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New Mixed-Valence Antimony Phosphates: α- and β-$Sb^{III}Sb^{V}(P_2O_7)_2$

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The compounds α- and β-$Sb^{III}Sb^{V}(P_2O_7)_2$ were obtained by heating at 923 K (α-type) or 773 K (β-type) a mixture of Sb_2O_5,nH_2O with an excess of $NH_4H_2PO_4$. α-$Sb^{III}Sb^{V}(P_2O_7)_2$ crystallizes in the monoclinic system, space group $P2_1/c$ with $a = 8.088(1)$ Å, $b = 16.015(3)$ Å, $c = 8.135(5)$ Å, $\beta = 90.17(2)°$, $Z = 4$. The β-type crystallizes in the orthorhombic system, space group $Pna2_1$, with $a = 8.018(1)$ Å, $b = 16.134(3)$ Å, $c = 8.029(5)$ Å, $Z = 4$. Both crystal structures were determined from reflections collected on a Nonius CAD4 automatic diffractometer with Mo$K\bar{\alpha}$ radiation. The final R index and weighted R_w index are 0.041 and 0.050, respectively, for α- and 0.041 and 0.052, respectively, for β-$Sb^{III}Sb^{V}(P_2O_7)_2$. Both structures are built up from corner-shared $Sb^{III}O_6$ or $Sb^{V}O_6$ octahedra and P_2O_7 groups. Each P_2O_7 group shares its six vertices with six different SbO_6 octahedra and each octahedron is connected with six P_2O_7 groups thus leading to two different three-dimensional frameworks. Nevertheless, both structures are closely related to that of the zirconium diphosphate ZrP_2O_7. © 1988 Academic Press, Inc.

Introduction

As part of a search for new materials likely to exhibit luminescence properties, several systems M_2O_3–M'_2O_5–P_2O_5 (M = Sb^{III}, Bi^{III}, Ln^{III} and M' = Sb^{V}, Nb^{V}, Ta^{V}) have been investigated and a new family of $MM'(P_2O_7)_2$ compounds has been prepared. The crystal structure of these materials is closely related to that of the zirconium diphosphate ZrP_2O_7 (*1*). This paper reports on the preparation and crystal structure determination of two members of this new family: α- and β-$Sb^{III}Sb^{V}(P_2O_7)_2$.

Experimental

Single crystals of α- and β-$Sb^{III}Sb^{V}(P_2O_7)_2$ were grown from mixtures of $(NH_4)H_2PO_4$ (GR grade, Merck) and Sb_2O_5,nH_2O, which was prepared and analyzed as described previously (*2*). The chemicals were weighed out in a molar ratio of 5 : 1 and the mixture was heated in air, in a platinum crucible, first at 473 K for 4 hr and then at 923 K (α-phase) or 773 K (β-phase) for 60 hr. In both cases the crystals are colorless thin rectangular platelets with large (010) faces. Their chemical analysis, conducted with an electron microprobe, leads to an atomic Sb to P ratio of 1 : 2. Actual compositions have been inferred from the crystal structure determinations. All attempts to prepare quantitatively the α- and β-phases led to mixtures of one of these phases with other antimony phosphates. A DTA experiment which has been undertaken on microcrystals of the β-phase shows that above 773 K it undergoes a decomposition, but the $\beta \rightarrow \alpha$ transformation is not evidenced.

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TABLE I

UNIT CELL CONSTANTS (AT 293 K)

	α-$Sb^{III}Sb^{V}(P_2O_7)_2$	β-$Sb^{III}Sb^{V}(P_2O_7)_2$
Crystal symmetry	Monoclinic	Orthorhombic
a (Å)	8.088(1)	8.018(1)
b (Å)	16.015(3)	16.134(3)
c (Å)	8.135(5)	8.029(5)
β (°)	90.17(2)	—
V (Å^3)	1053.8	1038.6
D_{calc} (g · cm^{-3})	3.73	3.78
Z	4	4
Space group	$P2_1/c$	$Pna2_1$
μ (cm^{-1}) for $\lambda_{MoK\overline{\alpha}}$ = 0.71069 Å	58.4	59.2

Single-crystal X-ray studies indicate monoclinic and orthorhombic symmetries, respectively, for α- and β-phases. For the β-phase, the possible space groups are $Pnam$ and $Pna2_1$ but according to the results of the structure solution the latter is retained unambiguously. Their unit cell parameters (Table I) were least-squares refined from 25 reflections automatically centered on a Nonius CAD4 diffractometer using graphite monochromated Mo$K\overline{\alpha}$ radiation. Diffraction intensities were measured with the diffractometer operating under the conditions given in Table II. The crystals used were 0.06 × 0.05 × 0.02 mm^3 (α-phase) and 0.08 × 0.06 × 0.01 mm^3 (β-phase) in dimensions. Intensities were corrected for absorption. For the data reductions, structure solutions, and refinements, the SDP-PLUS program chain (1982 version) of Enraf–Nonius, written by Frenz (*3*), was used.

