

Refinement

Refinement on F^2 $R(F) = 0.095$ $wR(F^2) = 0.082$ $S = 1.69$

5232 reflections

72 parameters

 $w = 1/\sigma^2(F^2)$ $(\Delta/\sigma)_{\max} = 0.10$ $\Delta\rho_{\max} = 2.2 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -2.3 \text{ e } \text{\AA}^{-3}$ Extinction correction: Becker
& Coppens (1974),
isotropic (type 1)Extinction coefficient:
 $3.2(5) \times 10^2$ Scattering factors from *Inter-*
national Tables for X-ray
Crystallography (Vol. IV)Table 1. Selected bond lengths (\AA)

V1—O1	1.998 (3)	V3—O3 ⁱⁱⁱ	2.005 (1)
V1—O1 ⁱ	1.968 (1)	V3—O3 ^{viii}	2.005 (1)
V1—O1 ⁱⁱ	1.968 (1)	V3—O6	1.643 (3)
V1—O4	1.854 (1)	V3—O7	1.954 (3)
V1—O5	1.990 (3)	Li1—O2 ^{ix}	2.032 (5)
V1—O6 ⁱⁱⁱ	2.022 (3)	Li1—O2 ^{vi}	2.009 (7)
V2—O2 ^{iv}	1.979 (1)	Li1—O3	2.031 (5)
V2—O2 ^v	1.979 (1)	Li1—O7 ^{iv}	1.960 (1)
V2—O3	2.007 (3)	Li1—O7 ^v	1.960 (1)
V2—O5	1.664 (3)	Li2—O1	2.06 (5)
V2—O7	1.956 (3)	Li2—O1 ^x	2.08 (5)
V2—O7 ^{vi}	2.201 (3)	Li2—O4 ^{iv}	1.99 (1)
V3—O2	1.985 (3)	Li2—O4 ^v	1.99 (1)
V3—O3 ^{vi}	2.321 (3)		

Symmetry codes: (i) $\frac{1}{2}-x, y-\frac{1}{2}, -z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, -z$; (iii) $1-x, y, -z$;
(iv) $x-\frac{1}{2}, y-\frac{1}{2}, z$; (v) $x-\frac{1}{2}, \frac{1}{2}+y, z$; (vi) $1-x, y, 1-z$; (vii) $\frac{1}{2}+x, y-\frac{1}{2}, z$;
(viii) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (ix) $x-1, y, z$; (x) $-x, y, -z$.

The large cell-parameter changes (described above) which occur during the lithiation process introduce severe stress and cracks in the crystal, resulting in poor crystal quality and weak broad peaks. The reflections were thus measured with a large-interval ω -step scan (70 steps of 0.05°). The net intensities obtained have large standard deviations due to the smeared-out character of the reflections. The structure was solved from a sequence of difference Fourier syntheses in space group $C2/m$, based on the atomic coordinates of V₆O₁₃ (Wilhelmi *et al.*, 1971). Some features of the refined model indicate that the structure should be described with lower symmetry. The disordered positions of Li2 close to a centre of symmetry show that, at least locally, the structure is non-centrosymmetric. Peaks in the range $0.8\text{--}2.2 \text{ e } \text{\AA}^{-3}$ close to the V-atom positions in the $\Delta\rho$ maps also indicate deficiencies in the model. Systematic refinements in the non-centrosymmetric space groups Cm and $C2$ did not improve the model significantly; moreover, displacement parameters for atoms breaking the $2/m$ symmetry acquired physically unreasonable large values. It is possible, nevertheless, that the structure does not have the space group $C2/m$; the present data cannot resolve this, however. A refinement of the final model based on averaged data but with a lower cut-off at $2\sigma(F^2)$ gave a weighted $wR(F^2)$ value of 0.0696.

Data collection: *DIF4* (Stoe & Cie, 1988). Cell refinement: *DIF4*. Data reduction: *STOEDATRED*, *LSQLIN* and *ABS-STOE* (Lundgren, 1983). Program(s) used to solve structure: *FORDUP* (Lundgren, 1983). Program(s) used to refine structure: *DUPALS* (Lundgren, 1983). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *DISTAN* (Lundgren, 1983).

