JOURNAL OF SOLID STATE CHEMISTRY 77, 102–111 (1988)

$Bi^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$: A New Type of $M_2(XO_4)_3$ Framework Related to Garnet and Nasicon

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Received March 31, 1988; in revised form June 20, 1988

The single-phase compound $Bi^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$ was prepared by solid-state reaction at 1173 K. It crystallizes in the rhombohedral system, space group $R\bar{3}$ with $a = 17.034(2)$ Å, $c = 21.260(4)$ Å, $Z = 24$. The structure was determined from 1487 reflections collected with a Nonius CAD4 diffractometer with Mo$K\bar{\alpha}$ radiation. The final R index and weighted R_w index are 0.034 and 0.040, respectively. This framework structure is built up from PO_4 tetrahedra sharing their four corners with three SbO_6 octahedra and one BiO_6 octahedron. The MO_6 octahedra (SbO_6 and BiO_6) share all their corners with PO_4 tetrahedra and they exhibit a nearly cubic-centered arrangement. This new type of $M_2(XO_4)_3$ framework is compared to those of garnet, nasicon, and $Sc_2(WO_4)_3$ in which the arrangement of octahedra is very similar.

Introduction

A number of oxides having the general compositional formula $A_nM_2(XO_4)_3$ adopt crystal structures containing a framework of corner-linked MO_6 octahedra and XO_4 tetrahedra such that each oxygen atom is bonded to one M atom and one X atom; i.e., each MO_6 tetrahedron is linked to four octahedra. The octahedra are then linked to each other via O–O "bonds" which are edges of tetrahedra and have been called T-bonds (*1*). Since each octahedron is connected to six tetrahedra via vertex-sharing, there are 18 such T-bonds between this octahedron and its neighboring octahedra. The manner in which they are distributed leads to various types of $M_2(XO_4)_3$ frameworks (garnet (*2*), nasicon (*3*), langbeinite (*4*), $Sc_2(WO_4)_3$ (*5*)) which are not simple distortions of each other. However, it has been shown recently (*1*) that garnet, nasicon, and $Sc_2(WO_4)_3$ frameworks are closely related: they all exhibit a cubic or nearly cubic-centered arrangement of octahedra and there is one T-bond between a given octahedron and each of the six next nearest neighboring octahedra which are the six centers of the next nearest cubes (Fig. 1). They differ from each other, as indicated in Fig. 1, by the distribution of the 12 remaining T-bonds between an octahedron and its eight neighboring octahedra at the apices of the cube.

In the langbeinite framework the arrangement of octahedra is not pseudo-cubic-centered. However, nasicon, $Sc_2(WO_4)_3$, and langbeinite structure types can be described as built up from the same type of $M_2X_3O_{18}$ units (two octahedra joined by three tetrahedra) (*1*).

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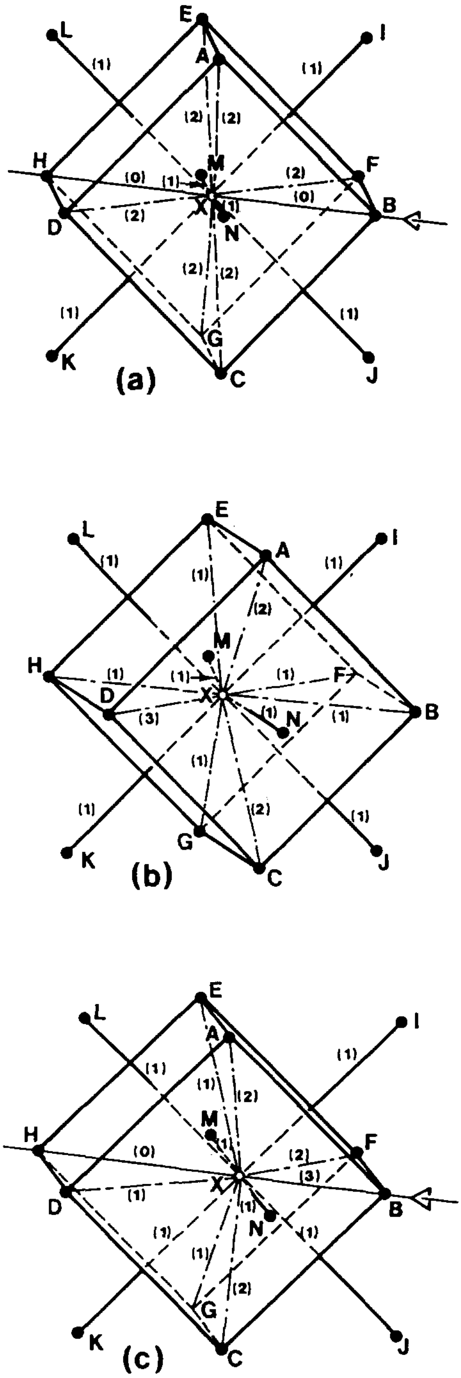