Refinement of the Structures

Refinements were carried out by the full-matrix least-squares method. The starting positional parameters for Sb atoms were inferred from the Patterson maps; successive

TABLE II

DATA COLLECTION AND REFINEMENT CONDITIONS

Data collection		
Equipment	Nonius CAD4 diffractometer	
Radiation (Å)	Mo$K\overline{\alpha}$ λ = 0.71069	
Scan mode	$\omega - 2\theta$	
Scan angle (°)	$\Delta\omega = 1.0 + 0.35 \tan\theta$	
Recording angular range (θ°)	1.5–30.0	
Number of reflections measured	6336 (α-phase)	3326 (β-phase)
Number of independent data with $\sigma(I)/I < 0.33$ (used in refinements)	1092 (α-phase)	858 (β-phase)
Agreement factor between equivalent F	0.022 (α-phase)	0.028 (β-phase)
Refinements		
	α-phase	β-phase
Number of variables (isotropic temperature factors)	82	81
$R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.046	0.041
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma wF_o^2]^{1/2}$ with $w = 1/(1 + [(F_{obs} - F_{aver})/F_{max}]^2)$	0.056	0.053
Number of variables with anisotropic temperature factors for	112 Sb and P atoms	91 Sb atoms
R =	0.041	0.041
R_w =	0.050	0.052
Extinction parameters refined g =	0.8(1) × 10^{-7}	0.3(1) × 10^{-7}

refinements and Fourier difference maps then gave the positions of the P and O atoms. Table II indicates the main results of the final refinements which include corrections for secondary extinction and account for anomalous dispersion (*3*). In order to keep a data to parameter ratio higher than 9 : 1, anisotropic temperature factors were not assigned to all atoms but to Sb and P atoms for the α-phase and to Sb atoms only for the β one.

The final Fourier difference maps are featureless with maxima and minima in the range ±1.6 $e\AA^{-3}$. Table III presents the final atomic coordinates and thermal parameters (structure factor tables will be sent upon request).

One can observe that, for the α-phase, at the completion of the refinement, several oxygen atoms exhibit unexpected high values for their thermal parameter. Data collected from another crystal of the α-phase led to almost the same results. Nevertheless, such high values for some *B* parameters of oxygen atoms cannot be fully explained from chemical bond considerations. They could be due either to a very weak triclinic distortion or to defects. However,

TABLE IIIa

FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS IN α-$Sb^{III}Sb^{V}(P_2O_7)_2$

Atom	x	y	z	B ($\AA^2$)
Sb(1)	0.1520(1)	0.12809(7)	0.4697(1)	0.69(1)*
Sb(2)	0.3729(1)	0.63266(8)	0.5193(1)	0.87(1)*
P(1)	0.0313(5)	0.3206(3)	0.5961(5)	0.92(7)*
P(2)	0.5379(5)	0.3315(3)	0.8855(5)	0.92(7)*
P(3)	0.2497(5)	0.4069(3)	0.3577(6)	1.12(7)*
P(4)	0.2214(5)	0.5718(3)	0.9317(6)	0.98(7)*
O(1)	0.072(1)	0.5834(7)	0.048(1)	1.0(2)
O(2)	0.229(1)	0.6278(9)	0.789(1)	1.5(2)
O(3)	0.373(1)	0.5864(8)	0.050(1)	1.4(2)
O(4)	0.376(1)	0.3281(7)	−0.017(1)	0.9(2)
O(5)	0.236(2)	0.4770(9)	0.887(2)	1.8(2)
O(6)	0.375(2)	0.3399(9)	0.368(2)	2.2(2)
O(7)	0.490(1)	0.6582(8)	0.296(2)	1.4(2)
O(8)	0.133(2)	0.333(1)	0.744(2)	3.2(3)
O(9)	0.147(1)	0.6617(8)	0.380(2)	1.4(2)
O(10)	0.354(1)	0.7596(8)	0.563(1)	1.1(2)
O(11)	0.163(2)	0.415(1)	0.189(2)	3.6(3)
O(12)	0.090(2)	0.385(1)	0.466(2)	4.8(4)
O(13)	0.308(3)	0.490(1)	0.411(3)	5.0(5)
O(14)	0.063(2)	0.237(1)	0.518(2)	4.1(4)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb(1)	0.00138(9)	0.00072(3)	0.0037(1)	−0.0003(2)	0.0008(2)	−0.0008(2)
Sb(2)	0.0039(1)	0.00091(3)	0.0024(1)	0.0002(2)	0.0000(2)	−0.0003(2)
P(1)	0.0021(5)	0.0013(2)	0.0033(5)	0.0002(5)	0.0018(9)	−0.0009(5)
P(2)	0.0019(5)	0.0013(2)	0.0034(6)	0.0018(5)	0.0022(9)	0.0010(5)
P(3)	0.0049(5)	0.0012(2)	0.0030(5)	0.0012(5)	−0.0002(9)	0.0004(5)
P(4)	0.0018(5)	0.0008(1)	0.0063(6)	−0.0006(5)	0.0005(9)	0.0001(6)

