JOURNAL OF SOLID STATE CHEMISTRY 118, 104–111 (1995)

Preparation and Crystal Structure of a New Form of $Sb_2(PO_4)_3$ and $M_{1/2}Sb^{V}_{3/2}(PO_4)_3$ (M = Y, In, and Sc)

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Received September 30, 1994; in revised form February 2, 1995; accepted February 6, 1995

A new form of mixed-valence antimony phosphate $Sb^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$ (β-$Sb_2(PO_4)_3$) has been prepared by the reaction of antimony pentachloride with a solution of antimony trichloride in phosphoric acid. The structure has been determined by single crystal X-ray study. Crystal data are as follows: space group $R\bar{3}$, $Z = 24$, $a = 16.880(2)$ Å, $c = 21.196(3)$ Å, and $V = 5230(1)$ Å. The structure is basically isotypic with $Bi^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$. The $Sb1^{III}$ atom is disordered in (0, 0, $\pm z$) positions as observed in $Bi^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$. Furthermore, some of the phosphorus and oxygen atoms are distributed in major and minor positions in the ratio of 5 : 1. Structural consideration has indicated that of the six oxygen atoms bonded with an $Sb1^{III}$ atom, five are at the major positions and one is at the minor position. This irregular coordination decreases the bond-order sum of the Sb1 atom to 3.07 and also gives a space for the lone-pair electrons. Similar preparations with yttrium trichloride, indium trichloride, and scandium nitrate have yielded $Y_{1/2}Sb^{V}_{3/2}(PO_4)_3$, $In_{1/2}Sb^{V}_{3/2}(PO_4)_3$, and $Sc_{1/2}Sb^{V}_{3/2}(PO_4)_3$, respectively. X-ray powder diffraction studies have shown that the yttrium compound has the $Bi^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$ structure while other two have the α-$Sb_2(PO_4)_3$ structure. © 1995 Academic Press, Inc.

INTRODUCTION

In the structural chemistry of the phosphates, antimony(III) and bismuth(III) show little similarity, probably due to the large difference in their sizes. Though several bismuth(III) phosphates have been reported (1), only two antimony(III) phosphates (2, 3) are known, and one of them is not isotypic with any of the bismuth(III) phosphates. However, the recent article on $M^{III}_{1/2}M'^{V}_{1/2}P_2O_7$($M^{III}$ = Sb, Bi, Nd; M'^{V} = Sb, Nb, Ta) revealed that the ZrP_2O_7-like structure can take both antimony(III) and bismuth(III) as the trivalent cation (4, 5). In this paper, we will report a mixed-valenced orthophosphate $Sb^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$ which is isotypic with the bismuth(III) analog $Bi^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$ (6) except for some details. It has the same composition as the phosphate reported recently by Jouanneaux *et al.* (8) but has a different structure. We will call the previously reported form of $Sb_2(PO_4)_3$ the α form and the form that we report here the β form.

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EXPERIMENTAL

Preparation of β-$Sb_2(PO_4)_3$

$SbCl_5$ (ca. 1.7 ml) was added to the solution of $SbCl_3$ (1.03 g) in 85% phosphoric acid (3.02 g) to yield a yellow solution. While the solution was heated with stirring at ca. 300°C, it became viscous with effervescence, and finally turned into a white solid. The solid was heated in an alumina boat under a nitrogen flow at 400°C for 2 days and at 500°C for a day, and became an amorphous intermediate. After being heated at 750°C for 3 days under a nitrogen flow, the amorphous intermediate became β-$Sb_2(PO_4)_3$ powder. The X-ray diffraction pattern showed the sample was pure. Colorless single crystals were obtained by heating the amorphous intermediate in a sealed silica tube at 750°C for 5 days. They have a nearly cubic shape, which is consistent with the rhombohedral cell parameters (a = 12.037 Å, α = 89.04°). Fluorescent X-ray spectra of the β-$Sb_2(PO_4)_3$ samples obtained with a Seiko SEA 2010 spectrometer (Rh target, 15 kV) indicated the samples did not contain a substantial amount of chlorine in the structure (Cl/P $\leq$ 0.003). When the temperature of the white solid obtained by the reaction of chlorides and phosphoric acid was rapidly increased to 750°C, the α form was obtained.

Preparation of Other $M^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$

The method of preparation of β-$Sb_2(PO_4)_3$ can be applied to the syntheses of other $M^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$ compounds. The reaction of $SbCl_5$ with the solution of $YCl_3 \cdot 6H_2O$, $InCl_3 \cdot 4H_2O$, or $Sc(NO_3)_3 \cdot 4H_2O$ in phosphoric acid (85%) and a small amount of hydrochloric acid followed by heating yielded $Y^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$, $In^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$, and $Sc^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$ as the major prod-

0022-4596/95 $12.00
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ucts, respectively. The ratio of the starting mixture was M : Sb : P = 1 : 3 : 6 (M = Y, In, Sc). The products were identified by powder X-ray diffraction and the cell parameters of the major products were determined from the data obtained with a Rigaku RINT2000 diffractometer equipped with a counterside monochromator. The reflection angles were corrected with the internal reference of silicon.