FIG. 1. Perspective views of the cubic-centered arrangements of octahedral cations in (a) garnet, (b) $Sc_2(WO_4)_3$, (c) nasicon. Figures between brackets indicate the number of T-bonds between the "central" atom X and its neighbors (A, B, . . . , N).

A number of $M_2(XO_4)_3$ frameworks are stable in the total absence of A cations. They are either $Sc_2(WO_4)_3$ or nasicon type but, to our knowledge, no example of the garnet framework without A cation exists. In connection with that it must be mentioned that the structure of $Fe_2(MoO_4)_3$ (*6–9*) is very frequently considered to be a garnet structure with the A sites unoccupied whereas it belongs to the $Sc_2(WO_4)_3$ type. $Sc_2(WO_4)_3$-related compounds include molybdates and tungstates of Al^{3+}, Sc^{3+}, Cr^{3+}, Fe^{3+}, In^{3+}, and the smaller rare-earth ions Ln^{3+} as well as the monoclinic form of ferric sulfate, $Fe_2(SO_4)_3$ (*10–18*) and the orthorhombic form of zirconium phosphatosulfate β-$Zr_2(PO_4)_2SO_4$ (*1*). Nasicon framework structures, with the A sites unoccupied, are observed for the $M^{\text{IV}}M'^{\text{V}}(PO_4)_3$ compounds (M = Ti, Ge and M' = Sb, Nb, Ta) (*19*) and in the rhombohedral form of ferric sulfate, $Fe_2(SO_4)_3$ (*17, 20*). The rhombohedral form of zirconium phosphatosulfate, α-$Zr_2(PO_4)_2SO_4$ is also assumed to be of this type (*21*).

Recently, we have shown (*22*) that chemical substitution at the Zr site of the ZrP_2O_7 structure by various cations gives rise to compounds corresponding to the compositional formula $M''^{\text{III}}_{1/2}M'^{\text{V}}_{1/2}P_2O_7$ (M' = Sb, Nb, Ta and M'' = Sb, Bi, Ln). In the same way, attempts have been undertaken to substitute the M^{IV} cation in the $M^{\text{IV}}M'^{\text{V}}(PO_4)_3$ phases mentioned above. We report here on the preparation and crystal structure determination of $Bi^{\text{III}}_{1/2}Sb^{\text{V}}_{3/2}(PO_4)_3$ which, formally, could be considered as one such phase. This compound exhibits in fact a new structural type which is compared to the garnet, nasicon, and $Sc_2(WO_4)_3$ frameworks.

Experimental

Single crystals of $Bi_{1/2}Sb_{3/2}(PO_4)_3$ were prepared by heating, in a platinum crucible, stoichiometric proportions of $NH_4H_2PO_4$,

TABLE I

$Bi^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$: UNIT CELL CONSTANTS

Crystal symmetry	Trigonal
a (Å)	17.034 (2)
c (Å)	21.260 (4)
V (Å^3)	5342.1
D_{calc} (g · cm^{-3})	4.266
Z	24
Space group	$R\bar{3}$
μ (cm^{-1}) for $\lambda K\bar{\alpha}$ = 0.71069 Å	150.2