Note. The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. Starred atoms were refined anisotropically. They are given in the form of the isotropic equivalent thermal parameter defined as $B = \frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\mathbf{a}_j$.

TABLE IIIb

FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS IN β-$Sb^{III}Sb^{V}(P_2O_7)_2$

Atom	x	y	z	B (Å)
Sb(1)	0.5194(1)	0.37770(9)	0.250	0.47(1)*
Sb(2)	0.5167(2)	0.13168(7)	0.7780(2)	0.66(2)*
P(1)	0.4284(7)	0.4289(4)	0.6333(7)	0.56(7)
P(2)	0.6120(7)	0.3264(3)	0.8717(7)	0.61(8)
P(3)	0.3916(7)	0.1863(4)	0.3781(8)	0.74(8)
P(4)	0.6248(7)	0.0939(4)	0.1549(7)	0.73(8)
O(1)	0.364(2)	0.842(1)	0.517(2)	1.5(3)
O(2)	0.470(3)	0.984(1)	0.617(3)	3.3(4)
O(3)	0.576(2)	0.720(1)	0.844(3)	1.9(3)
O(4)	0.457(3)	0.864(1)	0.810(3)	2.9(4)
O(5)	0.255(2)	0.665(1)	0.771(2)	1.4(3)
O(6)	0.031(2)	0.071(1)	0.476(2)	1.5(3)
O(7)	0.299(2)	0.429(1)	0.231(2)	1.1(2)
O(8)	0.440(2)	0.5905(9)	0.276(2)	0.8(2)
O(9)	0.367(2)	0.167(1)	0.557(2)	1.0(2)
O(10)	−0.008(2)	0.8285(9)	0.534(2)	0.9(2)
O(11)	0.439(2)	0.7434(9)	0.261(2)	1.1(2)
O(12)	0.119(2)	0.0226(9)	0.163(2)	0.6(2)
O(13)	0.282(2)	0.374(1)	0.637(2)	0.7(2)
O(14)	0.206(2)	0.664(1)	0.407(2)	0.8(2)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb(1)	0.0015(1)	0.00050(3)	0.0019(1)	0.0001(1)	−0.0001(3)	−0.0004(1)
Sb(2)	0.0028(1)	0.00060(3)	0.0025(1)	−0.0001(1)	−0.0005(3)	0.0003(2)

Note. Starred atoms were refined anisotropically. They are given in the form of the isotropic equivalent thermal parameter defined as $B = \frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\mathbf{a}_j$.

Table IV shows that all the interatomic distances are in very good agreement with previous knowledge of phosphates, Sb^{III} and Sb^{V} structural chemistry.

X-ray powder patterns are presented in Table V which gives the calculated interplanar distances along with the intensities calculated from the Lazy-Pulverix program (*4*) in the case of a Guinier–Hagg camera ($CuK\alpha_1$ radiation, quartz crystal monochromator; relative intensities less than 0.5 are not given).