Structure Analysis of β-$Sb_2(PO_4)_3$

The X-ray powder diffraction of β-$Sb_2(PO_4)_3$ indicated that it is isotypic with $Bi^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$ (trigonal, $R\bar{3}$) (6). Using the powder data obtained with Cu$K\alpha$ radiation with a Rigaku Geigerflex RAD-C system, we refined the structure by the Rietveld method with RIETAN (11) (R_f = 0.047, R_{wp} = 0.224). The refined cell constants were a = 16.900(2) Å and c = 21.211(2) Å (hexagonal axes).

A single-crystal study of β-$Sb_2(PO_4)_3$ has confirmed the above results. The crystallographic data are summarized in Table 1 with the descriptions of the data collection and the structure analysis. The starting positional parameters for antimony atoms were taken from the bismuth compound. Phosphorus and oxygen atoms were located by the Fourier method with SHELXS76 (9). All atoms were refined by the full-matrix least-squares method with ANYBLK (10). After the refinements of the structure, the Fourier maps showed a residual peak near the P2 atom and another near the P4 atom. Based on the distances to the surrounding oxygen atoms, the peaks were assigned to phosphorus atoms with fractional occupancies. The structure including these phosphorus atoms was successfully refined with the constraint that kept the sum of the occupancies of the neighboring phosphorus atoms at unity. Successive Fourier maps gave a new fractional oxygen atom bonded to each of the new phosphorus atoms. All of the occupation factors of the new atoms were refined as one parameter and converged at 0.187(6). In the final refinement, the occupation factor was fixed at $\frac{1}{6}$ from the structural consideration discussed below. Final atomic coordinates are listed in Table 2, and

TABLE 1
Summary of Crystal Data, Data Collection, and Refinement Parameters for β-$Sb_2(PO_4)_3$

Crystal data	
Crystal system and space group	Trigonal, $R\bar{3}$
Cell dimensions	a = 16.880(2) Å, c = 21.196(3) Å
(λ = 0.70926 Å)	V = 5230(1) Å^3
D_{calc}(g · cm^{-3})	4.021
Z	24
Data collection	
Crystal size	0.14 × 0.14 × 0.14 mm
Equipment and radiation	Rigaku AFC-5R, Mo$K\alpha$
Temperature	296 K
Scan mode and angle (°)	$\omega - 2\theta$, $\Delta\omega$ = 1.103 + .03 tan ω
2θ Range	3.0°–60.0°
Absorption correction	φ-Scan
Relative transmission factor	0.897–0.999
No. of reflections measured	3650
No. of independent reflections	3408
Agreement of equivalent reflections	R_{int} = 0.016
Refinement	
No. of reflections used for analysis	2907 ($F_o > 3\sigma(F_o)$)
No. of independent variables	226
R, R_w[a]	0.043, 0.028
Highest residual difference Fourier peak	1.49 e/Å^3

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$ ($w = 1/\sigma(F_o)^2$).

TABLE 2
Atomic Coordinates and Equivalent Isotropic Thermal Parameters for β-$Sb_2(PO_4)_3$

Atom	x/a	y/b	z/c	U(eq)
Sb1[a]	0	0	0.01467(7)	0.0123(7)
Sb2	1/2	0	0	0.0135(3)
Sb3	0	0	1/2	0.0056(4)
Sb4	0	0	0.28219(3)	0.0083(3)
Sb5	1/2	0	1/2	0.0068(2)
Sb6	0.51226(3)	0.02359(3)	0.23768(2)	0.0055(2)
P1	0.37484(12)	0.00571(12)	0.87719(8)	0.0091(7)
P2a[b]	0.1548(2)	0.1798(2)	0.20913(10)	0.0129(9)
P2b[c]	0.1182(7)	0.1138(7)	0.1624(4)	0.002(2)[d]
P3	0.14829(12)	0.02180(13)	0.38897(9)	0.0104(7)
P4a[b]	0.1681(2)	0.2226(2)	0.95784(10)	0.0112(9)
P4b[c]	−0.0566(7)	0.2375(7)	0.0396(4)	0.004(2)[d]
O1	0.1079(4)	0.0464(5)	0.3342(3)	0.036(3)
O2	0.0428(5)	0.4301(4)	0.2086(3)	0.030(3)
O3	0.2602(4)	0.4632(4)	0.2814(3)	0.042(3)
O4	0.1442(4)	0.4074(4)	0.6415(2)	0.020(2)
O5	0.0694(4)	0.1089(4)	0.5513(2)	0.022(3)
O6	0.0610(4)	0.1050(4)	0.2302(3)	0.019(2)
O7	0.0236(4)	0.5669(4)	0.1646(2)	0.018(2)
O8	0.1766(5)	0.4171(4)	0.0505(3)	0.033(3)
O9	0.2944(4)	0.1376(3)	0.0797(2)	0.018(2)
O10a[b]	0.2566(4)	0.0588(5)	0.7453(3)	0.023(3)
O10b[c]	0.379(2)	0.336(2)	0.6267(11)	0.002(5)[d]
O11	0.1983(4)	0.4620(4)	0.5230(2)	0.030(3)
O12	0.3547(5)	0.2888(4)	0.1547(3)	0.039(3)
O13	0.2095(4)	0.1285(4)	0.1946(3)	0.037(3)
O14	0.2519(4)	0.2220(4)	−0.0650(2)	0.024(3)
O15	0.3525(5)	0.0692(4)	0.6085(3)	0.037(3)
O16a[b]	0.1295(5)	0.0438(6)	0.0490(4)	0.041(4)
O16b[c]	0.066(2)	0.046(2)	0.1129(15)	0.024(8)[d]

[a] One-half of the sites are occupied.
[b] Five-sixths of the sites are occupied.
[c] One-sixth of the sites are occupied.
[d] The temperature factor was isotropically refined.

