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Synthesis, Thermal Stability, and Crystal Structure of Antimony(V) Phosphate $SbOPO_4$

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The compound $SbOPO_4$ was prepared two different ways: thermal decomposition of the phosphatoantimonic acid $HSbP_2O_8 \cdot xH_2O$ or synthesis at 1173 K from a stoichiometric mixture of $Sb_2O_5 \cdot xH_2O$ and $(NH_4)H_2PO_4$. At 1218 K $SbOPO_4$ undergoes a deoxidation process leading to the Sb(III) phosphate $SbPO_4$. $SbOPO_4$ crystallizes in the monoclinic system, space group $C2/c$ with $a = 6.791(1)$ Å, $b = 8.033(1)$ Å, $c = 7.046(1)$ Å, $\beta = 115.90(1)°$, $Z = 4$. The structure was determined from 481 reflexions collected on a NONIUS CAD4 automatic diffractometer with Mo$K\bar{\alpha}$ radiation. The final R index and weighted R_w index are 0.028 and 0.035, respectively. The structure is built up from chains of corner-shared SbO_6 octahedra, parallel to the c axis, crosslinked by corner-shared tetrahedra. Each phosphate group is bonded to four SbO_6 octahedra of which two belong to the same chain. This structure is closely related to that of β-$VOSO_4$ and β-$VOPO_4$.

Introduction

The existence of $SbOPO_4$ was first reported by Nevskaya *et al.* (*1*) and then, in a paper devoted to the As(V) and Sb(V) phosphates $M^VH(PO_4)_2 \cdot H_2O$, by Chernorukov *et al.* (*2*) who have obtained this compound as the final product in the thermogravimetric analysis of $HSbP_2O_8 \cdot nH_2O$ at 823 K. The $SbOPO_4$ powder spectrum given seems to be related to those of As_2O_5 and $AsOPO_4$ but there is no further structural information such as lattice parameters or crystal symmetry to support this comparison. By ionic exchange on $KSbP_2O_8$ (*3*), we recently prepared the phosphatoantimonic acid $HSbP_2O_8 \cdot nH_2O$ mentioned above (*4*) and performed its thermogravimetric analysis. When the layers reach condensation the compound obtained is $SbOPO_4$ but its powder spectrum is completely different from the one given in (*2*). Along with the synthesis, crystal growth, and thermal stability of $SbOPO_4$ this paper reports the refinement and description of its crystal structure.

Synthesis and Thermal Stability

The starting materials for synthesizing $SbOPO_4$ were $(NH_4)H_2PO_4$ (GR grade, Merck) and $Sb_2O_5 \cdot nH_2O$. Antimonic acid was prepared by stirring Sb_2O_3 (GR grade, Merck) in a 31% (by weight) H_2O_2 solution for 24 hr at 353 K. The resulting solid was then separated from the solution on a centrifuge, washed repeatedly with deionized water, and dried in an oven at 333 K. The water content of the material obtained was inferred from a thermogravimetric analysis.

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TABLE I

UNIT CELL CONSTANTS

Crystal symmetry	Monoclinic
a (Å)	6.791(1)
b (Å)	8.033(1)
c (Å)	7.046(1)
β (°)	115.90 (1)
V (Å^3)	345.76
d_{cal} (g · cm^{-3})	4.470
d_{obs} (g · cm^{-3})	4.42 ± 0.07
Z	4
Space group	$C2/c$
μ (cm^{-1}) for $\lambda K\bar{\alpha}$ = 0.71069 Å	83.7

The reactants were weighed out in the stoichiometric ratio and the mixture was heated in a platinum crucible at 473 K for 4 hr to decompose the $(NH_4)H_2PO_4$ before calcining at 1173 K for 12 hr in air. The crystals obtained are colorless thin needles elongated along the [102] direction. Single-crystal X-ray study indicates monoclinic symmetry. The parameters (Table I) were least-squares refined from a Guinier powder spectrum (Guinier-Nonius FR 552, $\lambda CuK\alpha_1$ = 1.54056 Å, quartz crystal monochromator, $Pb(NO_3)_2$ as standard) (Table II). The powder pattern includes the observed and calculated interplanar distances of the reflexion planes along with the intensities calculated from the Lazy-Pulverix program (*5*). The density of $SbOPO_4$ was determined experimentally by its apparent loss of weight in carbon tetrachloride. It was found to be 4.42 in fair agreement with the calculated value of 4.470 for four formula units in the unit cell.