Description of the Structures

In both α- and β-$Sb^{III}Sb^{V}(P_2O_7)_2$ crystal structures (Fig. 1) the oxygen coordination polyhedron for Sb^{III} can be considered, even very distorted, as an octahedron. In that way, these two structures can be described as built up from SbO_6 octahedra (either $Sb^{V}O_6$ or $Sb^{III}O_6$) sharing corners with P_2O_7 groups. Each P_2O_7 group shares its six vertices with six different SbO_6 octahedra and each octahedron is connected with six P_2O_7 groups thus leading to three-dimensional frameworks which are closely related to that of the zirconium diphosphate ZrP_2O_7 (*1*). This latter structure is NaCl-like and can be described as made up of two interpenetrating face-centered cubic lattices, one with ZrO_6 octahedra at each lattice point and the other with P_2O_7 groups (Fig. 2). In the structure of β-$Sb^{III}Sb^{V}$

$(P_2O_7)_2$, if one does not distinguish between $Sb^{III}O_6$ and $Sb^{V}O_6$ octahedra, the relative arrangement of P_2O_7 groups and octahedra is nearly the same as in ZrP_2O_7. It is much more distorted in the α-phase but the comparison with the zirconium diphosphate is still possible. From the schematic representations given in Figs. 3a to 3c it can be seen that the existence of two types of octahedra in the α- and β-phases leads to a doubling of one of the lattice parameters when going from ZrP_2O_7 to the α- or the β-phase. In both ZrP_2O_7 and β-phase structures each octahedron is surrounded by 12 octahedra at a distance of about $8/\sqrt{2}$ Å and is connected to each of them, in the same way, by

TABLE IV

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°)

