrum is very similar to that of onoratoite. The main difference is the lack in the onoratoite spectrum of any effect imputable to O—H bonds, whereas the second phase shows a band indicating the presence of water. Structure resolutions are in agreement with the above indications, suggesting for onoratoite (I) the formula $Sb_8O_{11}Cl_2$ and for the other phase (II) the formula $Sb_8O_{11}Cl_2.6H_2O$.

Experimental. Syntheses of (I) and (II) according to Belluomini, Fornaseri & Nicoletti (1967). Eight runs performed in the HCl concentration range = 0·11–0·09 mol dm^{-3}. Colourless transparent acicular crystals, about 0·1 × 0·15 × 0·4 mm, from Le Cetine (I) and preparation (II); Philips PW 1100 four-circle computer-controlled diffractometer (Centro di Studio per la Cristallografia Strutturale del CNR, Pavia, Italy); cell parameters from 25 independent reflections; three standard reflections checked each hour: (I) 080, $14\bar{2}$, $14\bar{2}$, intensity variation $\pm2\cdot8\%$; (II) 330, $3\bar{3}0$, 002, intensity variation $\pm1\cdot5\%$.†

(I): Twinned crystal, (001) as twin plane, reciprocal lattice of A and B individuals with c^* axes antiparallel, a_A^* axis making an angle $180°-2\beta^*$ with a_B^* axis. Intensity data sorted into two categories: one containing well-separated reflections ($h = 1,2,4,6,7,9,10,12,-14,15,17,18,20,22,23$); second grouping more or less overlapped reflections ($h = 0,3,5,8,11,13,16,19,21,24$).

From non-superimposed reflections relative volumes ($A/B = 10\cdot1$) computed, allowing subdivision of composite intensities. 2182 measured reflections; h 0–26, k 0–5, l 0–±14; $\theta < 30°$, ω-scan technique; $R_{int} = 0\cdot055$; 1230 independent; 828 with $F_o > 5\sigma(F_o)$.

(II): $R_{int} = 0\cdot036$; 884 measured reflections; h 0–13, k 0–18, l 0–5; $\theta < 30°$, ω–2θ scan technique; 470 independent; 347 with $I/\sigma(I) > 3$.

Absorption: max. 1·709 (I) and 1·433 (II), min. 0·964 (I) and 1·006 (II) (North, Phillips & Mathews, 1968) and Lp corrections; starting atomic parameters of Sb and Cl from Edstrand (1955b) (I) and Edstrand (1955a) (II); oxygen-atom coordinates from three-dimensional Fourier syntheses; H positions not detected; anisotropic full-matrix refinement on F, $w = 1/\sigma^2(F_o)$; parameters refined: atomic coordinates and anisotropic thermal parameters for all atoms, occupancy factors for oxygen atoms. Atomic scattering factors for all atoms, f' and f'' for antimony and chlorine from *International Tables for X-ray Crystallography* (1974); final $R = 0\cdot054$ (I) and 0·038 (II), $R_w = 0\cdot057$ (I) and 0·039 (II); max. $\Delta/\sigma = 1\cdot1$ (I), 1·0 (II); max. peak in final difference Fourier map = 4·1 (I) 2·0 (II) e Å^{-3} close to Sb. Honeywell computer (DPS 7 system) of Centro di Calcolo dell'Università di Firenze, local version of *ORFLS* (Busing, Martin & Levy, 1962), *BONDLA* (*XRAY* system; Stewart, Kruger, Ammon, Dickinson & Hall, 1972), *ORTEP* (Johnson, 1965).

Discussion. Table 1 reports atomic parameters for both (I) and (II).* There is substantial agreement between the present results and those achieved by Edstrand (1955a,b); however, the chemical formulae differ slightly, mainly in regard to hydroxyls and water molecules.

Both compounds show the same basic units: ladder-like chains built up of Sb and O atoms (see Fig. 1). In addition to the three ladder oxygens, each Sb links a fourth O atom to complete the characteristic SbO_4E coordination (E being the lone pair of electrons), with the shape of a trigonal bipyramid with an equatorial corner occupied by the lone pair. Similar Sb—O chains are also present in the low-temperature SbOF structure (Åström & Andersson, 1973) and in kermesite (Kupčik, 1967), where a fluorine and a sulphur atom each occupy one equatorial corner of the trigonal bipyramid around Sb. The ladder oxygens are linked to three Sb atoms, while the out-of-ladder atoms connect two Sb atoms of adjacent chains. In (I) four ladders are arranged to form a 'tube' parallel to [010] (Fig. 2a). In

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† In both (I) and (II) some diffraction effects, analogous to the 'weak zones' observed by Edstrand (1955a,b) and Belluomini *et al.* (1967), are present. These faint reflections seem to quadruple the 4 Å identity periods. However, their weakness and the difficulty of indexing them make their collection impossible.