The thermal analysis was performed on a Perkin-Elmer Model 1700 DTA system, Al_2O_3 as standard, heating rate 2 K.mn^{-1}, Model TGS-2 TGA system, heating rate 2 K.mn^{-1}. There is no thermal phenomenon before 1218 K. At this temperature a weight loss occurs corresponding to the change from $SbOPO_4$ to $SbPO_4$. This final product was identified by its X-ray powder spectrum (*6*). The observed weight loss of 6.9 ± 0.1% agrees well with the theoretical value of 6.87% calculated for the deoxidation process.

TABLE II

$SbOPO_4$ X-RAY POWDER DIFFRACTION DATA

$h\,k\,l$	d_{obs} (Å)	d_{calc} (Å)	I/I_0	$h\,k\,l$	d_{obs} (Å)	d_{calc} (Å)	I/I_0
1 1 0	4.850	4.863	100.0	$3\,1\,\bar{3}$		1.898	0.0
$1\,1\,\bar{1}$	4.740	4.734	12.5	0 2 3		1.870	0.5
0 2 0	4.020	4.016	28.6	2 0 2	1.836	1.835	1.3
0 2 1	3.390	3.393	8.3	1 3 2	1.792	1.793	4.2
1 1 1	3.339	3.338	6.0	$1\,3\,\bar{3}$		1.761	0.0
$1\,1\,\bar{2}$	3.216	3.215	64.5	$2\,0\,\bar{4}$	1.753	1.754	6.3
0 0 2	3.170	3.169	9.5	1 1 3		1.730	0.0
2 0 0	3.055	3.054	33.0	$2\,4\,\bar{1}$		1.728	0.1
$2\,0\,\bar{2}$	2.929	2.930	5.8	$3\,3\,\bar{1}$		1.720	0.1
$2\,2\,\bar{1}$	2.590	2.591	4.0	$3\,3\,\bar{2}$	1.703	1.703	3.2
0 2 2	2.489	2.488	27.0	0 4 2	1.696	1.696	10.3
1 3 0	2.451	2.452	23.7	$4\,0\,\bar{2}$		1.696	3.7
$1\,3\,\bar{1}$	2.433	2.435	0.0	3 1 1	1.690	1.692	0.5
2 2 0		2.431	9.3	$1\,1\,\bar{4}$		1.690	8.8
$2\,2\,\bar{2}$	2.366	2.367	8.0	2 4 0	1.677	1.678	5.0
1 1 2	2.313	2.313	9.7	2 2 2	1.669	1.669	12.0
$1\,1\,\bar{3}$		2.244	0.2	$2\,4\,\bar{2}$	1.656	1.656	11.6
1 3 1	2.163	2.163	3.0	3 3 0	1.621	1.621	11.1
$3\,1\,\bar{1}$		2.162	0.2	$3\,1\,\bar{4}$	1.612	1.613	3.7
$1\,3\,\bar{2}$	2.128	2.129	8.6	$2\,2\,\bar{4}$	1.607	1.608	6.5
$3\,1\,\bar{2}$		2.128	15.1	0 0 4	1.585	1.585	2.7
2 2 1		2.045	0.1	$3\,3\,\bar{3}$		1.578	0.2
0 4 0	2.008	2.008	6.1	$4\,2\,\bar{2}$	1.562	1.562	6.2
3 1 0	1.972	1.974	15.4	1 5 0	1.554	1.554	4.8
$2\,2\,\bar{3}$		1.969	3.1	$1\,5\,\bar{1}$		1.549	0.0
0 4 1		1.915	0.2				

TABLE III

DATA COLLECTION AND REFINEMENT CONDITIONS

Data collection	
Radiation (Å)	$MoK\bar{\alpha}$ λ = 0.71069
Scan mode	$\omega - 2\theta$
Scan angle (°)	$\Delta\omega = 1.0 + 0.35 \tan\theta$
Recording angular range (θ°)	1.5 − 35.0
Number of independent data observed with $\sigma(I)/I < 0.33$ (used in refinements)	481
Refinements	
Number of variables (Isotropic temperature factors)	15
$R = \Sigma\lvert F_0\rvert - \lvert F_c\rvert/\Sigma\lvert F_0\rvert$	0.032
$R_w = [\Sigma w(\lvert F_0\rvert - \lvert F_c\rvert)^2/\Sigma F_0^2]^{1/2}$ with $w = 1$	0.042
Number of variables (Anisotropic temperature factors)	36
R =	0.028
R_w = with $w = 1/(1 + [(F_{obs} - F_{av})/F_{max}]^2)$	0.035
Extinction parameter refined g =	$0.67(2) \times 10^{-5}$