Bi_2O_3 and $Sb_2O_5 \cdot xH_2O$ at 473 K for 4 hr to decompose the $NH_4H_2PO_4$ and at 1173 K for 24 hr to complete the reaction. The crystals obtained are colorless small hexagonal prisms. Single-crystal X-ray study indicates that the compound is of rhombohedral symmetry. The cell parameters (Table I) were refined by a least-squares procedure from powder diffraction data collected with a Guinier camera (Guinier Nonius FR552, quartz crystal monochromator, Cu$K\alpha_1$ = 1.54056 Å, $Pb(NO_3)_2$ as standard). The powder pattern (Table II) includes observed and calculated interplanar distances of the reflection planes along with the intensities calculated from the Lazy Pulverix program (*23*). Intensity data were collected with a Nonius CAD4 diffractometer operating under the conditions 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 (*24*), was used.

TABLE II

$Bi^{III}_{1/2}Sb^{V}_{3/2}(PO_4)_3$: X-RAY POWDER DIFFRACTION DATA

$h\ k\ l$	d_{obs} (Å)	d_{calc} (Å)	I/I_0
1 1 3	5.467	5.447	10
2 1 1	5.404	5.393	11
0 2 4	4.316	4.312	100
2 2 0	4.259	4.258	95
3 1 2	3.818	3.818	5
2 2 3	3.651	3.650	16
0 4 2	3.482	3.484	5
1 2 5	3.383	3.381	4
3 2 1	3.340	3.342	5
1 1 6	3.273	3.271	2
2 3 2	3.220	3.225	5
4 1 0		3.219	
4 0 4	3.029	3.030	63
3 1 5	2.948	2.948	4
4 1 3	2.928	2.931	6
0 5 1		2.922	
2 4 1	2.765	2.764	3
2 2 6	2.725	2.724	5
2 1 7	2.667	2.667	6
2 3 5	2.647	2.648	9
2 0 8	2.501	2.500	19
2 4 4	2.469	2.469	39
6 0 0	2.458	2.459	25
4 2 5	2.334	2.331	3
0 4 8	2.157	2.156	10
0 3 9	2.129	2.129	13
4 4 0			
2 2 9	2.066	2.066	2
0 2 10	2.043	2.043	3
0 6 6	2.020	2.020	2
2 6 2	2.008	2.009	4
4 2 8	1.924	1.924	19
6 2 4	1.908	1.909	22
4 3 7	1.894	1.895	3
0 7 5	1.888	1.888	3
5 3 5		1.888	
1 3 10		1.887	
7 1 3	1.882	1.884	3
5 4 1		1.881	
2 6 5	1.843	1.843	2
4 0 10		1.842	
4 4 6	1.824	1.825	2
6 3 3	1.797	1.798	3
2 7 1		1.796	
0 8 4	1.742	1.742	4
4 5 5	1.726	1.726	3
2 4 10	1.690	1.691	4
6 4 2	1.670	1.671	5
2 5 9		1.670	
2 2 12	1.635	1.636	12
2 6 8	1.620	1.621	13
4 6 4	1.612	1.610	17
2 8 0	1.610	1.609	16

TABLE III

DATA COLLECTION AND REFINEMENT CONDITIONS

Data collection	
Equipement	Nonius CAD4 diffractometer
Radiation (Å)	Mo$K\bar{\alpha}$ $\lambda = 0.71069$
Scan mode	ω-2θ
Scan angle (°)	$\Delta\omega = 1.0 + 0.35 \tan\theta$
Recording angular range (θ°)	1.5-35.0
Number of independent data observed with $\sigma(I)/I < 0.3$ (used in refinements)	1487
Refinements	
Number of variables (isotropic temperature factors)	93
$R = \Sigma(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/\Sigma \lvert F_o\rvert$	0.038
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w F_o^2]^{1/2}$ with $w = 1/(1 + [(F_o - F_{av})/F_{max}]^2)$	0.045
Number of variables (anisotropic temperature factors for Bi, Sb, and P atoms)	131
$R =$	0.034
$R_w =$	0.040
Extinction parameter refined $g =$	$1.4(2) \times 10^{-8}$

Refinement was carried out by the full-matrix least-squares method. The positional parameters of the bismuth and antimony atoms were determined from the three-dimensional Patterson map. Those of the phosphorus and oxygen atoms were then inferred from Fourier syntheses. In the final stage of refinement Bi, Sb, and P atoms were refined anisotropically. Refinement converged with $R = 0.034$ and $R_w = 0.040$. The final Fourier-difference map is featureless with maxima and minima in the range ±0.6 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 will be sent upon request).