* Lists of structure factors, anisotropic thermal parameters and Cl–Sb, Cl–O distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39487 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(II) each ladder is connected to two adjacent ones in a waving sheet parallel to (010) (Fig. 2b). In the wide spaces between the Sb—O blocks there are Cl atoms in (I) and Cl atoms with a similar environment and H_2O molecules in (II).

Table 1. *Fractional atomic coordinates, equivalent isotropic temperature factors ($Å^2$) and occupation factors (OF)*

$$B_{eq} = \tfrac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}	OF
(I) Onoratoite					
Sb(1)	0·27181 (7)	0	0·1737 (1)	2·34	1·0
Sb(2)	−0·00472 (8)	½	0·3005 (1)	2·03	1·0
Sb(3)	0·08770 (7)	0	−0·0103 (1)	1·71	1·0
Sb(4)	0·18592 (7)	½	0·3551 (1)	1·66	1·0
Cl	0·1158 (4)	0	0·5199 (7)	3·88	1·0
O(1)	0·229 (1)	½	0·202 (2)	3·68	0·84 (3)
O(2)	−0·035 (1)	0	0·219 (2)	4·56	0·89 (3)
O(3)	0·074 (1)	½	−0·101 (2)	3·17	0·72 (3)
O(4)	0·198 (1)	0	0·284 (3)	4·29	0·82 (3)
O(5)	0·192 (1)	0	−0·012 (1)	1·51	1·0
O(6)	0·082 (1)	½	0·240 (1)	2·13	1·0
(II) $Sb_8O_{11}Cl_2.6H_2O$					
Sb	0·18377 (7)	0·15356 (6)	0	2·47	1·0
Cl	½	½	0	4·46	1·0
O(1)	0·2798 (8)	0·2914 (8)	0	4·13	0·88 (3)
O(2)	0	0·2178 (10)	0	2·33	1·0
O(3)	0	0·399 (4)	0·364 (13)	13·97	0·50 (5)
O(4)	0	0·431 (4)	0	14·98	0·51 (4)

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

(I) Onoratoite

Sb(1)—O(1)	2·241 (10)	O(1)—Sb(1)—O(4)	65·5 (5)
Sb(1)—O(1ⁱⁱ)	2·241 (10)	O(1)—Sb(1)—O(5)	86·2 (5)
Sb(1)—O(4)	2·093 (29)	O(1)—Sb(1)—O(1ⁱⁱ)	129·5 (7)
Sb(1)—O(5)	1·991 (9)	O(4)—Sb(1)—O(5)	95·2 (7)
		O(4)—Sb(1)—O(1ⁱⁱ)	65·5 (5)
		O(5)—Sb(1)—O(1ⁱⁱ)	86·2 (5)
Sb(2)—O(2)	2·193 (7)	O(2)—Sb(2)—O(3ⁱⁱⁱ)	67·5 (4)
Sb(2)—O(2ⁱ)	2·193 (7)	O(2)—Sb(2)—O(6)	91·0 (6)
Sb(2)—O(3ⁱⁱⁱ)	2·024 (17)	O(2)—Sb(2)—O(2ⁱ)	135·0 (6)
Sb(2)—O(6)	1·957 (16)	O(6)—Sb(2)—O(3ⁱⁱⁱ)	90·0 (7)
		O(2ⁱ)—Sb(2)—O(3ⁱⁱⁱ)	67·5 (4)
		O(2ⁱ)—Sb(2)—O(6)	91·0 (6)
Sb(3)—O(3)	2·209 (8)	O(3)—Sb(3)—O(2ⁱᵛ)	67·0 (4)
Sb(3)—O(3ⁱⁱ)	2·209 (8)	O(3)—Sb(3)—O(5)	88·2 (5)
Sb(3)—O(2ⁱᵛ)	2·037 (19)	O(3)—Sb(3)—O(3ⁱⁱ)	133·0 (7)
Sb(3)—O(5)	1·992 (13)	O(5)—Sb(3)—O(2ⁱᵛ)	96·8 (7)
		O(2ⁱᵛ)—Sb(3)—O(3ⁱⁱ)	67·0 (4)
		O(5)—Sb(3)—O(3ⁱⁱ)	88·2 (5)
Sb(4)—O(4)	2·194 (12)	O(4)—Sb(4)—O(1)	67·7 (8)
Sb(4)—O(4ⁱ)	2·194 (12)	O(4)—Sb(4)—O(6)	89·9 (5)
Sb(4)—O(1)	2·016 (23)	O(4)—Sb(4)—O(4ⁱ)	134·9 (1·1)
Sb(4)—O(6)	1·923 (13)	O(1)—Sb(4)—O(6)	97·3 (6)
		O(1)—Sb(4)—O(4ⁱ)	67·6 (8)
		O(6)—Sb(4)—O(4ⁱ)	89·9 (5)

