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Crystal Structure of $KSbP_2O_8$

Y. PIFFARD,* S. OYETOLA, S. COURANT, AND A. LACHGAR

Laboratoire de Chimie des Solides, L.A. 279, 2, rue de la Houssinière, 44072 Nantes Cédex, France

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$KSbP_2O_8$ crystallizes in the rhombohedral system, space group $R\bar{3}$, with $a = 4.7623(4)$ Å, $c = 25.409(4)$ Å, and $Z = 3$. The structure was determined from 487 reflexions collected on a NONIUS CAD4 automatic diffractometer with Mo$K\bar{\alpha}$ radiation. The final R index and weighted R_w index are 0.030 and 0.038, respectively. This structure is built up from layers of SbO_6 octahedra and PO_4 tetrahedra sharing corners. These $(SbP_2O_8^-)_n$ layers are very similar to the $(ZrP_2O_8^{2-})_n$ layers in the well-known α-ZrP compound.

Introduction

A large number of phosphates of group IV and group V elements corresponding respectively to $M^{IV}(HPO_4)_2 \cdot H_2O$ and $M^{V}H(PO_4)_2 \cdot H_2O$ compositions are known (*1–3*). The X-ray diffraction patterns of these compounds and of the corresponding salts obtained by titration or ionic exchange are very similar and their structure was identified (*4, 5*) with that of $Zr(HPO_4)_2 \cdot H_2O$ (*6*) which presents a monoclinic symmetry. This structure is characterized by $(ZrP_2O_8^{2-})_n$ layers built up from ZrO_6 and PO_4 polyhedra linked by corners. The anhydrous double sulfates $A^{I}B^{III}(SO_4)_2$ (A^{I} = Cs, Rb, K, NH_4, Tl, and B^{III} = Al, Ga, Cr, Fe, In, Tl) exhibit the same type of layers which, however, lead to three different types of crystal symmetry: monoclinic, hexagonal, and rhombohedral (*7*). So far, such differences have not been evidenced for the above-mentioned phosphates.

During our investigations in the $K–Sb^{V}–P^{V}–O$ system, several phases have been identified (*8, 9*) including the compound $KSbP_2O_8$. This paper reports the refinement of its crystal structure which belongs to the rhombohedral system.

Experimental

$KSbP_2O_8$ was prepared by heating, in a platinum crucible, of stoichiometric proportions of $NH_4H_2PO_4$, KNO_3, and Sb_2O_3, at 200°C for 4 hr to decompose the

TABLE I

UNIT CELL CONSTANTS

Crystal Symmetry	Rhombohedral
a (Å)	4.7623(4)
c (Å)	25.409 (4)
V(Å^3)	499.06
d_{calc} (g · cm^{-3})	3.501
Z	3
Space group	$R\bar{3}$
μ(cm^{-1}) For λ $K\bar{\alpha}$ = 0.71069 Å	52.8

* To whom all correspondence should be addressed.

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TABLE II

$KSbP_2O_8$ 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
0 0 3	8.475	8.470	88.6	2 1 $\bar{1}$	1.556	1.556	2.3
0 0 6	4.237	4.235	7.5	1 2 $\bar{1}$			0.8
1 0 1	4.070	4.071	18.2	1 2 $\bar{2}$	1.547	1.547	0.6
0 1 2	3.928	3.923	8.1	2 1 $\bar{2}$			1.7
1 0 4	3.458	3.459	100.0	2 0 11	1.539	1.538	3.2
0 1 5	3.201	3.202	6.5	1 2 $\bar{4}$	1.514	1.514	6.7
0 0 9		2.823	0.3	2 1 4			7.8
1 0 7	2.724	2.725	8.2	2 1 $\bar{5}$	1.490	1.490	1.4
0 1 8	2.519	2.516	20.6	1 2 5			1.1
1 1 0	2.382	2.381	24.1	1 0 16	1.482	1.482	2.8
1 1 $\bar{3}$	2.293	2.292	0.2	2 1 7	1.432	1.432	1.0
1 1 3			5.8	1 2 $\bar{7}$			1.7
1 0 10	2.164	2.163	9.9	0 2 13		1.419	0.2
0 0 12		2.117	0.7	0 0 18		1.412	1.4
1 1 6	2.076	2.076	0.7	0 1 17		1.405	0.1
1 1 $\bar{6}$			13.4	1 2 8	1.399	1.399	4.8
0 2 1	2.056	2.055	2.0	2 1 $\bar{8}$			3.6
2 0 2	2.036	2.036	2.4	1 1 15	1.380	1.380	6.6
0 1 11	2.015	2.015	6.0	1 1 $\bar{15}$			2.0
0 2 4	1.962	1.961	13.0	3 0 0	1.375	1.375	10.1
2 0 5	1.911	1.911	3.6	2 0 14	1.362	1.362	2.3
1 1 9	1.821	1.820	0.9	3 0 3	1.357	1.357	1.9
1 1 $\bar{9}$			4.4	0 3 3			2.0
0 2 7	1.793	1.793	1.6	2 1 10	1.329	1.329	1.3
1 0 13		1.766	0.1	1 2 $\bar{10}$			2.6
2 0 8	1.730	1.730	9.5	3 0 6		1.308	0.9
0 0 15	1.693	1.694	1.3	0 3 6			1.0
0 1 14	1.662	1.661	5.5	1 2 11	1.292	1.292	2.6
0 2 10	1.601	1.601	3.6	2 1 $\bar{11}$			1.4
1 1 12	1.582	1.582	7.6				
1 1 $\bar{12}$			5.1				