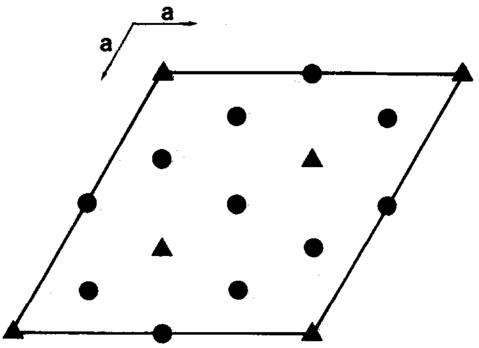

FIG. 2. Projection of the M cations (Bi and Sb) on the (001) plane showing the two types of files: (▲) type I, (●) type II.

Description of the Structure and Discussion

The structure of $Bi_{1/2}Sb_{3/2}(PO_4)_3$ is a new type of $M_2(XO_4)_3$ framework built up from MO_6 octahedra (BiO_6 and SbO_6) sharing all their corners with XO_4 tetrahedra, and XO_4 tetrahedra (PO_4) sharing all their corners with octahedra.

The M cations are located on two types of files running parallel to the c axis. In the first one they coincide with the threefold axes and in the second they go through the center of the hexagonal cell or equivalent sites (Fig. 2) so that there are three times as much files of type II as files of type I. If, then, the description includes the PO_4 tetrahedra around each M cation, the structure can be considered as a three-dimensional arrangement of two types of chains, parallel to the c axis. Such chains are represented on two figures. In Fig. 3, they have been artificially separated from each other in order to show more clearly the linkage between the MO_6 octahedra along each type of chain. The same chains, linked together to give an actual fragment of the structure, are shown in Fig. 4.

In this structure, the arrangement of the M cations and then of the MO_6 octahedra is pseudo-cubic-centered (Fig. 5). Therefore, $Bi_{1/2}Sb_{3/2}(PO_4)_3$ can be compared to the other $M_2(XO_4)_3$ frameworks exhibiting the same feature: garnet, nasicon, and $Sc_2(WO_4)_3$. In each of these three frameworks there is only one type of elementary cube or pseudo-cube (*1*) whereas there are six different ones in $Bi_{1/2}Sb_{3/2}(PO_4)_3$ (Fig. 5). They are centered on the six independent positions (Table IV) occupied by the M cat-

TABLE IV

FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS

Atom	x	y	z	B (Å^2)[a]
Bi(1)	0.0	0.0	0.0079(1)	1.09(3)
Bi(2)	0.5	0.0	0.0	0.83(1)
Sb(1)	0.0	0.0	0.5	0.33(2)
Sb(2)	0.0	0.0	0.28181(8)	0.32(2)
Sb(3)	0.5	0.0	0.5	0.39(2)
Sb(4)	0.50980(6)	0.02409(5)	0.23722(5)	0.31(1)
P(1)	0.3403(2)	0.0393(2)	0.7899(2)	0.37(6)
P(2)	0.0247(2)	0.1783(2)	0.2063(2)	0.57(6)
P(3)	0.1479(3)	0.1226(3)	0.3892(2)	0.78(7)
P(4)	0.0554(3)	0.2254(3)	0.9580(2)	0.94(7)
O(1)	0.1093(8)	0.0579(8)	0.3329(6)	1.2(2)*
O(2)	0.0956(8)	0.3693(8)	0.1306(6)	1.5(2)*
O(3)	0.2020(9)	0.4683(9)	0.2796(7)	1.8(2)*
O(4)	0.2620(8)	0.4075(8)	0.6404(6)	1.3(2)*
O(5)	0.0438(8)	0.1098(8)	0.5503(6)	1.2(2)*
O(6)	0.0465(7)	0.1051(7)	0.2283(6)	1.1(2)*
O(7)	0.0246(8)	0.4546(8)	0.1632(6)	1.2(2)*
O(8)	0.2356(9)	0.4164(9)	0.0503(7)	1.9(2)*
O(9)	0.2983(7)	0.1602(7)	0.0799(6)	1.1(2)*
O(10)	0.2549(7)	0.1964(7)	0.7493(6)	1.1(2)*
O(11)	0.2594(9)	0.4657(9)	0.5248(7)	2.0(2)*
O(12)	0.3071(8)	0.2627(8)	0.1793(7)	1.6(2)*
O(13)	0.2098(8)	0.0781(8)	0.1932(6)	1.5(2)*
O(14)	0.2280(8)	0.2585(8)	0.0627(6)	1.4(2)*
O(15)	0.3219(8)	0.0487(9)	0.7242(7)	1.6(2)*
O(16)	0.1342(8)	0.0899(8)	0.0517(6)	1.4(2)*