α-$Sb^{III}Sb^{V}(P_2O_7)_2$		β-$Sb^{III}Sb^{V}(P_2O_7)_2$	
	$Sb^{V}O_6$ octahedron		
Sb(1)–O(1)	1.95(1)	Sb(1)–O(3)	1.91(2)
–O(4)	1.95(1)	–O(5)	1.94(1)
–O(5)	1.94(1)	–O(6)	2.00(2)
–O(8)	1.95(2)	–O(7)	1.96(1)
–O(11)	1.91(2)	–O(10)	1.91(2)
–O(14)	1.92(2)	–O(12)	1.93(1)
O(1)–Sb(1)–O(4)	178.8(5)	O(3)–Sb(1)–O(5)	92.7(7)
–O(5)	88.9(5)	–O(6)	90.3(8)
–O(8)	88.9(6)	–O(7)	91.1(7)
–O(11)	88.8(6)	–O(10)	89.7(7)
–O(14)	90.0(7)	–O(12)	178.0(8)
O(4)–Sb(1)–O(5)	90.3(5)	O(5)–Sb(1)–O(6)	91.4(7)
–O(8)	90.6(6)	–O(7)	175.5(7)
–O(11)	92.0(6)	–O(10)	88.6(7)
–O(14)	90.6(6)	–O(12)	86.6(6)
O(5)–Sb(1)–O(8)	88.7(6)	O(6)–Sb(1)–O(7)	86.3(7)
–O(11)	89.9(7)	–O(10)	180.0(7)
–O(14)	171.3(7)	–O(12)	87.8(6)
O(8)–Sb(1)–O(11)	177.3(7)	O(7)–Sb(1)–O(10)	93.7(6)
–O(14)	82.7(8)	–O(12)	89.5(6)
O(11)–Sb(1)–O(14)	98.7(8)	O(10)–Sb(1)–O(12)	92.2(6)
	$Sb^{III}O_6$ octahedron		
Sb(2)–O(2)	2.49(1)	Sb(2)–O(1)	2.19(2)
–O(6)	2.27(1)	–O(2)	2.74(2)
–O(7)	2.10(1)	–O(9)	2.22(2)
–O(9)	2.20(1)	–O(11)	2.05(1)
–O(10)	2.07(1)	–O(13)	2.41(1)
–O(13)	2.50(2)	–O(14)	2.13(1)
O(2)–Sb(2)–O(6)	94.2(5)	O(1)–Sb(2)–O(2)	129.8(6)
–O(7)	170.5(5)	–O(9)	153.1(6)
–O(9)	93.9(4)	–O(11)	78.1(6)
–O(10)	81.0(5)	–O(13)	92.0(6)
–O(13)	100.6(6)	–O(14)	83.9(6)
O(6)–Sb(2)–O(7)	84.5(5)	O(2)–Sb(2)–O(9)	76.8(6)
–O(9)	155.5(5)	–O(11)	148.1(6)
–O(10)	78.8(5)	–O(13)	82.3(6)
–O(13)	120.4(6)	–O(14)	109.2(6)
O(7)–Sb(2)–O(9)	83.7(5)	O(9)–Sb(2)–O(11)	77.9(6)
–O(10)	89.6(5)	–O(13)	96.3(5)
–O(13)	88.1(6)	–O(14)	82.6(6)
O(9)–Sb(2)–O(10)	79.6(5)	O(11)–Sb(2)–O(13)	81.6(5)
–O(13)	80.7(6)	–O(14)	86.1(5)
O(10)–Sb(2)–O(13)	160.3(6)	O(13)–Sb(2)–O(14)	167.7(5)
	$P(1)O_4$ tetrahedron		
P(1)–O(8)	1.47(2)	P(1)–O(6)	1.50(2)
–O(9)	1.48(1)	–O(8)	1.59(2)
–O(12)	1.56(2)	–O(12)	1.58(2)
–O(14)	1.51(2)	–O(13)	1.47(1)
O(8)–P(1)–O(9)	114.4(8)	O(6)–P(1)–O(8)	104.0(9)
–O(12)	107(1)	–O(12)	104.7(9)
–O(14)	111(1)	–O(13)	117.1(9)
O(9)–P(1)–O(12)	105.0(9)	O(8)–P(1)–O(12)	103.8(8)
–O(14)	113.2(9)	–O(13)	113.5(8)
O(12)–P(1)–O(14)	105(1)	O(12)–P(1)–O(13)	112.5(8)
	$P(2)O_4$ tetrahedron		
P(2)–O(3)	1.59(1)	P(2)–O(8)	1.60(2)
–O(4)	1.53(1)	–O(10)	1.55(2)
–O(7)	1.50(1)	–O(11)	1.49(2)
–O(10)	1.50(1)	–O(14)	1.49(2)
O(3)–P(2)–O(4)	104.3(7)	O(8)–P(2)–O(10)	104.2(8)
–O(7)	107.4(7)	–O(11)	105.9(8)
–O(10)	106.3(7)	–O(14)	105.4(8)
O(4)–P(2)–O(7)	112.6(7)	O(10)–P(2)–O(11)	111.7(9)
–O(10)	109.7(7)	–O(14)	111.3(9)
O(7)–P(2)–O(10)	116.3(7)	O(11)–P(2)–O(14)	117.2(9)
	$P(3)O_4$ tetrahedron		
P(3)–O(6)	1.48(2)	P(3)–O(3)	1.55(2)
–O(11)	1.55(2)	–O(4)	1.56(2)
–O(12)	1.60(2)	–O(5)	1.50(2)
–O(13)	1.48(2)	–O(9)	1.48(2)
O(6)–P(3)–O(11)	114.7(9)	O(3)–P(3)–O(4)	108(1)
–O(12)	112(1)	–O(5)	105(1)
–O(13)	115(1)	–O(9)	114(1)
O(11)–P(3)–O(12)	98(1)	O(4)–P(3)–O(5)	107(1)
–O(13)	109(1)	–O(9)	110(1)
O(12)–P(3)–O(13)	108(1)	O(5)–P(3)–O(9)	113.7(9)
	$P(4)O_4$ tetrahedron		
P(4)–O(1)	1.55(1)	P(4)–O(1)	1.51(2)
–O(2)	1.47(1)	–O(2)	1.50(2)
–O(3)	1.58(1)	–O(4)	1.56(2)
–O(5)	1.57(1)	–O(7)	1.57(2)
O(1)–P(4)–O(2)	116.4(7)	O(1)–P(4)–O(2)	117(1)
–O(3)	102.4(7)	–O(4)	108(1)
–O(5)	108.5(7)	–O(7)	113.1(9)
O(2)–P(4)–O(3)	111.3(7)	O(2)–P(4)–O(4)	108(1)
–O(5)	113.7(8)	–O(7)	109(1)
O(3)–P(4)–O(5)	103.2(7)	O(4)–P(4)–O(7)	99(1)
	P–O–P angles		
P(1)–O(12)–P(3)	140(1)	P(1)–O(8)–P(2)	133.3(9)
P(2)–O(3)–P(4)	132.5(9)	P(3)–O(4)–P(4)	146(2)