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Rubidium Antimony(V) Titanium Oxide, Rb₅Sb₇TiO₂₂

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Abstract

In the title compound, three Sb atoms have octahedral coordination and there is a 50/50 disorder of Sb and Ti at a site with trigonal-bipyramidal coordination. These polyhedra form an open network with the Rb⁺ ions in two types of channels, both types running in perpendicular directions, along [110] and [1 $\bar{1}$ 0]. The structure is pseudo-tetragonal and similar to the cubic pyrochlore structure.

Comment

Attempts to prepare a homologue of rubidium titanil arsenate, RbTiOAsO_4 (RTA), with Sb at the As site resulted in a novel rubidium antimony(V) titanium oxide, $\text{Rb}_5\text{Sb}_7\text{TiO}_{22}$. RTA belongs to the KTiOPO_4 isomorphous family of materials with high non-linear optical coefficients, used, for example, for efficient frequency doubling of the Nd:YAG 1064 nm laser beam (Bierlein & Vanherzeele, 1989). The arsenate analogues have a higher transmission in the infrared (Cheng *et al.*, 1993) favourably combined with low ionic conductivity (Bolt *et al.*, 1997).

Previously reported materials with the same constituents as $\text{Rb}_5\text{Sb}_7\text{TiO}_{22}$, except for titanium, are RbSbO_3 and Rb_3SbO_4 (Duquenois, 1974), and $\text{Rb}_4\text{Sb}_2\text{O}_7$ (Josien & Duquenois, 1980). These compounds were investigated by X-ray powder diffraction and no atomic coordinates were given. Electron-probe microanalysis of

four different crystals of the title compound from two batches gave the chemical formula $\text{Rb}_{5.1}\text{Sb}_{7.02}\text{Ti}_{0.94}\text{O}_{22}$, which is consistent with the formula determined from the X-ray diffraction data.

The $\text{Rb}_5\text{Sb}_7\text{TiO}_{22}$ structure (Fig. 1) is pseudotetragonal and similar to the cubic pyrochlore structure, which has the space group $Fd\bar{3}m$ and a unit-cell edge of approximately 10.4 Å (Perrault, 1968). The pyrochlore structure has four crystallographically non-equivalent kinds of atoms and a general formula $A_2B_2O_6O'$. In the BO_3 network, B has octahedral coordination while the anion has twofold coordination. The A and residual O atoms can be viewed either as interstitials or as a linearly coordinated network. The compound reported here is compared with the pyrochlore phase of $\text{Hg}_2\text{Sb}_2\text{O}_7$ (Sleight, 1968) shown in Fig. 1. The title compound has four different Sb sites, three with octahedral coordination and one with trigonal-bipyramidal coordination. There is a 50/50 disorder of antimony and titanium at the trigonal-bipyramidal site. The octahedra are slightly distorted and the different bond lengths vary as in Sb_2O_5 , which is also composed of distorted octahedra (Jansen, 1979). In the trigonal bipyramid, one apical bond to O [$\text{Sb4/Ti1—O8} = 2.136(5) \text{ \AA}$] is longer than the other bonds and the Sb4/Ti1 site is shifted by $0.177(2) \text{ \AA}$ out of the equatorial plane towards O7. Furthermore, one of the equatorial bonds to O is significantly elongated [$\text{Sb4/Ti1—O8}^v = 1.967(4) \text{ \AA}$; symmetry code as in Table 1] and the O9—Sb4—O10 angle [$123.5(3)^\circ$] is somewhat wider than the other two equatorial angles (Table 1).

The octahedra are linked by corners and edges. Together with the trigonal bipyramids, they form an open network containing two types of oval channels. The larger channel is formed by eight polyhedra, two with edge-sharing links, and has an average width of approximately 6 Å. The smaller channel is formed by six corner-sharing polyhedra, giving a channel approximately 5 Å wide. The network found in the pyrochlore structure is built of channels formed by six corner-linked octahedra. In $\text{Rb}_5\text{Sb}_7\text{TiO}_{22}$, the Rb atoms are located in the channels, with Rb1 in the narrow channels, Rb3 in the wider ones, and Rb2 in both types. Both channels run along $[110]$ and $[\bar{1}\bar{1}0]$. Rb1 and Rb2 are each coordinated by ten O atoms and Rb3 is coordinated by nine O atoms. Rb—O bond distances are in the range $2.673(5)–3.575(7) \text{ \AA}$ and are comparable to the metal–oxygen distances in RTA. The open network structure may indicate the possibility for ion exchange of Rb for other alkali metal ions, an experiment which has not yet been carried out.