Data Collection and Structure Determination

The intensity data were collected from a small needle-shaped crystal (0.02 × 0.02 × 0.10 mm^3) on a Nonius CAD4 automatic diffractometer using graphite monochromated Mo$K\bar{\alpha}$ radiation. Conditions for data collection are given in Table III. For $SbOPO_4$ the calculated linear absorption coefficient μ is 83.7 cm^{-1} and as the crystal was very small no absorption correction was applied. For the data reduction, structure solution, and refinement, the SDP-PLUS program chain (1982 version) of Enraf-Nonius, written by B. Frenz (*7*), was used.

The positional parameters for the antimony atoms were determined from the three-dimensional Patterson map. In the first stage of refinement, the isotropic temperature factor of the unique Sb atom was refined. With use of these data, a Fourier difference map was computed which revealed the positions of the phosphorus and oxygen atoms. In the subsequent stage of refinement the positional parameters and isotropic temperature factors were refined to $R = 0.032$ and $R_w = 0.042$. Then anisotropic temperature factors were assigned to all atoms. The final stage of refinement with corrections for secondary extinction and anomalous dispersion converged to final $R = 0.028$ and $R_w = 0.035$. The final Fourier difference map is featureless with maxima and minima in the range ±0.8 e/Å^3. Details of the different stages of refinement are given in Table III. Table IV presents the final atomic coordinates and thermal parameters (structure factor table to be sent upon request).

Description and Discussion of the Structure

The crystal structure of $SbOPO_4$ may be described as consisting of chains of corner-sharing SbO_6 octahedra running parallel to the *c* axis. The chains are linked together by PO_4 tetrahedra thus giving a three-dimensional network (Fig. 1). Each PO_4 tetra-

TABLE IV

FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS

Atom	Position	x	y	z	B_{eq}[a] (Å^2)
Sb	4a	0	0	0	0.387(6)
P	4e	0	0.3348(3)	$\frac{1}{4}$	0.54 (4)
O(1)	4e	0	0.9105(9)	$\frac{1}{4}$	0.7 (1)
O(2)	8f	0.5884(7)	0.2751(6)	0.6254(7)	0.74 (8)
O(3)	8f	0.1848(7)	0.4440(7)	0.4012(8)	0.93 (8)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb	0.00317(6)	0.00127(5)	0.00242(6)	0.0009(3)	0.00280(9)	0.0004(3)
P	0.0043 (4)	0.0011 (3)	0.0043 (3)	0	0.0038 (5)	0
O(1)	0.007 (1)	0.0018 (8)	0.003 (1)	0	0.004 (2)	0
O(2)	0.0052 (8)	0.0022 (6)	0.0064 (8)	0.004 (1)	0.007 (1)	0.004 (1)
O(3)	0.0041 (8)	0.0035 (6)	0.0080 (8)	−0.003 (1)	0.006 (1)	−0.004 (1)

Note. Expression for anisotropic temperature factors:

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)].$$

[a] $B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\vec{a}_i\vec{a}_j$.

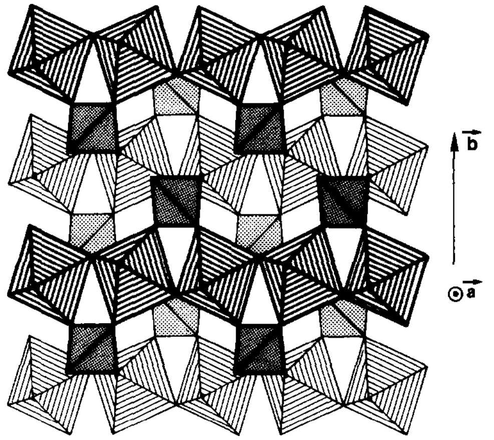

FIG. 1. [100] view of $SbOPO_4$. The polyhedra with dark and light outlines lie at the levels $x = \frac{1}{2}$ and $x = 0$, respectively.