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Bi(1)	0.00061(3)	β_{11}	0.00122(6)	β_{11}	0	0
Bi(2)	0.00068(2)	0.00102(2)	0.00047(1)	0.00061(3)	0.00033(5)	−0.00013(4)
Sb(1)	0.00048(5)	β_{11}	0.00009(4)	β_{11}	0	0
Sb(2)	0.00033(3)	β_{11}	0.00022(3)	β_{11}	0	0
Sb(3)	0.00033(3)	0.00044(3)	0.00031(2)	0.00049(5)	0.00024(8)	0.00065(6)
Sb(4)	0.00018(2)	0.00026(2)	0.00027(1)	0.00013(4)	−0.0005(5)	0.00008(3)
P(1)	0.00046(9)	0.00022(9)	0.00034(7)	0.0005(1)	0.0000(1)	−0.0002(1)
P(2)	0.0005(1)	0.0005(1)	0.00042(7)	0.0004(1)	−0.0004(2)	−0.0001(2)
P(3)	0.0005(1)	0.0012(1)	0.00041(7)	0.0006(2)	−0.0002(2)	0.0002(2)
P(4)	0.0005(1)	0.0021(1)	0.00026(7)	0.0012(2)	0.0000(2)	0.0004(2)

Note. The form of the anisotropic thermal parameter is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $B_{eq} = 4/3\ \Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\mathbf{a}_j$.

ions (Bi(1), Bi(2), and Sb(1) to Sb(4)). In each of the six pseudo-cubes the central octahedron is connected to each of the next nearest neighboring octahedra (which are the six centers of the next nearest cubes) via one T-bond. Therefore, the comparison of the six pseudo-cubes between themselves and with the elementary cubes or pseudo-cubes in garnet, nasicon, and $Sc_2(WO_4)_3$ structures amounts to the distri-

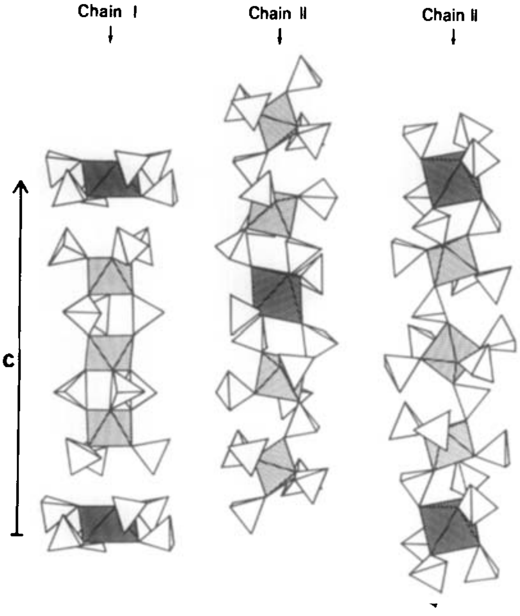

FIG. 3. [120] view of the chains (see text) artificially separated from each other.