TABLE V

CALCULATED X-RAY POWDER PATTERN

hkl	d_{calc} (Å)	I/I_o	*hkl*	d_{calc} (Å)	I/I_o
		α-$Sb^{III}Sb^{V}(P_2O_7)_2$			
020	8.008	6.0	113	2.536	7.5
011	7.253	7.3	160	2.535	2.1
110	7.220	2.3	$23\bar{2}$	2.529	7.1
021	5.707	1.0	$31\bar{1}$	2.529	12.0
120	5.690	0.8	311	2.525	15.2
$11\bar{1}$	5.407	24.8	232	2.523	6.9
111	5.393	26.8	052	2.516	1.0
$12\bar{1}$	4.667	43.6	250	2.511	13.7
121	4.658	28.1	$12\bar{3}$	2.450	29.6
031	4.463	1.8	123	2.446	5.3
130	4.455	1.0	$32\bar{1}$	2.440	1.2
002	4.067	80.8	321	2.436	9.8
200	4.044	4.1	$16\bar{1}$	2.421	15.1
040	4.004	100.0	161	2.419	11.5
012	3.942	8.2	330	2.407	1.3
210	3.921	70.9	152	2.402	2.5
$13\bar{1}$	3.910	1.9	251	2.398	0.7
131	3.905	6.3	$24\bar{2}$	2.334	3.6
$10\bar{2}$	3.638	6.2	242	2.329	1.3
102	3.630	6.4	$13\bar{3}$	2.318	2.7
220	3.610	13.5	133	2.315	6.0
041	3.592	12.6	$33\bar{1}$	2.309	9.8
$11\bar{2}$	3.548	10.2	331	2.306	8.9
112	3.540	6.3	$30\bar{2}$	2.250	5.2
$21\bar{1}$	3.536	4.9	043	2.245	0.9
$12\bar{2}$	3.312	3.2	302	2.244	0.8
122	3.306	3.3	340	2.236	2.6
$22\bar{1}$	3.303	6.4	$21\bar{3}$	2.233	1.5
221	3.296	9.8	260	2.228	2.2
$14\bar{1}$	3.285	9.3	071	2.202	2.0
141	3.281	4.1	223	2.165	2.8
032	3.235	5.0	$14\bar{3}$	2.165	1.5
230	3.223	17.0	322	2.161	1.1
132	3.001	1.4	$34\bar{1}$	2.158	1.1
$23\bar{1}$	2.999	2.5	341	2.155	0.7
051	2.980	1.0	$25\bar{2}$	2.138	8.0
$20\bar{2}$	2.872	3.5	252	2.135	8.0
202	2.864	1.5	$17\bar{1}$	2.125	1.3
042	2.853	26.1	171	2.125	7.2
240	2.845	0.9	332	2.069	0.7
$21\bar{2}$	2.827	14.9	004	2.034	2.3
212	2.819	23.3	400	2.022	4.4
$15\bar{1}$	2.797	10.0	014	2.018	4.3
151	2.796	8.6	153	2.004	3.2
222	2.696	0.5	080	2.002	4.1
300	2.696	0.5	$35\bar{1}$	2.000	3.2
$14\bar{2}$	2.693	1.4	351	1.998	1.9
013	2.674	0.6	072	1.994	1.0
060	2.669	1.6	270	1.991	6.5
023	2.568	1.4	420	1.961	0.7
$11\bar{3}$	2.541	1.1	081	1.944	1.5

