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Preparation and Crystal Structure of K_2SbPO_6

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The single phase compound K_2SbPO_6 was prepared by a solid-state reaction. It crystallizes in the orthorhombic system, space group *Pnma* with $a = 9.429(4)$ Å, $b = 5.891(3)$ Å, $c = 11.030(5)$ Å, $Z = 4$. The structure was determined from 561 reflexions collected on a Nonius CAD4 automatic diffractometer with MoK$\bar{\alpha}$ radiation. The final R index and weighted R_w index are 0.038 and 0.044, respectively. The structure is built up from rutile-like strings of edge shared SbO_6 octahedra to which phosphate groups are linked by two of their vertices. These chains, running parallel to the b-axis, are separated from each other by potassium atoms.

Introduction

Within a research program devoted to compounds likely to exhibit fast alkali-ion mobility, our structural studies of phases occurring in the K_2O–Sb_2O_5–P_2O_5 system have found some promising materials:

—$K_3Sb_3P_2O_{14}$ (*1*) and $KSbP_2O_8$ (*2*) in which potassium atoms are situated between covalent layers.

—KSb_2PO_8 (*3*) and $K_5Sb_5P_2O_{20}$ (*4, 5*) which have three-dimensional frameworks delimiting large channels wherein potassium atoms are situated.

This paper reports the preparation and crystal structure determination of a new compound isolated in the course of our investigations in the K_2O–Sb_2O_5–P_2O_5 system: K_2SbPO_6.

Experimental

The starting materials for synthesizing K_2SbPO_6 were $K_2HPO_4 \cdot 3H_2O$ (GR Grade, Merck) and $Sb_2O_5 \cdot nH_2O$ which was prepared and analyzed as has been described previously (*6*). The chemicals were weighed out in the stoichiometric ratio and the mixture was heated, in a platinum crucible, at 1173 K for 12 hr. The crystals obtained are colorless thin needles elongated along the [010] direction. Single crystal X-ray study indicates that the compound is of orthorhombic symmetry. The cell parameters (Table I) were least-squares refined

TABLE I

UNIT CELL CONSTANTS

Crystal symmetry	Orthorhombic
a (Å)	9.429(4)
b (Å)	5.891(3)
c (Å)	11.030(5)
V (Å^3)	612.72
d_{calc} (g · cm^{-3})	3.53
d_{obs} (g · cm^{-3})	3.50 ± 0.05
Z	4
Space group	*Pnma*
μ (cm^{-1}) for $\lambda K\bar{\alpha} = 0.71069$ Å	61.0

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from a Guinier powder spectrum (Guinier-Nonius FR 552, quartz crystal monochromator, $\lambda CuK\alpha_1$ = 1.54056 Å, $Pb(NO_3)_2$ as standard) (Table II). The powder pattern includes observed and calculated interplanar distances of the reflexion planes along with the intensities calculated from the Lazy-Pulverix program (*7*). The density of K_2SbPO_6 was determined experimentally by its apparent loss of weight in carbon tetrachloride. It was found to be 3.50 g cm^{-3} in fair agreement with the calculated value of 3.53 g cm^{-3} for four formula units in the unit cell. Intensity data were collected from a needle-shaped crystal (0.02 × 0.01 × 0.12 mm^3) rotating along the [010] axis, on a Nonius CAD4 diffractometer using the conditions for data collection given in Table III. For the data reduction, structure solution and refinement, the SDP-PLUS program chain (1982 version) of Enraf-Nonius, written by Frenz, was used (*8*).

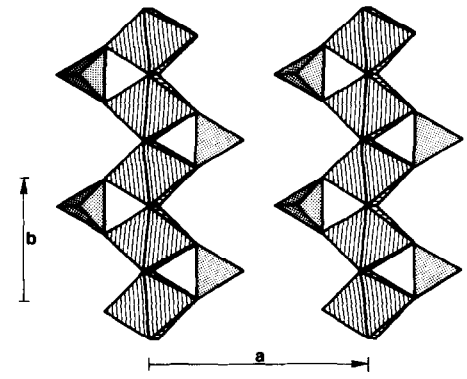

FIG. 1. [001] view of two $(SbPO_6^{2-})_n$ chains corresponding to antimony atoms lying at $z = 0$.