bution of 12 T-bonds between an octahedron and its eight neighboring octahedra at the apices of the cube. In order to describe the different possible distributions, one can consider first that the number of T-bonds between a given octahedron and one of its eight neighboring octahedra can vary from 0 to 3 and then that there are k, l, m, and n such neighbors which are linked to the central octahedron by 0, 1, 2, and 3 T-bonds, respectively. A distribution can therefore be written ($k\ l\ m\ n$) with:

$$k + l + m + n = 8 \text{ (number of neighbors)}$$

$$l + 2m + 3n = 12 \text{ (number of T-bonds)}.$$

According to this way of writing distributions, those which have been evidenced in garnet, $Sc_2(WO_4)_3$, and nasicon are (2060), (0521), and (1331), respectively (see Fig. 1). In $Bi_{1/2}Sb_{3/2}(PO_4)_3$ the distributions which are observed around the six nonequivalent MO_6 octahedra are the following (see Fig. 6):

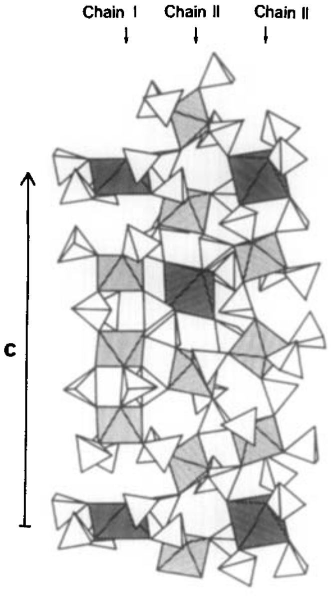

FIG. 4. [120] view of a fragment of the structure corresponding to the chains represented in Fig. 3.

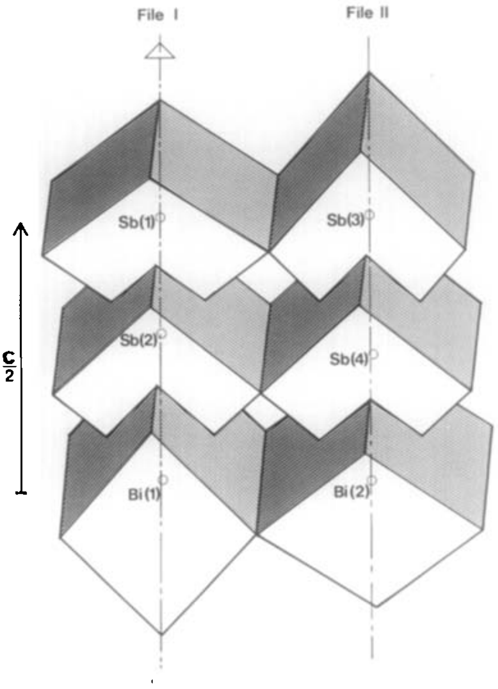

FIG. 5. Perspective view showing the pseudo-cubic-centered arrangement of the Bi and Sb atoms (each apex of the pseudo-cubes corresponds either to a Bi or a Sb atom).