hedron is bonded to four different SbO_6 octahedra of which two belong to the same chain (Fig. 2), and each octahedron is bonded to four tetrahedra and two octahedra. This disposition of the polyhedra was also found in β-$VOSO_4$ (*8*), β-$VOPO_4$ (*9*) and in many monohydrated sulfates or selenates $MM'O_4 \cdot H_2O$ (*10–16*). For these monohydrates, a systematic study of the packing of octahedra and tetrahedra (in equal number) was carried out (*17*). It leads to only eight possible types of structures and this classification can also apply to most of the $MM'O_5$ compounds where M and M′ are, respectively, octahedrally and tetrahedrally coordinated to oxygen atoms. According to this theoretical study compounds such as $MoOPO_4$ (*18*), $NbOPO_4$ (*19*), $VOMoO_4$ (*20*), α-$VOSO_4$ (*21*) belong to the second structural type in which each tetrahedron links, via its four vertices, four chains of corner-sharing octahedra. Among the $MM'O_5$ above mentioned β-$VOSO_4$, β-$VOPO_4$ and $SbOPO_4$ belong to the third

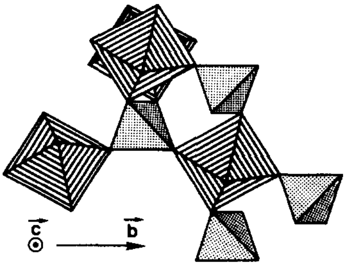

FIG. 2. [001] view of a fragment of $SbOPO_4$ showing a tetrahedron linking three chains of octahedra and an octahedron bonded to four tetrahedra.

TABLE V

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR THE COORDINATION POLYHEDRA

Sb–O(1)(×2)	1.903(3)	O(1)–Sb–O(1)	180.0(4)
Sb–O(2)(×2)	1.985(5)	O(1)–Sb–O(2)(×2)	93.1(2)
Sb–O(3)(×2)	1.992(5)	O(1)–Sb–O(2)(×2)	86.9(2)
		O(1)–Sb–O(3)(×2)	88.5(2)
		O(1)–Sb–O(3)(×2)	91.5(2)
		O(2)–Sb–O(2)	180.0(3)
		O(2)–Sb–O(3)(×2)	91.1(2)
		O(2)–Sb–O(3)(×2)	88.9(2)
		O(3)–Sb–O(3)	180.0(3)
P–O(2)(×2)	1.540(5)	O(2)–P –O(2)	110.0(4)
P–O(3)(×2)	1.520(5)	O(2)–P –O(3)(×2)	109.8(3)
		O(2)–P –O(3)(×2)	108.8(3)
		O(3)–P –O(3)	109.5(5)

O(1)–O(2)(×2)	2.674(6)	O(1)–O(2)(×2)	2.823(8)	O(1)–O(3)(×2)	2.789(5)
O(1)–O(3)(×2)	2.719(6)	O(2)–O(3)(×2)	2.840(7)	O(2)–O(3)(×2)	2.784(7)
O(2)–O(2)	2.523(9)	O(2)–O(3)	2.504(7)	O(2)–O(3)	2.488(7)
O(3)–O(3)	2.483(9)				

structural type defined in (*17*) whereas As_2O_5 (*22*) does not correspond to any of them. In this latter compound each tetrahedron is linked to four different AsO_6 octahedra belonging to two chains of corner-sharing octahedra. Such a combination, which needs highly distorted polyhedra, leads to the same synoptic formula as for types 2 and 3 in (*17*) but cannot enter the classification which assume for the idealized structures, O–O distances in the $M'O_4$ tetrahedra shorter than the O–O distances in the MO_6 octahedra.

For $SbOPO_4$ a list of bond distances and bond angles along with their standard deviations is given in Table V. It can be seen from this table that all distances are reasonable and in good agreement with previous knowledge of phosphate and antimony(V) structural chemistry. The phosphate group is almost a regular tetrahedron with two P–O distances of 1.540(5) Å and two of 1.520(5) Å while the O–O distances are ranging from 2.483(9) to 2.523(9) Å. These values give an average O–P–O angle within the tetrahedron of 109.5°. The SbO_6 octahedron is distorted with three pairs of Sb–O distances: 1.992(5), 1.985(5), and 1.903(3) Å. This latter value corresponds to the oxygen atom bonded to two antimony atoms. Despite these two shorter distances the SbO_6 octahedron is more regular than the VO_6 octahedron in β-$VOSO_4$ (*8*) and β-$VOPO_4$ (*9*).

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