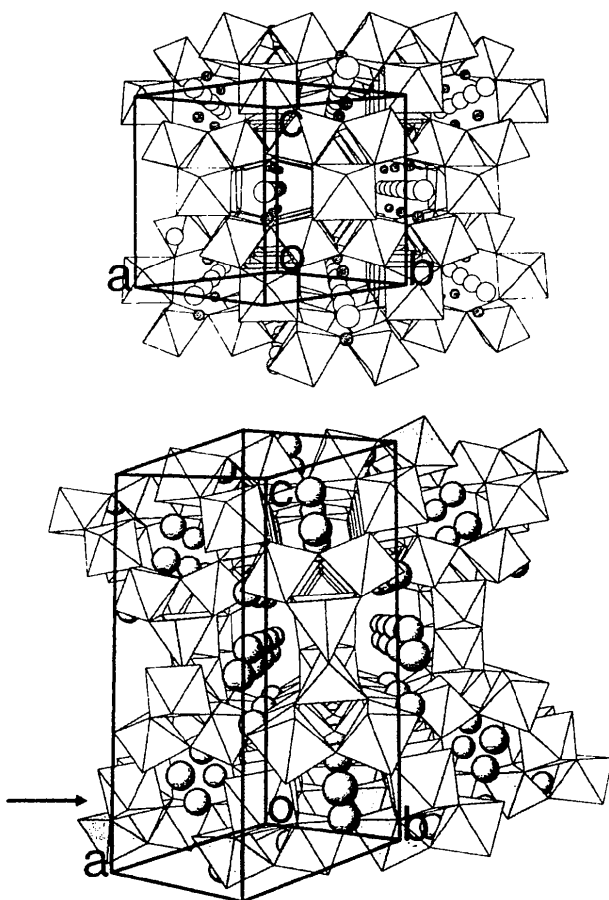


Fig. 1. The structure of $\text{Rb}_5\text{Sb}_7\text{TiO}_{22}$ (below) projected on the (110) plane. The trigonal bipyramids are shaded darkly and the Rb atoms are plotted as spheres with a radius of 0.65 \AA . An arrow indicates the pyrochlore-like building block of four octahedra forming a pyramid. The pyrochlore structure of $\text{Hg}_2\text{Sb}_2\text{O}_7$ (Sleight, 1968) is shown above. The interstitial atoms are Hg (white, plot radius 0.5 \AA) and O (dark, plot radius 0.3 \AA).

Experimental

Crystals of different compositions were synthesized by spontaneous crystallization using the method of RTA flux growth from Rb_2CO_3 , TiO_2 and As_2O_5 (Cheng *et al.*, 1994). The

As₂O₅ constituent in the recipe for RTA growth was replaced with various molar ratios of Sb₂O₅. The starting materials were all powders that were mixed thoroughly and placed in a pure platinum crucible before being heated in a chamber furnace. A flux melt was obtained when the powder mixture was heated to 1473 K, and crystallization was achieved after rapid cooling to 1173 K, slower cooling to 1123 K at a rate of 0.5 K h⁻¹, and finally to room temperature at a rate of 70 K h⁻¹. Crystals were recovered by flux dissolution in hot dilute hydrochloric acid. The phases formed were analysed by powder diffraction. Up to 10 mol% of Sb₂O₅ in the flux resulted in RTA [orthorhombic with space group *Pna*2₁ (Thomas *et al.*, 1992)], while 25 to 50 mol% gave only Rb₅Sb₇TiO₂₂. Attempts to further increase the Sb₂O₅ flux content did not give any visible crystals. It was not possible to detect any mixed compounds of Rb₅Sb₇TiO₂₂ and RTA, and the border between the two phase fields lies somewhere between 10 and 25 mol% of Sb₂O₅ in the flux.