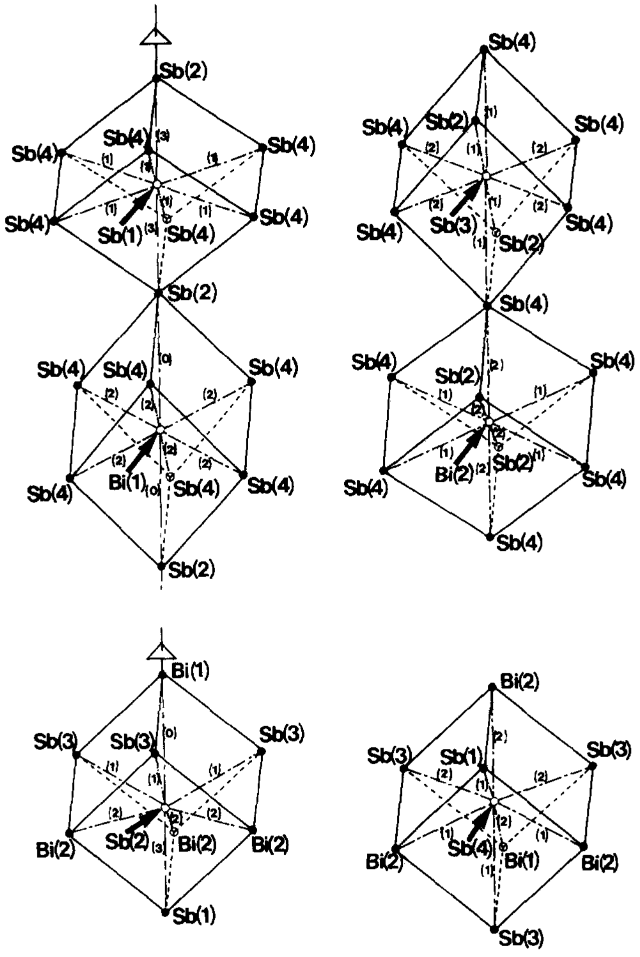

FIG. 6. Perspective views of the pseudo-cubic-centered arrangements of octahedral cations in Bi$_{1/2}$Sb$_{3/2}$(PO$_4$)$_3$. Figures between parentheses indicate the number of T-bonds between the central octahedron and its eight neighboring octahedra (as in Fig. 1).

Bi(1)O$_6$ → (2060)
Bi(2)O$_6$ → (0440)
Sb(1)O$_6$ → (0602)
Sb(2)O$_6$ → (1331)
Sb(3)O$_6$ → (0440)
Sb(4)O$_6$ → (0440)

The pseudo-cubes centered on Bi(1) and Sb(2) are similar to those observed, respectively, in garnet and nasicon. The four others have never been encountered before. Three of them (around Bi(2), Sb(3), and Sb(4)) exhibit the same (0440) distribution. However, only those around Bi(2) and Sb(3) are strictly identical in terms of relative positions of octahedra linked by 1 and 2 T-bonds (see Fig. 6).

Bi(1)O$_6$ and Sb(2)O$_6$ octahedra are not linked by T-bonds and the 6c site (0, 0, z with z = 0.13) located halfway between Bi(1) and Sb(2) is about 2.6 Å from the nearest oxygen atoms (Figs. 5 and 6). This site is nearly the same as that of Na in NaZr$_2$(PO$_4$)$_3$ (*3*).

For $Bi_{1/2}Sb_{3/2}(PO_4)_3$ a list of bond distances 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 bismuth (III), antimony (V), and phosphate structural chemistry. Within the $Bi(1)O_6$ octahedra Bi(1) occupies statistically (at 50%) an off-centered 6c position very close to a $\bar{3}$ site. This situation leads to two groups of three Bi(1)–O(16) distances instead of six equal ones and accounts for the stereochemical activity of the Bi^{III} $6s^2$ lone pair. This activity is less sensible for Bi(2) which occupies an inversion center. The SbO_6 octahedra are rather regular. The most distorted one is $Sb(4)O_6$ with Sb(4)–O distances ranging from 1.906(6) to 1.970(5) Å and O–Sb(4)–O angles from 85.1 to 94.6°. Each PO_4 tetrahedron is connected to three