TABLE 3
Main Interatomic Distances (Å) and Angles (°) of $\beta Sb_2(PO_4)_3$

Sb1	O16a	O16a^{i}	O16a^{iii}	O16a^{iv}	O16a^{v}	O16b^{ii}
O16a	**2.059(7)**	3.336(13)	4.376(15)	2.831(12)	2.831(12)	2.651(4)
O16a^{i}	108.2(2)	**2.059(7)**	2.831(12)	4.376(15)	2.831(12)	3.09(3)
O16a^{iii}	165.67(8)	79.6(3)	**2.351(8)**	3.336(13)	3.336(13)	4.00(3)
O16a^{iv}	79.6(3)	165.67(8)	90.4(3)	**2.351(8)**	3.336(13)	3.66(3)
O16a^{v}	79.6(3)	79.6(3)	90.4(3)	90.4(3)	**2.351(8)**	4.47(3)
O16b^{ii}	74.4(9)	90.1(9)	118.3(9)	103.7(8)	147.4(8)	**2.31(3)**

Sb2	O3^{ix}	O3^{x}	O10a^{viii}	O10b^{viii}	O15^{viii}	O15^{xv}
O3^{ix}	**2.246(6)**	4.492(12)	3.149(9)	3.75(3)	3.133(8)	3.164(9)
O3^{x}	180.	**2.246(6)**	3.317(10)	3.25(3)	3.164(9)	3.133(8)
O10a^{viii}	87.0(3)	93.0(3)	**2.327(7)**	4.78(2)	3.284(9)	3.127(9)
O10b^{viii}	98.3(5)	81.7(5)	143.7(5)	**2.70(2)**	4.32(3)	2.38(2)
O15^{viii}	89.4(2)	90.6(2)	92.8(2)	123.0(5)	**2.206(6)**	4.411(12)
O15^{xv}	90.6(2)	89.4(2)	87.2(2)	57.0(5)	180.	**2.206(6)**

Sb3	O5	O5^{i}	O5^{ii}	O5^{iii}	O5^{iv}	O5^{v}
O5	**1.944(5)**	2.792(9)	2.792(9)	3.889(10)	2.707(9)	2.707(9)
O5^{i}	91.8(2)	**1.944(5)**	2.792(9)	2.707(9)	3.889(10)	2.707(9)
O5^{ii}	91.8(2)	91.8(2)	**1.944(5)**	2.707(9)	2.707(9)	3.889(10)
O5^{iii}	180.	88.2(2)	88.2(2)	**1.944(5)**	2.792(9)	2.792(9)
O5^{iv}	88.2(2)	180.	88.2(2)	91.8(2)	**1.944(5)**	2.792(9)
O5^{v}	88.2(2)	88.2(2)	180.	91.8(2)	91.8(2)	**1.944(5)**

Sb4	O1	O1^{i}	O1^{ii}	O6	O6^{i}	O6^{ii}
O1	**1.928(6)**	2.740(11)	2.740(11)	2.693(8)	3.824(7)	2.714(8)
O1^{i}	90.5(3)	**1.928(6)**	2.740(11)	2.714(8)	2.693(8)	3.824(7)
O1^{ii}	90.5(3)	90.5(3)	**1.928(6)**	3.824(7)	2.714(8)	2.693(8)
O6	89.5(2)	90.4(3)	179.1(3)	**1.896(5)**	2.671(9)	2.671(9)
O6^{i}	179.1(3)	89.5(2)	90.4(3)	89.6(2)	**1.896(5)**	2.671(9)
O6^{ii}	90.4(3)	179.1(3)	89.5(2)	89.6(2)	89.6(2)	**1.896(5)**

Sb5	O9^{viii}	O9^{xv}	O12^{viii}	O12^{xv}	O13^{viii}	O13^{xv}
O9^{viii}	**1.937(4)**	3.874(9)	2.737(7)	2.724(7)	2.791(8)	2.700(7)
O9^{xv}	180.	**1.937(4)**	2.724(7)	2.737(7)	2.700(7)	2.791(8)
O12^{viii}	90.3(2)	89.7(2)	**1.925(5)**	3.849(11)	2.722(9)	2.751(9)
O12^{xv}	89.7(2)	90.3(6)	180.	**1.925(5)**	2.751(9)	2.722(9)
O13^{viii}	91.9(2)	88.1(2)	89.4(3)	90.6(3)	**1.946(5)**	3.892(11)
O13^{xv}	88.1(2)	91.9(2)	90.6(3)	89.4(3)	180.	**1.946(5)**

Sb6	O2^{ii}	O4^{x}	O7^{ii}	O8^{ix}	O11^{x}	O14^{viii}
O2^{ii}	**1.928(5)**	2.767(7)	2.656(7)	2.676(8)	2.723(9)	3.859(7)
O4^{x}	91.0(2)	**1.950(5)**	3.879(7)	2.829(8)	2.674(7)	2.761(8)
O7^{ii}	87.0(2)	176.6(2)	**1.930(5)**	2.685(8)	2.726(8)	2.770(7)
O8^{ix}	88.3(3)	94.1(2)	88.6(3)	**1.914(5)**	3.839(7)	2.664(8)
O11^{x}	90.0(3)	87.3(2)	90.0(2)	177.8(2)	**1.925(5)**	2.824(8)
O14^{viii}	175.7(3)	90.6(2)	91.6(2)	87.6(3)	94.1(3)	**1.934(5)**

main interatomic distances and angles are given in Table 3.