TABLE V—*Continued*

hkl	d_{calc} (Å)	I/I_o	*hkl*	d_{calc} (Å)	I/I_o
		α-$Sb^{III}Sb^{V}(P_2O_7)_2$			
$17\bar{2}$	1.937	1.2	430	1.891	0.7
172	1.935	0.8	$18\bar{1}$	1.890	2.7
$42\bar{1}$	1.907	2.7	181	1.890	1.5
421	1.905	0.8	323	1.857	5.0
$31\bar{3}$	1.901	1.9	$16\bar{3}$	1.853	11.7
034	1.900	2.3	163	1.851	2.8
313	1.896	2.4	134	1.849	1.1
		β-$Sb^{III}Sb^{V}(P_2O_7)_2$			
020	8.067	4.1	331	2.294	0.6
011	7.188	2.0	062	2.234	2.9
110	7.180	5.9	203	2.226	4.4
121	4.641	100.0	170	2.215	3.3
031	4.468	1.8	213	2.205	1.9
130	4.466	2.8	312	2.204	0.8
040	4.033	71.7	261	2.152	1.1
002	4.014	55.5	341	2.147	0.7
200	4.009	66.1	223	2.146	0.6
131	3.903	0.5	322	2.145	0.9
210	3.891	2.9	171	2.135	0.9
140	3.603	9.5	252	2.131	1.0
022	3.594	15.7	233	2.057	1.3
201	3.587	16.8	332	2.056	2.8
112	3.504	2.1	080	2.017	2.3
141	3.287	13.0	004	2.007	2.7
122	3.280	13.3	400	2.005	2.7
221	3.277	9.7	276	1.998	0.8
230	3.214	3.8	351	1.994	0.9
051	2.994	2.1	410	1.989	2.4
150	2.993	1.5	180	1.956	0.7
132	2.986	1.6	024	1.948	0.8
042	2.845	28.5	401	1.945	0.6
240	2.843	21.9	172	1.939	0.8
202	2.837	27.4	114	1.933	2.4
212	2.794	3.6	181	1.900	0.7
142	2.682	0.8	424	1.891	1.7
241	2.680	1.5	313	1.878	0.7
222	2.676	1.7	430	1.878	1.8
160	2.549	0.7	163	1.846	12.9
250	2.514	0.6	361	1.845	17.3
232	2.509	1.1	223	1.841	11.1
113	2.508	0.6	253	1.832	0.8
311	2.505	1.4	352	1.832	1.7
161	2.430	35.9	082	1.802	10.4
123	2.422	41.3	280	1.802	7.2
321	2.419	36.5	044	1.797	7.3
152	2.400	0.6	440	1.795	6.1
251	2.399	1.1	204	1.795	7.4
033	2.396	3.1	402	1.793	7.7
330	2.393	0.9	272	1.789	0.6
242	2.320	30.8	214	1.784	1.4
133	2.296	2.1	412	1.782	2.5

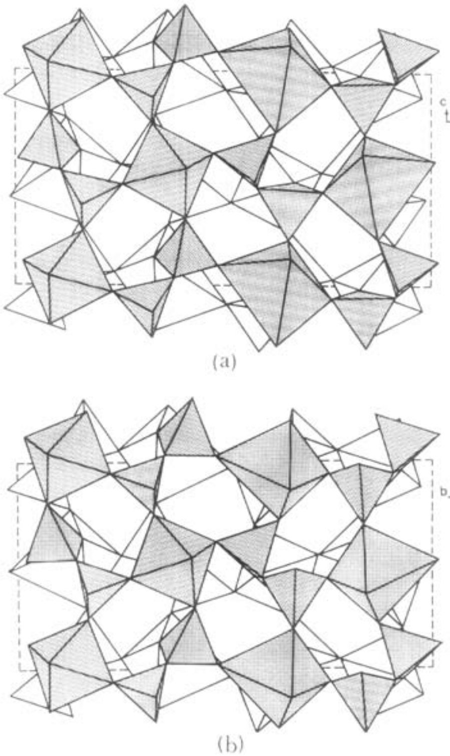

FIG. 1. Projection of the structures of (a) α-$Sb^{III}Sb^{V}(P_2O_7)_2$ along [100] and (b) β-$Sb^{III}Sb^{V}(P_2O_7)_2$ along [001].

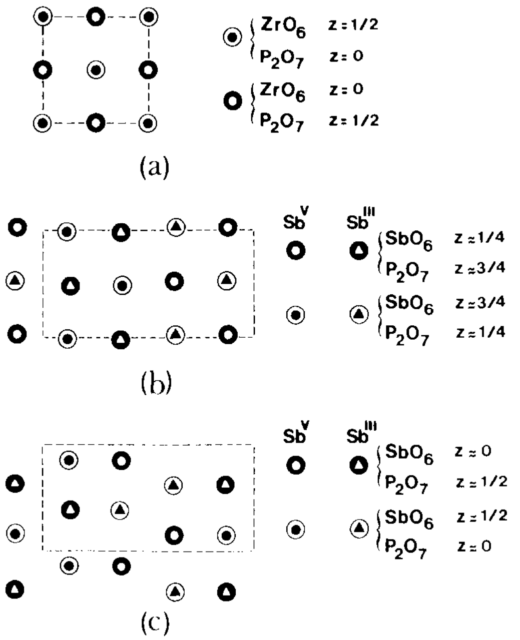

FIG. 3. Schematic representation ([001] views) of (a) ZrP_2O_7, (b) β-$Sb^{III}Sb^{V}(P_2O_7)_2$, (c) α-$Sb^{III}Sb^{V}(P_2O_7)_2$.