$NH_4H_2PO_4$ and at 950°C for 24 hr to complete the reaction. The bulk of the crystals obtained are hexagonal-shaped platelets with some thin needles. Single crystal X-ray study indicates that the compound is of rhombohedral symmetry. The cell parameters (Table I) were least-squares refined from a Guinier powder spectrum (Guinier–Nonius FR 552, quartz crystal monochromator, λ Cu$K\bar{\alpha}_1$ = 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 (*10*). Intensity data were collected from a needle-shaped crystal rotating along the [1$\bar{1}$1] 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 B. Frenz (*11*) was used.

Refinement of the Structure

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

TABLE III

DATA COLLECTION AND REFINEMENT CONDITIONS

Data collection	$KSbP_2O_8$
Equipment	CAD4 Nonius diffractometer
Radiation (Å)	Mo$K\bar{\alpha}$, graphite monochromator, $\lambda = 0.71069$
Scan mode	$\omega - 2\theta$
Scan angle (°)	$\Delta\omega = 1.2 + 0.35$ tg θ
Recording angular range (θ°)	1.5–35.0
Number of independant data observed with ($\sigma(I)/I \leq 0.33$ (used in refinements)	487
No absorption correction	
Refinements	
Number of variables (isotropic temperatures factors)	12
$R = \Sigma[\lvert F_o\rvert - \lvert F_c\rvert]/\Sigma\lvert F_o\rvert$	0.061
$R_w = [\Sigma_w(\lvert F_o\rvert - F_c\rvert)^2/\Sigma F_o^2)^{1/2}$ with $w = 1$	0.070
Number of variables (anisotropic temperature factors)	21
R =	0.030
R_w = with $w = 1(1 + [(F_o - F_{aver})/F_{max}]^2)$	0.038
Extinction parameter refined g =	$0.323(2) \times 10^{-4}$

TABLE IV

FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS

Atom	Position	x	y	z	B_{eq}[a] (Å^2)
Sb	3*a*	0	0		0.447(4)
K	3*b*	0	0	$\frac{1}{2}$	2.16 (3)
P	6*c*	0	0	0.26473(5)	0.68 (1)
O(1)	6*c*	0	0	0.2067 (2)	1.43 (5)
O(2)	18*f*	0.9556(5)	0.3050(5)	0.04565(9)	0.92 (3)

	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb	0.0040(1)	β_{11}	0.00031(1)	β_{11}	0	0
K	0.0313(7)	β_{11}	0.00085(3)	β_{11}	0	0
P	0.0096(3)	β_{11}	0.00029(1)	β_{11}	0	0
O(1)	0.026 (1)	β_{11}	0.00029(5)	β_{11}	0	0
O(2)	0.0098(7)	0.0111(7)	0.00053(3)	0.011(1)	−0.0001(2)	−0.0011(2)