RESULTS AND DISCUSSION

Structure Description of β-$Sb_2(PO_4)_3$

The β-form of $Sb_2(PO_4)_3$ ($=Sb^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$) is nearly isotypic with $Bi^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$ (6), whose structure has been described by Oyetola *et al.* (6). The structure belongs to the family of $M_2(TO_4)_3$-type structures that includes NASICON, $Sc_2(WO_4)_3$, and garnet, where the *M* and T atoms are surrounded by oxygen atoms octahedrally and tetrahedrally, respectively. All of these structures have a nearly centered-cubic arrangement (bcc arrangement) of the *M* atoms as discussed by Oyetola *et al.* (6) and Piffard *et al.* (7). To emphasize the centered-cubic arrangement of the antimony atoms, we have shown the structure of the β-$Sb_2(PO_4)_3$ in a rhombohedral cell which

TABLE 3—*Continued*

P1	O2^{x}	O7^{v}	O12^{iv}	O15^{viii}
O2^{x}	**1.528(6)**	2.403(7)	2.463(8)	2.464(8)
O7^{v}	103.2(3)	**1.539(5)**	2.465(7)	2.500(8)
O12^{iv}	108.5(4)	108.1(3)	**1.507(6)**	2.470(8)
O15^{viii}	111.1(4)	112.9(3)	112.6(4)	**1.461(6)**
P2a	O6	O10a^{v}	O11^{xiii}	O13
O6	**1.517(5)**	2.497(8)	2.377(7)	2.453(8)
O10a^{v}	112.8(4)	**1.482(7)**	2.549(8)	2.601(9)
O11^{xiii}	102.4(3)	115.4(4)	**1.535(5)**	2.454(8)
O13	104.7(3)	116.2(4)	103.9(4)	**1.581(6)**
P2b	O6	O11^{xiii}	O13	O16b
O6	**1.695(11)**	2.377(7)	2.453(8)	2.70(3)
O11^{xiii}	97.2(6)	**1.469(11)**	2.454(8)	2.42(4)
O13	96.6(6)	106.7(7)	**1.588(11)**	2.72(3)
O16b	116.3(14)	110.5(15)	125(2)	**1.48(3)**
P3	O1	O3^{xv}	O5^{iv}	O8^{vii}
O1	**1.506(6)**	2.481(9)	2.430(8)	2.359(8)
O3^{xv}	112.5(4)	**1.477(6)**	2.499(8)	2.501(9)
O5^{iv}	106.4(4)	112.6(3)	**1.527(5)**	2.490(7)
O8^{vii}	102.3(4)	112.9(4)	109.4(3)	**1.523(6)**
P4a	O4^{xiii}	O9^{v}	O14	O16a^{v}
O4^{xiii}	**1.525(5)**	2.431(7)	2.415(7)	2.547(9)
O9^{v}	105.0(3)	**1.539(5)**	2.475(7)	2.504(9)
O14	106.0(3)	109.1(3)	**1.499(6)**	2.458(9)
O16^{v}	115.0(4)	111.2(4)	110.3(4)	**1.496(8)**
P4b	O4^{viii}	O9^{i}	O10b^{xiii}	O14^{v}
O4^{viii}	**1.554(11)**	2.431(7)	2.61(2)	2.415(7)
O9^{i}	100.5(6)	**1.607(11)**	2.68(3)	2.475(7)
O10b^{xiii}	117.9(11)	119.9(11)	**1.49(3)**	2.31(3)
O14^{v}	106.6(7)	107.6(6)	103.5(12)	**1.458(11)**

Sb4–O1–P3	142.6(4)	Sb6^{i}–O2–P1^{vi}	142.0(4)
Sb2^{vi}–O3–P3^{xiv}	144.0(4)	Sb6^{vi}–O4–P4a^{xiii}	146.6(4)
Sb6^{vi}–O4–P4b^{xi}	136.6(5)	Sb3–O5–P3^{v}	145.6(4)
Sb4–O6–P2a	143.4(3)	Sb4–O6–P2b	126.5(4)
Sb6^{i}–O7–P1^{iv}	141.5(3)	Sb6^{ix}–O8–P3^{xii}	145.4(3)
Sb5^{xi}–O9–P4a^{iv}	137.4(3)	Sb5^{xi}–O9–P4b^{ii}	125.1(5)
Sb2^{xi}–O10–P2a^{iv}	143.7(4)	Sb2^{xi}–O10a–P4b^{xiii}	159.5(14)
Sb6^{vi}–O11–P2a^{xiii}	140.3(4)	Sb6^{vi}–O11–P2b^{xiii}	163.8(5)
Sb5^{xi}–O12–P1^{v}	160.9(4)	Sb5^{xi}–O13–P2a	134.6(4)
Sb5^{xi}–O13–P2b	136.0(5)	Sb6^{xi}–O14–P4a	149.8(4)
Sb6^{xi}–O14–P4b^{iv}	162.4(6)	Sb2^{xi}–O15–P1^{xi}	133.7(4)
Sb1–O16–P4a^{iv}	150.7(5)	Sb1^{iii}–O16–P4a^{iv}	137.6(5)
Sb1–O16a–P2b	154(2)		