TABLE II

K_2SbPO_6 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 0 1	7.178	7.167	100.0	4 0 2	2.167	2.168	13.6
0 0 2	5.511	5.515	59.0	1 0 5	2.148	2.148	2.4
0 1 1		5.197	0.0	4 1 1		2.147	0.3
1 0 2		4.760	0.0	3 2 1		2.110	0.7
2 0 0	4.719	4.715	11.3	3 0 4		2.073	0.3
1 1 1	4.551	4.551	4.5	2 2 3	2.066	2.066	0.9
2 0 1		4.335	0.0	0 1 5		2.066	1.0
1 1 2		3.703	0.6	4 1 2		2.034	1.0
2 1 0		3.681	1.2	1 1 5		2.018	0.1
2 0 2	3.581	3.584	16.7	0 2 4	2.013	2.013	11.4
2 1 1		3.492	0.6	3 2 2		2.003	1.2
1 0 3	3.424	3.425	36.4	2 0 5		1.998	0.3
0 1 3		3.119	0.4	4 0 3		1.984	0.3
2 1 2	3.062	3.062	10.4	1 2 4		1.969	0.0
3 0 1	3.021	3.023	39.4	3 1 4		1.955	0.4
1 1 3	2.962	2.961	16.4	0 3 1		1.933	0.0
0 2 0		2.946	0.6	1 3 1		1.894	0.0
2 0 3		2.899	0.6	2 1 5		1.892	0.0
0 0 4	2.755	2.757	5.1	4 1 3		1.881	0.0
3 0 2	2.724	2.731	0.8	5 0 1	1.858	1.859	6.0
1 2 1		2.725	42.0	3 2 3		1.856	15.6
3 1 1		2.689	1.6	2 2 4	1.850	1.851	13.8
1 0 4		2.647	1.3	4 2 0	1.840	1.841	7.4
2 1 3	2.597	2.610	0.9	0 0 6		1.838	5.9
0 2 2		2.598	18.9	1 3 2	1.815	1.815	0.0
1 2 2		2.505	0.7	4 2 1		1.815	1.8
2 2 0	2.499	2.498	7.8	2 3 0		1.813	0.0
3 1 2		2.478	0.7	3 0 5	1.806	1.806	6.3
2 2 1		2.436	0.0	1 0 6		1.804	0.0
1 1 4		2.414	0.4	4 0 4	1.792	1.792	5.2
3 0 3		2.389	0.9	2 3 1		1.789	0.0
2 0 4		2.380	1.3	5 0 2		1.784	0.0
4 0 0	2.358	2.357	3.4	5 1 1		1.773	0.0
4 0 1	2.305	2.305	2.8	4 2 2	1.746	1.746	4.8
2 2 2	2.276	2.276	9.7	1 2 5	1.736	1.736	14.2
1 2 3	2.232	2.233	11.5	0 3 3		1.732	0.2
3 1 3		2.214	0.2	3 1 5		1.726	0.3
2 1 4		2.207	0.2	1 1 6		1.725	0.3
4 1 0		2.189	0.2	2 3 2	1.714	1.714	2.2

Refinement of the Structure

Refinement was carried out by the full-matrix least-squares method. The posi-

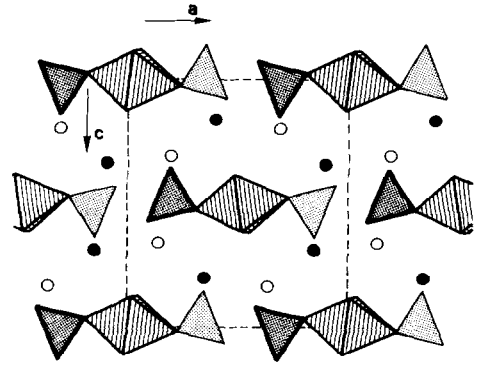

FIG. 2. [010] view of K_2SbPO_6. The tetrahedra with dark and light outlines correspond to phosphorus atoms lying at levels $y = \frac{3}{4}$ and $y = \frac{1}{4}$, respectively. For the same y levels potassium atoms are represented by black and white circles, respectively.

TABLE III

DATA COLLECTION AND REFINEMENT CONDITIONS

Data collection	
Equipment	Nonius CAD4 diffractometer
Radiation (Å)	$\lambda MoK\bar{\alpha}$ $\lambda = 0.71069$
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)	561
No absorption correction	
Refinements	
Number of variables (isotropic temperature factors)	28
$R = \Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|$	0.063
$R_w = [\Sigma\, w(\|F_o\| - \|F_c\|)^2/\Sigma\, F_o^2]^{1/2}$ with $w = 1$	0.069
Number of variables (anisotropic temperature factors)	59
R =	0.038
R_w =	0.044
with $w = 1/(1 + [(F_{obs} - F_{av})/F_{max}]^2)$	
Extinction parameter refined g =	$0.26(3) \times 10^{-6}$

TABLE IV

FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS

Atom	Position	x	y	z	B_{eq}[a] (Å^2)
Sb	4a	0	0	0	0.743(7)
K(1)	4c	0.1724(4)	¼	0.3060(3)	1.80 (6)
K(2)	4c	0.1192(4)	¼	0.6606(3)	1.70 (5)
P	4c	0.8038(3)	¼	0.5094(4)	0.85 (4)
O(1)	4c	0.467 (1)	¼	0.3817(9)	0.8 (1)
O(2)	4c	0.501 (2)	¼	0.6167(8)	1.0 (1)
O(3)	4c	0.929 (1)	¼	0.426 (1)	1.5 (2)
O(4)	4c	0.830 (1)	¼	0.644 (1)	1.9 (2)
O(5)	8d	0.2893(6)	0.538(1)	0.5270(7)	1.5 (1)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb	0.00178(4)	0.0036(1)	0.00225(3)	−0.0001(3)	−0.0001(2)	0.0003(4)
K(1)	0.0036 (3)	0.015 (1)	0.0042 (2)	0	−0.0002(5)	0
K(2)	0.0037 (3)	0.0141(9)	0.0037 (2)	0	0.0009(5)	0
P	0.0016 (2)	0.0050(6)	0.0027 (2)	0	0.0002(6)	0
O(1)	0.0029 (9)	0.002 (2)	0.0020 (6)	0	−0.001 (1)	0
O(2)	0.0031 (7)	0.006 (2)	0.0022 (5)	0	0.000 (2)	0
O(3)	0.0023 (9)	0.009 (3)	0.0051 (9)	0	0.003 (2)	0
O(4)	0.005 (1)	0.017 (4)	0.0038 (8)	0	0.002 (2)	0
O(5)	0.0010 (4)	0.009 (2)	0.0058 (7)	−0.001 (1)	0.0010(8)	0.003 (2)