TABLE V

BOND DISTANCES (Å) FOR THE COORDINATION POLYHEDRA

$Bi(1)O_6$ octahedron			$Bi(2)O_6$ octahedron		
Bi(1) -O(16)	(3×)	2.222(6)	Bi(2) -O(3)	(2×)	2.360(6)
-O(16)	(3×)	2.382(6)	-O(10)	(2×)	2.410(5)
			-O(15)	(2×)	2.276(5)
O(16)-O(16)	(6×)	3.494(8)			
O(16)-O(16)	(6×)	2.984(9)	O(3) -O(10)	(2×)	3.269(7)
			-O(10)	(2×)	3.474(8)
			-O(15)	(2×)	3.275(7)
			-O(15)	(2×)	3.283(8)
			O(10)-O(15)	(2×)	3.285(7)
			-O(15)	(2×)	3.344(8)
$Sb(1)O_6$ octahedron			$Sb(2)O_6$ octahedron		
Sb(1)-O(5)	(6×)	1.951(5)	Sb(2)-O(1)	(3×)	1.945(5)
			-O(6)	(3×)	1.926(5)
O(5) -O(5)	(6×)	2.825(8)			
-O(5)	(6×)	2.691(8)	O(1) -O(1)	(3×)	2.794(9)
			-O(6)	(3×)	2.757(7)
			-O(6)	(3×)	2.706(7)
			O(6) -O(6)	(3×)	2.691(8)
$Sb(3)O_6$ octahedron			$Sb(4)O_6$ octahedron		
Sb(3)-O(9)	(2×)	1.926(4)	Sb(4)-O(2)		1.934(6)
-O(12)	(2×)	1.918(5)	-O(4)		1.953(5)
-O(13)	(2×)	1.962(5)	-O(7)		1.970(5)
			-O(8)		1.906(6)
O(9) -O(12)	(2×)	2.697(7)	-O(11)		1.933(6)
-O(12)	(2×)	2.738(7)	-O(14)		1.942(5)
-O(13)	(2×)	2.816(7)			
-O(13)	(2×)	2.681(7)	O(2) -O(4)		2.800(7)
O(12)-O(13)	(2×)	2.741(7)	-O(7)		2.641(7)
-O(13)	(2×)	2.746(7)	-O(8)		2.709(7)
			-O(11)		2.711(8)
			O(4) -O(8)		2.788(8)
			-O(11)		2.659(7)
			-O(14)		2.784(7)
			O(7) -O(8)		2.738(7)
			-O(11)		2.789(8)
			-O(14)		2.804(7)
			O(8) -O(14)		2.641(7)
			O(11)-O(14)		2.849(7)

TABLE V—*Continued*

$P(1)O_4$ tetrahedron		$P(2)O_4$ tetrahedron	
P(1) -O(2)	1.547(6)	P(2) -O(6)	1.541(5)
-O(7)	1.532(5)	-O(10)	1.475(5)
-O(12)	1.525(5)	-O(11)	1.550(6)
-O(15)	1.457(6)	-O(13)	1.544(5)
O(2) -O(7)	2.412(7)	O(6) -O(10)	2.502(7)
-O(12)	2.502(8)	-O(11)	2.345(7)
-O(15)	2.487(7)	-O(13)	2.495(7)
O(7) -O(12)	2.461(7)	O(10)-O(11)	2.552(7)
-O(15)	2.489(7)	-O(13)	2.535(7)
O(12)-O(15)	2.479(7)	O(11)-O(13)	2.496(8)
$P(3)O_4$ tetrahedron		$P(4)O_4$ tetrahedron	
P(3) -O(1)	1.535(5)	P(4) -O(4)	1.535(5)
-O(3)	1.453(6)	-O(9)	1.558(5)
-O(5)	1.542(5)	-O(14)	1.548(5)
-O(8)	1.556(6)	-O(16)	1.483(6)
O(1) -O(3)	2.508(7)	O(4) -O(9)	2.466(7)
-O(5)	2.488(7)	-O(14)	2.439(7)
-O(8)	2.379(7)	-O(16)	2.552(7)
O(3) -O(5)	2.482(7)	O(9) -O(14)	2.524(7)
-O(8)	2.509(8)	-O(16)	2.503(7)
O(5) -O(8)	2.518(7)	O(14)-O(16)	2.502(7)

SbO_6 octahedra and one BiO_6 octahedron. The three oxygen atoms bonded to antimony lead to P–O distances ranging from 1.525(5) to 1.558(5) Å. The fourth, bonded to Bi, leads to a shorter P–O distance (average value: 1.467 Å for the four nonequivalent PO_4 tetrahedra).

In $Bi_{1/2}Sb_{3/2}(PO_4)_3$ the shortest Bi–Bi distance is 8.5 Å. This feature is of great interest since we have shown recently that it is possible to substitute Bi with Nd to get $Nd_xBi_{1/2-x}Sb_{3/2}(PO_4)_3$ materials ($0 < x < 1/2$). As a matter of fact it has been shown that the degree of concentration quenching in Nd laser materials is determined by the linkage between the NdO_y polyhedra (*25*), and especially by the Nd–Nd distance. The luminescence properties of $Nd_xM^{III}_{1/2-x}Sb_{3/2}(PO_4)_3$ materials (M = Bi, Sb) are presently being investigated.

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