(II) $Sb_8O_{11}Cl_2.6H_2O$

Sb—O(1ᵛ)	2·192 (4)	O(1)—Sb—O(1ᵛ)	68·5 (2)
Sb—O(1ᵛⁱ)	2·192 (4)	O(1)—Sb—O(1ᵛⁱ)	68·5 (2)
Sb—O(1)	2·034 (10)	O(1)—Sb—O(2)	91·5 (4)
Sb—O(2)	1·959 (6)	O(1ᵛ)—Sb—O(1ᵛⁱ)	137·0 (3)
		O(1ᵛ)—Sb—O(2)	90·1 (3)
		O(2)—Sb—O(1ᵛⁱ)	90·1 (3)

Symmetry code: (i) x, $1+y$, z; (ii) x, $−1+y$, z; (iii) $−x$, $1−y$, $−z$; (iv) $−x$, $−y$, $−z$; (v) $\tfrac{1}{2}−x$, $\tfrac{1}{2}−y$, $\tfrac{1}{2}−z$; (vi) $\tfrac{1}{2}−x$, $\tfrac{1}{2}−y$, $−\tfrac{1}{2}−z$.

In Table 2 bond distances and angles of (I) and (II) are listed. The coordination polyhedra around all Sb atoms are similar. In each polyhedron there are, along the ladder, two Sb—O bond distances of about 2·2 Å [2·192 (4) to 2·24 (1) Å] and perpendicularly two of about 2·0 Å [1·92 (1) to 2·09 (3) Å], the shortest always being the Sb—O distance involving the 'out-of-ladder' oxygen atom, which is linked only to two Sb atoms. In the scheme of Särnstrand (1978), these distances are characteristic for the 'more representative trigonal bipyramid' around Sb. The greatest O—Sb—O angle is the one involving the two farthest oxygens along the 'axis' of the bipyramids.

The Sb—Cl distances, ranging from 3·217 (7) to 3·837 (8) Å, are rather long for covalent or ionic bonds. Indeed, in SbOCl (Edstrand, 1953) covalent sheets of $(Sb_6O_6Cl_4)^{2+}$ are present, with Sb—Cl distances of about 2·3 Å; the sheets are bound together by another Cl atom with 0·6 Å longer distances and bonds with more ionic character. On the other hand, the Sb—Cl distances in (I) and (II) are in agreement with those found in nadorite (Giuseppetti & Tadini, 1973) and with the intermolecular Sb—Cl distances in $SbCl_3$ (Lipka, 1979).

The formulae of both title compounds were in doubt until the end of the structure resolution. Two occupancy problems, concerning oxygen atoms, are present. The ladder oxygens of both structures have an occupancy of about 88%, which indicates one vacancy in eight positions; since Sb atoms show full occupancy, this means that three out of eight Sb atoms, in turn, would be only three coordinated. The good agreement of the occupancy data for both structures raises the reliability of this feature, which is uncommon in Sb compounds.

The second occupancy problem concerns the water molecules of (II). In the first structure determination of this compound (Edstrand, 1955a) the water oxygen was supposed to be at special position 4(h) $(0,y,\tfrac{1}{4})$. In the Fourier syntheses of the present study a diffuse residue can be seen; the oxygen position proposed by Edstrand is not evident on these maps, but two relative maxima imputable to water oxygen atoms are present. Nevertheless, these positions, O(3) and O(4) in Table 1,
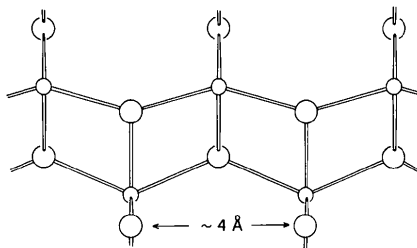