two of its vertices, via one edge of a PO_4 tetrahedron for one vertex and two edges from a P_2O_7 group for the other. As a consequence of its more distorted structure, in the α-phase there are three types of connections between one octahedron and its 12 nearest neighbors and not a single one as in ZrP_2O_7 and β-$Sb^{III}Sb^{V}(P_2O_7)_2$. These three types are indicated as I, II, and III in Fig. 4. This difference between α- and β-phase structures shows that α-phase is not a simple distortion of the β-phase. Figures 1 and 4 clearly show the difference. The left-hand side of the α-unit cell (Fig. 1a) is almost identical with the corresponding half of the β-unit cell (Fig. 1b) but according to the symmetry the two remaining halves (right-hand side Figs. 1a and 1b) are different. Both structures can then be divided into slabs parallel to the *a–c* plane. These are equivalent but not linked together in the same way in both structures. Within each slab the connections between one octahedron and its nearest neighbors are all of type I. At the junction between A and B slabs in the α-phase (Fig. 4a) the connec-

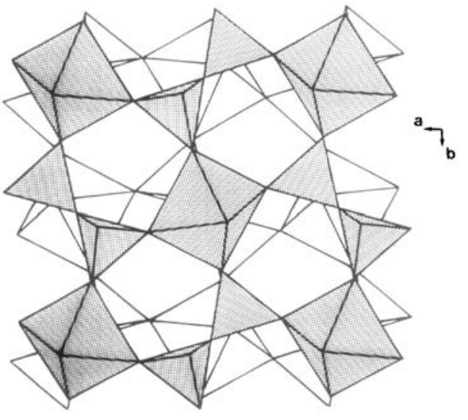

FIG. 2. Structure of ZrP_2O_7 (*1*).

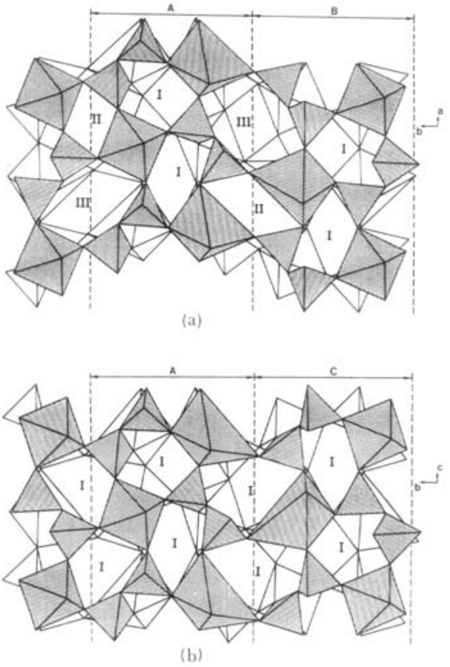

FIG. 4. Projection of the structures of (a) α-$Sb^{III}Sb^{V}(P_2O_7)_2$ along [001] and (b) β-$Sb^{III}Sb^{V}(P_2O_7)_2$ along [100] showing the A, B, and C slabs and the three different types of connections between polyhedra.

tions are of types II and III whereas they remain of type I between A and C slabs in the β-phase (Fig. 4b).

From Table IV which reports the main bond distances and bond angles for the different coordination polyhedra it can be seen that in both α- and β-$Sb^{III}Sb^{V}(P_2O_7)_2$ structures the $Sb^{III}O_6$ octahedra are very distorted and even to a higher extent in the β-form. In fact, in both structures there are four oxygen atoms at an average distance of 2.15 Å from Sb^{III} and two oxygen atoms at a larger distance (2.49(1) and 2.50(2) Å in the α-phase and 2.41(1) and 2.74(2) Å in the β-phase). This situation accounts for the stereochemical activity of the Sb^{III} lone pair which leads to a 4 + E trigonal bipyramid arrangement.

The $Sb^{V}O_6$ octahedra are nearly regular in both structures with Sb^{V}–O distances ranging from 1.91(2) to 2.00(2) Å. The values of the P–O–P bridging angles in the different P_2O_7 groups range from 132.5(9) to 146(2)°. The P–O distances are rather irregular; the shortest ones (1.47(2) to 1.50(2) Å) correspond to oxygen atoms which are also bonded to Sb^{III} atoms and the longest (1.56(2) to 1.60(2) Å) are those in which the oxygen bridging atoms are involved. Such features seem to be quite usual in the pyrophosphates crystal chemistry.

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