Note. Symmetry codes are as follows. (i) $-y, x-y, z$; (ii) $-x+y, -x, z$; (iii) $-x, -y, -z$; (iv) $y, -x+y, -z$; (v) $x-y, x, -z$; (vi) $x+\frac{2}{3}, y+\frac{1}{3}, z+\frac{1}{3}$; (vii) $-y+\frac{2}{3}, x, -y+\frac{1}{3}, z+\frac{1}{3}$; (viii) $-x+y+\frac{2}{3}, -x+\frac{1}{3}, z+\frac{1}{3}$; (ix) $-x+\frac{2}{3}, -y+\frac{1}{3}, -z+\frac{1}{3}$; (x) $x+\frac{1}{3}, y+\frac{2}{3}, z+\frac{2}{3}$; (xi) $-y+\frac{1}{3}, x-y+\frac{2}{3}, z+\frac{2}{3}$; (xii) $-x+y+\frac{1}{3}, -x+\frac{2}{3}, z+\frac{2}{3}$; (xiii) $-x+\frac{1}{3}, -y+\frac{2}{3}, -z+\frac{2}{3}$; (xiv) $y+\frac{1}{3}, -x+y+\frac{2}{3}, -z+\frac{2}{3}$; (xv) $x, -y+\frac{1}{3}, x+\frac{2}{3}, -z+\frac{2}{3}$.

contains eight centered-cubic subcells (see Fig. 1). In Fig. 2, all independent atoms are drawn.

The structure of the β-$Sb_2(PO_4)_3$ has two types of disorder: (A) the position of a trivalent antimony atom Sb1 and (B) the positions of P2, P4, O10, and O16 atoms. The structure is isotypic with $Bi^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$ if the second type of disorder is neglected. The disorder of the (A)-type will be described in this section, and the (B)-type disorder will be discussed in the next section.

All of the antimony atoms are coordinated by six oxy-

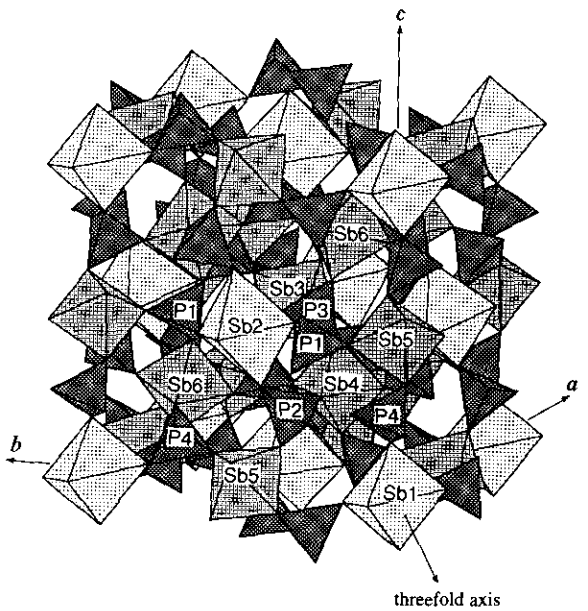

FIG. 1. A rhombohedral unit cell of β-$Sb_2(PO_4)_3$. Sb^{III} polyhedra, Sb^{V} octahedra, and PO_4 tetrahedra are shaded light, medium, and dark, respectively. The tetrahedra around the minor positions of the phosphorus atoms (P2b and P4b) are omitted. The unit cell contains eight cubic-centered subcells of metal atoms as discussed by Oyetola *et al.* (6).

gen atoms. The coordination polyhedra around pentavalent antimony atoms (Sb3–Sb6) are close to perfect octahedra. However, the trivalent antimony atoms have deformed octahedral coordination. Especially, the octahedra around the Sb1 atom are very deformed and modified by the oxygen disorder discussed below. The phosphorus atoms are tetrahedrally bonded with four oxygen atoms. Each oxygen atom is bonded with a phosphorus atom and with an antimony atom.

The trivalent Sb1 atom is located at $(0, 0, \pm z)$ positions (trigonal axes) with an occupancy of $\frac{1}{2}$. The positions are close to an inversion center and related to each other through it. The distance between the two positions is much longer in the antimony compound (0.62 Å) than in the bismuth analog (0.34 Å) (6). This disorder leads to a deformed coordination of the Sb1 atom. Six O16 atoms surround the inversion center near the Sb1 atom to form a trigonal antiprism compressed along the three-fold axis, and the disorder of the Sb1 atom shifts the atom from the center of the antiprism, yielding three longer Sb1–O bonds (2.35 Å) and three shorter bonds (2.06 Å). The coordination of the atom is further modified by the second type of disorder.

Disorder of Phosphorus and Oxygen

The X-ray structural study has revealed that P2, P4, O10, and O16 atoms are distributed in two positions, respectively. Each of these atoms occupies one of the positions with probability ca. $\frac{5}{6}$ and the other with probability ca. $\frac{1}{6}$. We will call the positions occupied in the larger probability major positions and denote them by the atomic name followed by the letter "a," such as P2a. Similarly, the other positions will be called minor positions and are denoted by the letter "b," such as P2b.