Fig. 1. The Sb—O ladder present in both structures. This configuration accounts for the period of about 4 Å: along **b** in (I) and **c** in (II). Larger circles are oxygen atoms.
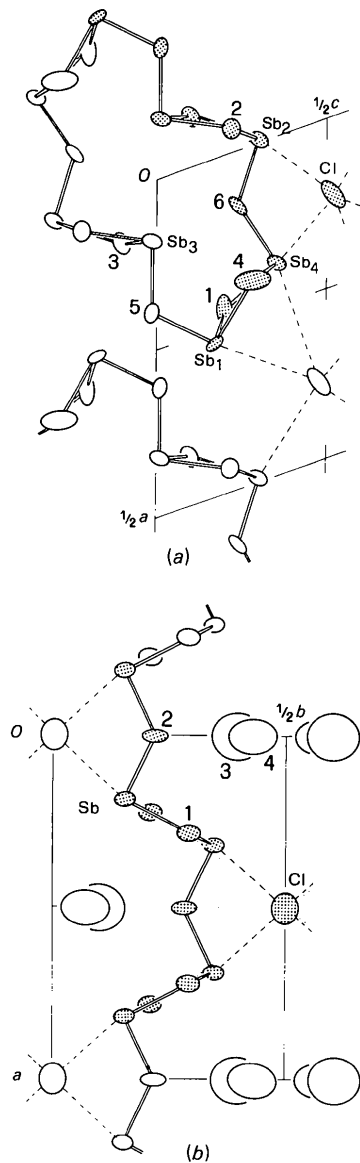
Fig. 2. *ORTEP* drawings of (*a*) (I) and (*b*) (II) with boundary ellipses at the 50% probability level. Dotted atoms indicate the portions of the structures topologically equivalent in the two compounds. Dashed and dotted lines join Sb and O atoms, respectively, to the Cl atom (within 3·9 Å).
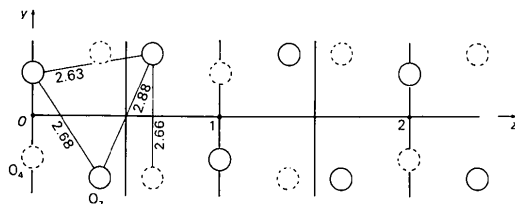

Fig. 3. Water oxygen atoms in (II). Heavy lines are mirror planes. The four distances (Å, e.s.d. 0·07) shown are possible H bridges.

cannot be fully occupied because of steric hindrance. The refinement confirms this assumption; the thermal parameters for these oxygens are too high and the formal site occupancy is found to be about 50%. The two sites, a total of twelve positions in the whole cell, are thus only half occupied in a disordered way. Water molecules form a curtain perpendicular to the Sb—O layers. Inside the curtain the actual symmetry is not kept; a possible arrangement of the oxygen atoms is drawn in Fig. 3 (full circles). This configuration requires a doubled period in the z direction. On the other hand, the symmetrical arrangement (dashed circles) is equally possible, so that a mean symmetry, *i.e.* the actual symmetry, may be respected. This disorder in oxygen sites does not permit location of the hydrogen atoms, which are, in addition, masked by the heavy atoms. From the distances quoted in Fig. 3 a net of strong H bonds can be imagined inside the curtain of water, but no more precise hypothesis may be stated. It is possible that some hydrogens will be directed towards O(2); two reasonable distances, O(3)—O(2) 2·80 (5) and O(4)—O(2) 2·80 (6) Å, are in fact observed. Together with Cl—Sb interactions, these bridges probably hold the structure together, no other bonds between Sb—O sheets being present.

A similar situation is found in (I): the Sb—O tubes are connected by Cl atoms, which are located in channels of about 7 Å diameter. Thus, the acicular habit of the crystals results.

Synthetic onoratoite and $Sb_8O_{11}Cl_2.6H_2O$ have a common origin: the first crystallizes from a boiling solution of Sb_2O_3 and HCl, the second from the same solution after cooling and filtration. In view of this, it is likely that the Sb—O ladder units, together with a Cl atom (Fig. 2), form part of the structure that, reasonably, already exists in solution and that polymerizes in a different way for the two phases, depending mainly on the crystallization temperature.