Crystal data

Rb₅Sb₇TiO₂₂
M_r = 1679.50
 Monoclinic
*C*2/*c*
a = 10.263 (2) Å
b = 10.270 (2) Å
c = 20.420 (2) Å
 β = 98.38 (3)°
V = 2129.31 (6) Å³
Z = 4
D_x = 5.239 Mg m⁻³
D_m not measured

Data collection

Siemens SMART CCD
 diffractometer
 3° ω rotation frame
 exposure
 Absorption correction:
 Gaussian (see below)
T_{min} = 0.092, *T_{max}* = 0.381
 18 648 measured reflections

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.050
wR (*F*²) = 0.100
S = 1.273
 4303 reflections
 162 parameters
w = 1/[σ²(*F_o*²) + (0.0607*P*)²]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.003

Sb1—O10	2.030 (5)	Sb3—O9	2.046 (6)
Sb2—O1	1.917 (5)	Sb4—O10	1.823 (6)
Sb2—O4	1.919 (5)	Sb4—O9	1.827 (5)
Sb2—O7	1.953 (5)	Sb4—O7 ^{iv}	1.871 (6)
Sb2—O2	1.992 (5)	Sb4—O8 ^v	1.967 (4)
Sb2—O2 ⁱⁱ	1.996 (5)	Sb4—O8	2.136 (5)
Sb2—O8	2.079 (4)		
O6—Sb1—O1	91.7 (2)	O10—Sb4—O7 ^{iv}	95.5 (3)
O6—Sb1—O10	90.9 (3)	O9—Sb4—O7 ^{iv}	93.5 (3)
O1—Sb1—O10	89.7 (2)	O10—Sb4—O8 ^v	117.9 (3)
O1—Sb2—O4	99.7 (2)	O9—Sb4—O8 ^v	115.7 (3)
O1—Sb2—O8	91.4 (2)	O7 ^{iv} —Sb4—O8 ^v	98.1 (2)
O4—Sb2—O8	91.7 (2)	O10—Sb4—O8	88.6 (2)
O6—Sb3—O4	94.9 (2)	O9—Sb4—O8	89.5 (2)
O6—Sb3—O9	92.5 (3)	O7 ^{iv} —Sb4—O8	172.4 (2)
O4—Sb3—O9	86.2 (2)	O8 ^v —Sb4—O8	74.3 (2)
O10—Sb4—O9	123.5 (3)		

Symmetry codes: (i) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (ii) $2 - x, -y, 1 - z$; (iii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $x - \frac{1}{2}, \frac{1}{2} + y, z$; (v) $\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$.

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 6872
 reflections
 θ = 2.02–34.28°
 μ = 20.553 mm⁻¹
T = 293 (2) K
 Square plate
 0.16 × 0.16 × 0.05 mm
 Colourless

A first data collection was made with imaging plates at beamline X7B at the National Synchrotron Light Source, Brookhaven National Laboratories, USA. This was used for determining the space group and unit-cell dimensions. To complete the structural solution, new data were needed due to problems with the absorption correction. For this, a Siemens CCD camera area detector was used. As absorption is severe, two methods of absorption correction were applied. Face indexing was carried out but half of the O atoms showed odd anisotropy of the atomic displacement parameters. Therefore, this correction was compared to a multi-scan correction based on the whole sphere of diffraction spots, using the program *SADABS* (Sheldrick, 1994). This gave the same result as the Gaussian absorption correction. A third data set was collected on a CAD-4 diffractometer which showed the same refined structure, including the odd anisotropic displacement parameters. A new crystal from the same batch was also studied; CAD-4 data gave the same result as before. We tried to refine the structure in the non-centrosymmetric space group *Cc*, but that did not improve the result. An attempt was also made to refine third-order anharmonic tensors for heavy atoms using the program *JANA98* (Petříček & Dušek, 1997). This, however, did not result in any improvements. The Sb4 site could not have full occupation of Sb, and Ti atoms were thus refined at the trigonal-bipyramidal coordination site. The total occupancy factor was set to 1, and Sb4 and Ti1 occupancies were allowed to change within this constraint. These refined closely to 50/50 disorder [the Sb4 occupancy was 0.490 (3) and the Ti equivalent was 0.510 (3)] and both occupation factors were set to 0.5 in the final refinements. Atomic coordinates and displacement parameters for Ti1 were set to the values of Sb4. Final maximum and minimum Δρ values were found near the Sb atoms.