The P2 atom exists at either the P2a position or P2b position. At both positions, the P2 atom is surrounded tetrahedrally by four oxygen atoms. Three oxygen atoms (O6, O11, and O13) are common to the coordination tetrahedra around P2a and around P2b as shown in Fig. 3. The two tetrahedra are related approximately by the mirror plane that passes the three common oxygen atoms. The fourth oxygen atom for position P2a and that for position P2b are far apart, and they are connected to different antimony atoms. The P2 atom at the P2a position is bonded to the oxygen atom at the O10a position while the atom at the P2b position is connected to the oxygen atom at O16b. Each of the oxygen atoms is connected to a phosphorus atom and an antimony atom, and the linkages are:

Major positions	P2a–O10a–Sb2;	P4a–O16a–Sb1.
Minor positions	P2b–O16b–Sb1;	P4b–O10b–Sb2.

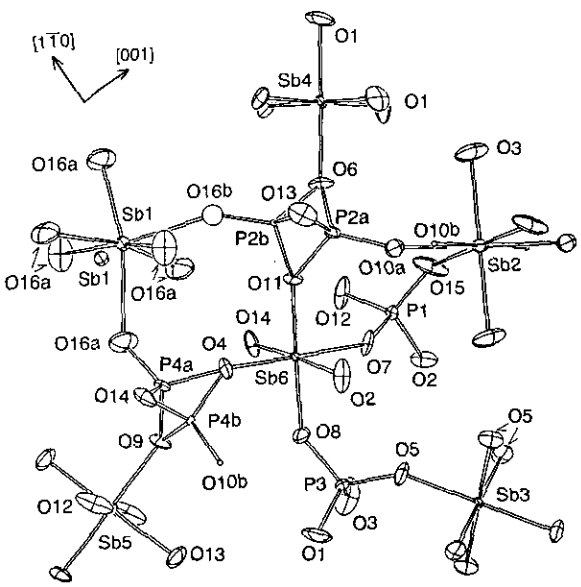

FIG. 2. ORTEP drawing of β-$Sb_2(PO_4)_3$ with 50% thermal ellipsoids projected along [110] of the hexagonal cell (i.e., projected along [101] of the rhombohedral cell). All independent atoms are drawn in the figure. The atoms Sb2 and Sb3 are on the inversion center while Sb1, Sb3, and Sb4 are on the threefold axis. Due to the disorder of oxygen atom O16, the coordination around Sb1 is very complicated, and only one of the O16b positions is drawn. Details of the coordination of the Sb1 atom are shown in Fig. 5. The positions of antimony atoms illustrate the diagonal plane of the cubic-centered subcells of metal atoms discussed by Oyetola *et al.* (6).

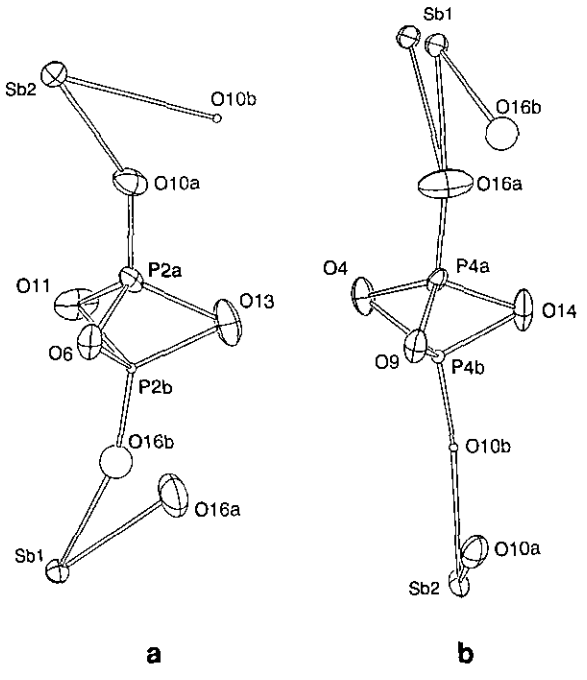

FIG. 3. The disorder around (a) the P2 atom and (b) the P4 atom. The P4a and O16a are the major positions ($\frac{5}{6}$ occupied) while the P4b and O10b are the minor positions ($\frac{1}{6}$ occupied).

The P2 atom at the P2a position is connected to the Sb2 atom through an oxygen atom and the P2 atom at the P2b position is connected to the Sb1 atom. Similarly, the P4 atom at the P4a position is connected to the Sb1 while the atom at P4b is connected to the Sb2 atom. Thus, the position of the phosphorus atoms affects the coordination of the Sb1 and Sb2 atoms and must be selected so that the coordinations around the Sb1 and Sb2 atoms are appropriate. In other words, the choice of the phosphorus and oxygen positions propagates through the antimony atoms. If a P2 atom is at the P2b position, the oxygen atom bonded with it must be at O16b, and the P2 atom is connected with the Sb1 atom through the oxygen atom. Then, the Sb1 atom cannot have an oxygen atom at the O16a position due to the small distance between O16a and O16b (1.60 Å), and the P4 atom neighboring the Sb1 atom must be at the P4b position because the P4a position would require the oxygen to be at the O16a position (Fig. 4). This choice forces the P4 atom to be connected with other antimony atom (Sb2) through the O10b position. In short, the coordination of the $P2O_4$ tetrahedron to the Sb1 atom expels the $P4O_4$ tetrahedron from the coordination of the Sb1 atom, and the $P4O_4$ tetrahedron must shift toward the neighboring Sb2 atom and coordinate to it. The choice of the positions propagates as

P2b occupied
→ O16b on Sb1 occupied
(=O16a not occupied)
→ P4b occupied → O10b on Sb2 occupied
(=O10a not occupied)
→ P2b occupied → · · · .