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Refinement of Barium Tetratitanate, BaTi4O9, and Hexabarium 17-Titanate, Ba6Ti17O40

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Abstract. $BaTi_4O_9$: $M_r = 472.9$, orthorhombic, *Pmmn*, $a = 14.527$ (2), $b = 3.794$ (1), $c = 6.293$ (1) Å, $V = 346.8$ Å^3, $Z = 2$, $D_x = 4.53$ Mg m^{-3}, $\lambda(Mo\,K\alpha) = 0.71069$ Å, $\mu = 10.00$ mm^{-1}, $F(000) = 431.9$, $T = 293$ K, final $R = 0.033$ for 1614 unique reflexions. $Ba_6Ti_{17}O_{40}$: $M_r = 2278.3$, monoclinic, $C2/c$, $a = 9.887$ (1), $b = 17.097$ (2), $c = 18.918$ (2) Å, $\beta = 98.72$ (2)°, $V = 3160.9$ Å^3, $Z = 4$, $D_x = 4.79$ Mg m^{-3}, $\lambda(Mo\,K\alpha) = 0.71069$ Å, $\mu = 11.47$ mm^{-1}, $F(000) = 3958.9$, $T = 293$ K, final $R = 0.051$ for 6945 unique reflexions. Single crystals from both compounds were grown from the melt. The $BaTi_4O_9$ compound is best described as a '4.0 Å' structure similar to many alkali titanates, in which the long axes of the octahedra are lined up parallel to the short cell constant. The $Ba_6Ti_{17}O_{40}$ compound can be described as a hexagonal closest packing of Ba and O atoms, with Ti in octahedral interstices.

Introduction. With the determination of the crystal structure of $Ba_2Ti_9O_{20}$ (Tillmanns, Hofmeister & Baur, 1983) all the structures of the compounds in the system $BaO-TiO_2$ are known. Structure determinations have been reported for $BaTi_4O_9$ by Lukaszewicz (1957) and Templeton & Dauben (1960) and for $Ba_6Ti_{17}O_{40}$ by Tillmanns & Baur (1970). In the course of an investigation of the crystal chemistry of the barium titanate system a refinement of these structures proved necessary in order to obtain more precise coordinates and distances. With bond distances from these newly refined structures a statistically significant dependence of mean bond lengths on octahedral distortions can be established for the titanates (Tillmanns, Hofmeister & Baur, 1984).

Experimental. Single crystals of $Ba_6Ti_{17}O_{40}$ and $BaTi_4O_9$ were taken from a sample of composition $BaO:TiO_2 = 1:3$ partly melted on a platinum plate at about 1673 K and quenched. Three-dimensional X-ray diffraction intensities were collected with a Nonius CAD-4 computer-controlled diffractometer. For $Ba_6Ti_{17}O_{40}$: crystal irregularly shaped, approximate diameter 0.2 mm; 25 reflexions with $20 < \theta < 30°$ used for determination of lattice parameters; a total of 7464 reflexions collected in range $0.03 < \sin\theta/\lambda < 0.81$ Å^{-1} with $0 \le h \le 15$, $0 \le k \le 27$ and $-30 \le l \le 30$ giving 6945 unique reflexions ($R_{int} = 0.038$) of which 699 considered unobserved ($I < 2\sigma_I$); intensities of three standard reflexions monitored after every 6 h, their orientation after every 400 reflexions, measurement instability 0.008; min. and max. transmission factors for absorption correction 0.09 and 0.27; function minimized $\sum w(|F_o| - |F_c|)^2$, where w for each reflexion is set to $1/\sigma^2(F)$; ratio of max. least-squares shift to error in final cycle 0.2; after a secondary extinction correction ($g = 0.0005$) final $R = 0.051$, $R_w = 0.053$; final difference synthesis had max. $\Delta\rho$ excursions of -1.9 e Å^{-3} at the Ba positions and 1.1 e Å^{-3} at distances of 0.6–0.7 Å. Atomic scattering factors and real and imaginary anomalous-dispersion coefficients from *International Tables for X-ray Crystallography* (1974).

Most experimental conditions were the same for $BaTi_4O_9$: orthorhombic prism with dimensions $0.15 \times 0.1 \times 0.325$ mm; min. and max. transmission factors 0.23 and 0.40; a total of 1614 unique reflexions collected between $0.02 < \sin\theta/\lambda < 0.90$ Å^{-1} (measurement instability 0.008, $0 \le h \le 28$, $0 \le k \le 7$, $0 \le l \le 12$) of which 75 considered unobserved; ratio of