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

tional 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 potassium, phosphorus, and oxygen atoms. In the subsequent stage of refinement the positional parameters and isotropic temperature factors of the nine unique atoms were refined to $R = 0.063$ and $R_w = 0.069$. 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 $R = 0.038$ and $R_w = 0.044$. 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 will be sent upon request).

Description and Discussion of the Structure

In the structure of K_2SbPO_6 the SbO_6 octahedra and PO_4 tetrahedra are arranged in infinite chains running parallel to the *b*-axis. The SbO_6 octahedra are linked together by sharing edges thus forming a somewhat staggered string (Fig. 1). In this rutile-like string, each outwardly pointing vertex O(5), as yet unshared, of every SbO_6 octahedron joins with one PO_4 tetrahedron, so that each tetrahedron links two octahedra and has two unshared vertices. The $(SbPO_6^{2-})_n$ chains are separated from each other by the potassium atoms (Fig. 2).

A list of bond distances and bond angles

TABLE V

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

Sb—O(1)(×2)	1.995(8)		O(1)—Sb—O(1)	180.0(7)			
Sb—O(2)(×2)	1.958(8)		O(1)—Sb—O(2)(×2)	82.8(3)			
Sb—O(5)(×2)	2.023(6)		O(1)—Sb—O(2)(×2)	97.2(3)			
			O(1)—Sb—O(5)(×2)	91.4(5)			
			O(1)—Sb—O(5)(×2)	88.6(5)			
			O(2)—Sb—O(2)	180.(9)			
			O(2)—Sb—O(5)(×2)	89.5(5)			
			O(2)—Sb—O(5)(×2)	90.5(5)			
			O(5)—Sb—O(5)	180.0(5)			
P—O(3)	1.50 (1)		O(3)—P—O(4)	118.2(8)			
P—O(4)	1.50 (1)		O(3)—P—O(5)(×2)	106.4(5)			
P—O(5)(×2)	1.579(7)		O(4)—P—O(5)(×2)	110.1(5)			
			O(5)—P—O(5)	104.6(5)			
K(1)—O(1)	2.90 (1)	K(1)—O(1)	2.84 (1)	K(1)—O(2)(×2)	3.969(9)		
K(1)—O(3)	2.65 (1)	K(1)—O(3)	3.53 (1)	K(1)—O(4)(×2)	3.003(2)		
K(1)—O(5)(×2)	3.171(8)	K(1)—O(5)(×2)	3.343(9)				
K(2)—O(1)(×2)	3.914(8)	K(2)—O(2)	3.63 (1)	K(2)—O(2)	2.70 (1)		
K(2)—O(3)	3.15 (1)	K(2)—O(3)(×2)	3.136(5)	K(2)—O(4)	2.73 (1)		
K(2)—O(4)	2.94 (1)	K(2)—O(5)(×2)	2.764(8)				
O(1)—O(2)(×2)	2.61 (1)	O(1)—O(2)(×2)	2.97 (1)	O(1)—O(5)(×2)	2.88 (1)		
O(1)—O(5)(×2)	2.81 (1)	O(2)—O(5)(×2)	2.80 (1)	O(2)—O(5)(×2)	2.83 (1)		
O(3)—O(4)	2.58 (2)	O(3)—O(5)(×2)	2.47 (1)	O(4)—O(5)(×2)	2.53 (1)		
O(5)—O(5)	2.50 (1)						

along with their standard deviations is given for K_2SbPO_6 in Table V. It can be seen from this table that all distances are reasonable and in good agreement with previous knowledge of phosphate, potassium, and antimony(V) structural chemistry. The SbO_6 octahedron is slightly distorted with three pairs of Sb–O distances: 1.958(8), 1.995(8), and 2.023(6) Å. The length of the shared edge, O(1)–O(2), is 2.61(1) Å. This distance is significantly shorter than the other O–O distances within the octahedron which are ranging from 2.80(1) to 2.97(1) Å. In the case of the phosphate group, the two unshared oxygen atoms, i.e., not bonded to antimony, form two P–O bonds (1.50(1) Å) significantly shorter than the two others (1.579(7) Å). These values are very close to those which have been found in $K_3Sb_3P_2O_{14}$ (*1*) and $KSbP_2O_8$ (*2*).

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