However, it does not propagate infinitely. It localizes as shown in Fig. 4 because the propagation of the choice of the positions makes a loop. If the choice of position were not localized, the lattice would have a superstructure.

The disorder of the O16 atoms is related to the coordination of the trivalent antimony atom Sb1. The structural determination has shown that about one-sixth of the O16 atoms are located at the O16b position and the rest are at the O16a position. The O16a positions surrounding an Sb1 atom make a trigonal antiprism compressed along the three-fold axis, and the O16b positions an elongated one (Fig. 5). The Sb1 atom is not at the center of the antiprisms, but is shifted by 0.31 Å along the three-fold axis

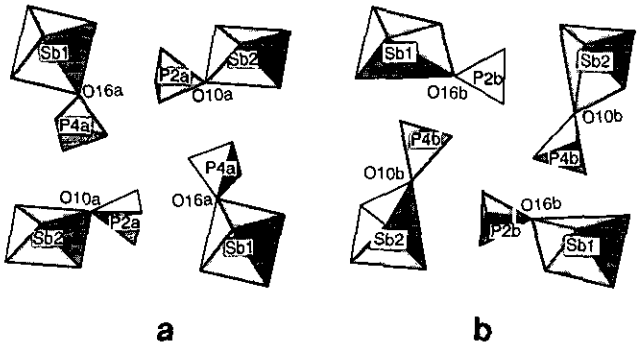

FIG. 4. The propagation of the choice of the disordered positions: (a) major positions; (b) minor positions.

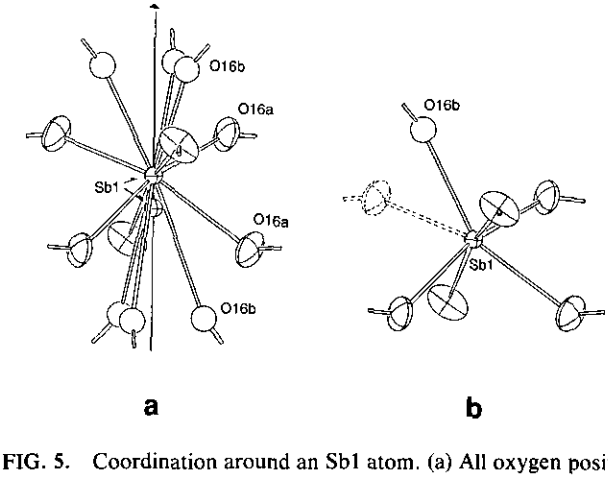

FIG. 5. Coordination around an Sb1 atom. (a) All oxygen positions surrounding an Sb1 atom. (b) A possible coordination with a space for the lone-pair electron of the Sb1 atom.

due to the (A)-type disorder. Three of the O16a positions are at an appropriate distance (2.350 Å) from the Sb1 atom, and the other three are at a distance of 2.058 Å, which is a little shorter than normal. On the other hand, three of the O16b positions are too far from the Sb1 atom (2.886 Å) to bond with it, and other three have an appropriate distance (2.313 Å). Because the three allowed O16b positions are too close to each other (1.72 Å) to be occupied at the same time, only one of the six O16b positions around an Sb1 atom can be occupied. From this restriction, the occupation factor of the O16b position must be equal to or less than one-sixth. If it is less than one-sixth, some Sb1 atoms must be surrounded by six oxygen atoms at the O16a positions and have three shorter bonds (2.058 Å). This tight coordination is relaxed by the occupation of one of the three O16b positions. The valence calculated by the bond–valence method (12) is +3.07 for the Sb1 atom surrounded by five oxygen atoms at the O16a positions and one at the O16b position. If all oxygen atoms are at the O16a positions, the calculated valence is +3.47. Another reason for the occupation of the O16b position is that it makes a suitable space for the lone-pair electron on the Sb1 atom, as shown in Fig. 5. The occupation of one of the O16b positions is very favorable for the Sb1 atom due to the bond distances and also due to the stereochemistry of the lone pair electrons. Therefore, we have concluded that the occupation factor of the minor positions is $\frac{1}{6}$.

The disorder of the O10 atom affects the coordination of the Sb2 atom. Because an Sb2 atom is bonded to two O10 atoms, the occupation of one-sixth of the O10b positions affects only one-third of the Sb2 atoms. The occupation of the O10b position gives a suitable space for the lone pair of the Sb2 atom, as shown in Fig. 6. However, the bond distance becomes too long. The calculated valence of the Sb2 atom is +2.54 if one of the O10b positions is occupied, and is +2.79 if only O10a positions are occupied. The occupation of the disordered positions of the oxygen atoms is not very advantageous to the Sb2 atoms. Therefore, the driving force of the disorder of the P2, P4, O10, and O16 atoms may be the favorable coordination of oxygen atoms around the Sb1 atoms.

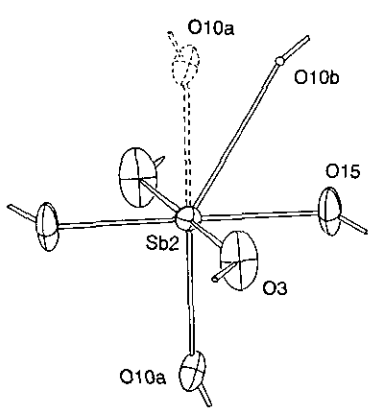

FIG. 6. A possible coordination around an Sb2 atom.