Data collection: *SMART* (Siemens, 1994). Cell refinement: *SMART*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

Table 1. Selected geometric parameters (Å, °)

Sb1—O5 ⁱ	1.913 (5)	Sb3—O5	1.910 (5)
Sb1—O6	1.928 (6)	Sb3—O6	1.941 (6)
Sb1—O3	1.970 (5)	Sb3—O12	1.957 (3)
Sb1—O11	1.974 (3)	Sb3—O3 ⁱⁱⁱ	1.961 (5)
Sb1—O1	1.981 (5)	Sb3—O4	1.983 (5)

We are grateful to Dr Jon C. Hanson at Brookhaven National Laboratories for help with the first data collection and the initial structure solution, and to Dr Vratislav Langer at the University of Gothenburgh for help with the Siemens diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1383). Services for accessing these data are described at the back of the journal.

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A Mixed Zinc–Nickel *cyclo*-Tetraphosphate, ZnNiP₄O₁₂

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Abstract

Zinc nickel *cyclo*-tetraphosphate is composed of cyclic [P₄O₁₂] groups forming sheets parallel to the crystallographic (100) plane. These sheets are separated by zigzag chains of alternating NiO₆ or ZnO₆ octahedra that share a common edge, the cations being statistically disordered. The chains are extended along the *c*

axis and link two consecutive sheets, thus ensuring the cohesion of the structure.

Comment

The structures of the tetrametaphosphates of bivalent ions, M₂P₄O₁₂ (M = Mg, Mn, Fe, Co, Ni, Zn and Cd), are well known (Beucher & Grenier, 1968; Shchegrov *et al.*, 1989; Nord, 1982; Nord *et al.*, 1990; Averbuch-Pouchot & Durif, 1983). They crystallize in the monoclinic system with the same space group, C2/c. However, only the structures of Cu₂P₄O₁₂ and Mg₂P₄O₁₂ are based on single-crystal measurements (Nord & Lindberg, 1975*a,b*; Läggt *et al.*, 1972; Genkina *et al.*, 1985). In these structures, the metal ions occupy two octahedral sites with different symmetries: 1̄ for M^I and 2 for M^{II}. Moreover, the M^IO₆ site is generally slightly smaller than the M^{II}O₆ site. The frameworks of all the M₂P₄O₁₂ structures show a succession of planes formed by the cyclic P₄O₁₂ groups, linked by chains of alternating edge-sharing M^IO₆ and M^{II}O₆ octahedra.

The magnetic study of the phosphates M₂P₄O₁₂ (M = Mn, Co, Ni and Cu) reveals the existence of chains of paramagnetic ions that confer monodimensional magnetic behaviour (Gunsser *et al.*, 1989). Exceptionally, Cd₂P₄O₁₂ presents a high-pressure phase in which the structure is composed of long chains of polyphosphates instead of P₄O₁₂ *cyclo*-tetraphosphates (Averbuch-Pouchot & Durif, 1983).

Unlike the aforementioned monometallic phosphates, the tetrametaphosphates of mixed bivalent ions have been scarcely studied. NiCoP₄O₁₂ and NiZnP₄O₁₂ have been studied by neutron powder diffraction (Nord, 1983). They belong to the same family as the monometallic phosphates M₂P₄O₁₂, with monoclinic symmetry C2/c. They show two mixed cationic sites, M^IO₆ and M^{II}O₆, unequally occupied. The smaller ions, Ni²⁺, prefer to lodge in the M^I sites, while the Zn²⁺ or Co²⁺ ions have a tendency to occupy the larger M^{II} sites. We must point out that the NiCoP₄O₁₂ and NiZnP₄O₁₂ samples prepared by Nord (1983) were quenched in liquid nitrogen. Consequently, the Zn²⁺, Co²⁺ and Ni²⁺ ions are partially disordered over both kinds of sites. We thus thought it useful to prepare single crystals of the mixed tetrametaphosphate NiZnP₄O₁₂ in order to establish whether a cationic structural order was achieved.

During the crystal structure solution and refinement it was not possible to distinguish the Zn²⁺ and Ni²⁺ cations and mixed-atom sites were therefore considered with *x*Zn + *y*Ni on site I, denoted M^I, and (½ - *x*)Zn + (½ - *y*)Ni on site II, denoted M^{II}, where *x* + *y* = ½. Best refinement results were obtained for *x* = *y* = ¼, indicating that the Zn²⁺ and Ni²⁺ cations are fully disordered on the M^I and M^{II} sites. This partition can be related to the thermodynamic conditions necessary for the preparation of the single crystals, which were obtained by a slow decrease of the temperature, allowing