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

[b] Expression for anisotropic temperature factors: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

positional parameters for Sb, K, and P atoms were taken by analogy with those of Tl^{III}, Rb, and S, respectively, in the structure of $RbTl(SO_4)_2$ (*7*) and, since there are three formula units in the unit cell, in keeping with the possible unique positions of $R\bar{3}$ space group. In the first stage of refinement, z parameter for unique P atom and the isotropic temperature factors for Sb, K, and P unique atoms were refined. With use of these data, a Fourier difference map was computed which revealed the positions of the oxygen atoms. In the subsequent stage of refinement the positional parameters and isotropic temperature factors of the five unique atoms were refined to $R = 0.061$ and $R_w = 0.070$. Then anisotropic temperature factors were assigned to all atoms. Refinement converged with $R = 0.030$ and $R_w = 0.038$. The final Fourier difference map is featureless with maxima and minima in the range ± 0.35 $e/Å^3$. Details of the different stages of refinement are given in Table III. Table IV presents the final atomic coordinates and thermal parameters. (Structure factor tables will be sent upon request.)

Results and Discussion

$KSbP_2O_8$ has a layered structure. The $(SbP_2O_8^-)_n$ infinite layers are built up from SbO_6 octahedra and PO_4 tetrahedra sharing corners. Three oxygens of each tetrahedral phosphate are linked to three antimony atoms so that each antimony is octahedrally coordinated with six oxygens of six different phosphate groups (Figs. 1 and 2). The fourth oxygen of each phosphate group is unshared and points into the interlayer space. These $(SbP_2O_8^-)_n$ layers are very similar to the $(ZrP_2O_8^{2-})_n$ layers in the well-known α-ZrP compound. Each of the potassium atoms is octahedrally coordinated to six of the unshared oxygen atoms (Fig. 2). The SbO_6 octahedron is quite regular with six equal Sb–O distances of 1.951(2) Å and O–Sb–O bond angles very close to 90°. In the case of the PO_4 group, the unshared oxygen, i.e., not bonded to antimony, forms a P–O bond significantly shorter than the three others. A list of bond distances and bond angles is given in Table V.

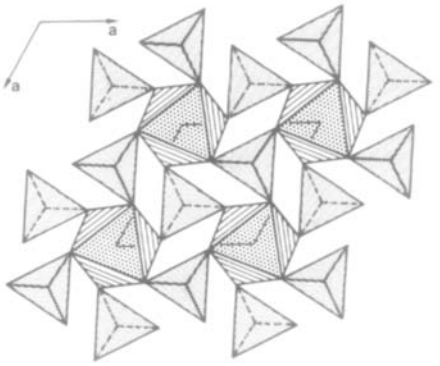

FIG. 1. Projection along the c axis of a $(SbP_2O_8^-)_n$ layer.

TABLE V

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

Sb–O(2)(×6)	1.951(2)	O(2)–Sb–O(2)(×3)			180.00(7)
		O(2)–Sb–O(2)(×6)			88.28(7)
		O(2)–Sb–O(2)(×6)			91.72(7)
P–O(1)	1.474(3)	O(1)–P –O(2)(×3)			111.93(7)
–O(2)(×3)	1.561(2)	O(2)–P –O(2)(×3)			106.90(7)
K–O(1)(×6)	2.932(1)	O(1)–O(2)	2.515(3)	O(2)–O(2)	2.718(3)
K–O(2)	3.544(2)	O(2)–O(2)	2.508(3)	O(2)–O(2)	2.801(3)

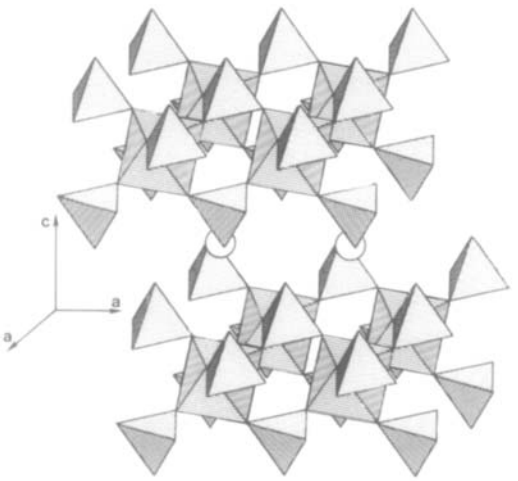

FIG. 2. Perspective drawing of two $(SbP_2O_8^-)_n$ layers showing two potassium atoms in the interlayer space.

This type of structure favors alkali ion mobility and ionic exchange behavior is expected with $KSbP_2O_8$. The study of its ionic exchange and conductivity properties is in progress.

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