The oscillation and Weissenberg photographs with the [100] axis of the rhombohedral cell did not show any indication of superstructure.

Comparison of α and β Forms of $Sb_2(PO_4)_3$

As described above, β-$Sb_2(PO_4)_3$ is nearly isotypic with $Bi^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$, and the structure of α-$Sb_2(PO_4)_3$ is basically of the $Sc_2(WO_4)_3$-type (7). Both structures are made of SbO_6 octahedra and PO_4 tetrahedra, and each SbO_6 octahedron shares an oxygen atom with four neighboring PO_4 tetrahedra. Therefore, local structures of both compounds are similar. Furthermore, both structures belong to the $M_2(TO_4)_3$ structural family described above, and the arrangement of antimony atoms are centered-cubic in both structures. However, the topological connectivities of these structures are different. Since the relation between the $Sc_2(WO_4)_3$ and $Bi^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$ structures has been well discussed (6, 8), we will mention here only a difference that can be easily described. In the $M_2(TO_4)_3$-type structures, some MO_6 octahedra are connected with another MO_6 octahedron through three TO_4 bridges. In α-$Sb_2(PO_4)_3$, every SbO_6 octahedron is connected with another SbO_6 octahedron through such bridges to make Sb–$(PO_4)_3$–Sb groups. In β-$Sb_2(PO_4)_3$, trivalent antimony atoms (Sb1 and Sb2), Sb5, and Sb6 do not have such triply bridged neighbors while Sb3 and Sb4 make a triply bridged triplet of Sb4–$(PO_4)_3$–Sb3–$(PO_4)_3$–Sb4.

Because α and β forms have different connectivities, their interconversion requires breaks and reconnections of Sb–O bonds and/or P–O bonds, and is expected to occur only at very high temperatures. Indeed, we have never observed any conversion between them. At present, therefore, the thermodynamic relation between them is not clear. However, the preparative methods described under Experimental give some hints about the thermodynamic or kinetic stability. The α form is prepared by the rapid increase of the reaction temperature while the preparation of the β form requires preheating at 400–500°C. These facts indicate that the α form is made thermodynamically or kinetically at higher temperatures and the β form at lower temperatures.

Structure of $M^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$

The powder X-ray diffractions have shown that $Y_{1/2}Sb^{V}_{3/2}(PO_4)_3$ is isotypic with $Bi^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$. Because we have not been able to obtain single crystals of this compound, it has not been determined whether the yttrium compound has a similar disorder, as observed in β-

TABLE 4
Cell Parameters of $M^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_2$ Compounds

M^{III}	Type[a]	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)	$r(M^{III})$[b]
Sc	S	11.810(6)	8.616(4)	8.400(5)	90.80(1)	854.6(6)	0.885
Sb[c]	S	11.936(1)	8.7354(8)	8.3185(8)	91.12(2)	867.14	0.90
Sb[d]	B	16.880(2)		21.196(3)		5230(1)	0.90
In	S	11.792(3)	8.622(3)	8.379(3)	90.91(2)	851.8(3)	0.940
Y	B	17.019(2)		21.233(6)		5326(2)	1.04
Bi[e]	B	17.034(2)		21.260(4)		5342.1	1.17

[a] Type S: α-$Sb_2(PO_4)_3$ structure (monoclinic, $P2_1/n$). Type B: $Bi_{1/2}Sb_{3/2}(PO_4)_3$ structure (trigonal, $R\bar{3}$) including the β-$Sb_2(PO_4)_3$ structure.
[b] Crystal radius of the trivalent metal cation from Ref. (13).
[c] From Ref. (8).
[d] From the single crystal data of this work.
[e] From Ref. (6).

$Sb_2(PO_4)_3$. On the other hand, $In_{1/2}Sb^{V}_{3/2}(PO_4)_3$ and $Sc_{1/2}SB^{V}_{3/2}(PO_4)_3$ are found to have the α-$Sb_2(PO_4)_3$ structure. The cell parameters of the new compounds, as determined by X-ray powder diffraction, are given in Table 4.

Jouanneaux *et al.* have pointed out that $M^{III}_{1/2}M'^{V}_{3/2}(PO_4)_3$ takes the $Bi^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$ structure when the ratio of $r(M)/r(M')$ is large (14). Though the ratios $r(Y)/r(Sb^V)$, $r(In)/r(Sb^V)$, and $r(Sc)/r(Sb^V)$ are close to the borderline, their structures are in agreement with this expectation. Table 4 suggests that the lower limit of the $r(M)$ of $M^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$ with the $Bi^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$ structure is between r(In) (0.94 Å) and r(Y) (1.04 Å). However, Sb^{III}, which is smaller than indium, takes both the $Bi^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$-like structure and the α-$Sb_2(PO_4)_3$ structure. The reason why β-$Sb_2(PO_4)_3$ can exist may be that the structure is stabilized for Sb^{III} atoms through the disorder discussed above.

ACKNOWLEDGMENTS

We thank Professor T. Iwamoto for providing the facility for the X-ray powder diffraction measurement of β-$Sb_2(PO_4)_3$. We are indebted to Rigaku Co. for the measurements of powder diffractions of the compounds containing Y, In, and Sc.

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