

Structures of  $\text{Pb}_3\text{GeGa}_{10}\text{O}_{20}$  and  $\text{Ba}_3\text{SnFe}_{10}\text{O}_{20}$ 

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**Abstract.**  $\text{Pb}_3\text{GeGa}_{10}\text{O}_{20}$ :  $M_r = 1711.3$ ,  $I2/m$ ,  $a = 14.751$  (5),  $b = 11.695$  (5),  $c = 5.106$  (3) Å,  $\beta = 90.23$  (3)°,  $V = 881$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 6.45$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $T = 291$  K, single-crystal X-ray diffraction,  $R = 0.031$  for 1161 observed reflections. The compound is isostructural with  $\text{Pb}_3\text{GeAl}_{10}\text{O}_{20}$  and  $\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$ . The crystal structure of the also isostructural  $\text{Ba}_3\text{SnFe}_{10}\text{O}_{20}$  was determined by a Rietveld refinement of neutron powder diffraction data collected at 873 K, with the results of the structure determination of  $\text{Pb}_3\text{GeGa}_{10}\text{O}_{20}$  as starting parameters:  $M_r = 1409.2$ ,  $I2/m$ ,  $a = 15.4430$  (5),  $b = 11.9068$  (4),  $c = 5.2473$  (2) Å,  $\beta = 90.945$  (2)°,  $V = 964.7$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 4.85$  Mg m<sup>-3</sup>,  $R_I = 0.051$  for 208 measured reflections,  $\mu R = 0.275$ . The structure consists of a framework of six-membered rings of tetrahedra, which form a ribbed plane. These planes are connected by a string of octahedra and by an  $M^{2+}$  ion in octahedral coordination. The other  $M^{2+}$  ion is situated inside the rib of the ribbed plane and has irregular seven or eight coordination, which is best described as a mono- or bicapped trigonal prism. ( $M^{2+}$  is  $\text{Pb}^{2+}$  or  $\text{Ba}^{2+}$ .)

**Introduction.** During investigations in the system  $\text{BaO-SnO}_2\text{-Fe}_2\text{O}_3$  the compound  $\text{Ba}_3\text{SnFe}_{10}\text{O}_{20}$  was obtained (Cadée & IJdo, 1981). The occurrence of compounds with almost the same unit-cell dimensions and similar formulae,  $\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$  (Guha, Kolar & Volavsek, 1976) and  $\text{Pb}_3\text{GeAl}_{10}\text{O}_{20}$  (Vinek, Völlenke & Nowotny, 1970), suggests that all these compounds are isostructural. Because single crystals of  $\text{Ba}_3\text{SnFe}_{10}\text{O}_{20}$  were not available an attempt was made to determine the structure using the neutron powder-profile-refinement technique (Rietveld, 1969), with the atomic parameters of  $\text{Pb}_3\text{GeAl}_{10}\text{O}_{20}$  as trial parameters (Vinek *et al.*, 1970). This attempt met with no success. Therefore, single crystals of the isostructural  $\text{Pb}_3\text{GeGa}_{10}\text{O}_{20}$  were prepared in order to redetermine the structure and to clarify why a successful refinement of the neutron powder diffraction data was not possible. Using the results of the structure determination of  $\text{Pb}_3\text{GeGa}_{10}\text{O}_{20}$  as trial parameters the neutron powder diffraction data of  $\text{Ba}_3\text{SnFe}_{10}\text{O}_{20}$  and  $\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$  could be refined.

The crystal structure of  $\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$  was published recently (Cadée, IJdo & Blasse, 1982) and consists of

rings of six corner-sharing tetrahedra, with their apices all in the same direction, that form strings parallel to the  $c$  axis. The tetrahedra share the apices of tetrahedra of two other strings, in which the apices point in the opposite direction. These strings thus form a ribbed plane of tetrahedra; the twofold axes generate the other planes. Between the planes are situated a string of octahedra and the large Ba atoms, which occupy a site with octahedral coordination and a site with irregular nine coordination. Besides the crystal structure, luminescence properties of  $\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$  and some of its isomorphs and the unit-cell dimensions of 15 isomorphs were reported.

**Experimental.** (a)  $\text{Pb}_3\text{GeGa}_{10}\text{O}_{20}$ : prepared by hydrothermal reaction of a mixture of yellow  $\text{PbO}$ ,  $\text{GeO}_2$  and  $\text{Ga}_2\text{O}_3$  in the appropriate ratios, in a sealed platinum tube. Because of the reaction between  $\text{PbO}$  and Pt, 5% excess of  $\text{PbO}$  was used. Heating time 2 d at 870 K, pressure about 0.2 G Pa, stainless steel autoclave, Tempress hydrothermal equipment. Colourless plates,  $0.15 \times 0.09 \times 0.03$  mm, Enraf-Nonius four-circle diffractometer, graphite-monochromated  $\text{Mo } K\alpha$  radiation, 24 reflections used for determination of unit-cell dimensions, space group  $C2/m$ , transferred to  $I2/m$  in order to diminish correlation effects. Observed unit-cell dimensions are in good agreement with data found for  $\text{Pb}_3\text{GeGa}_{10}\text{O}_{20}$  prepared by solid-state reaction at 1070 K for 4d in air, in an alumina crucible (Cadée *et al.*, 1982). 3779 reflections measured at 291 K,  $2^\circ < \theta < 32^\circ$ , 1587 independent, 1161 significant [ $I > 2\sigma(I)$ ]; range of  $h$  -21 to 21, of  $k$  -6 to 16, of  $l$  -3 to 7; standard reflections 080, 004 and  $\bar{3}03$ , intensity variation 5.3%, the observed reflections were corrected for this variation, e.s.d. of the standard reflections 1.0%; Lp correction, absorption correction (de Graaff, 1973),  $\mu = 49.1$  mm<sup>-1</sup>, minimum and maximum transmission 0.051 and 0.331; scattering factors from *International Tables for X-ray Crystallography* (1974) with correction for the real and imaginary part of the anomalous dispersion. Function minimized during the least-squares refinement process:  $\sum w_f(|F_o| - |F_c|)^2$ ,  $w_f = \sigma(F)^{-2}$ ,  $\sigma(F)$  is the estimated standard deviation calculated from counting statistics and errors in various correction factors. Leiden University Amdahl computer, computer programs written or modified by Mrs E. W. Rutten-Keulemans and Dr R. A. G. de Graaff.

A refinement with the atomic parameters of Pb<sub>3</sub>GeAl<sub>10</sub>O<sub>20</sub> in *I2/m* (Vinek *et al.*, 1970) as starting parameters met with no success. A Patterson synthesis revealed the positions of the Pb atoms. From this result it appeared that the parameters of Vinek *et al.*, correspond to a cell with  $\beta < 90^\circ$  ( $\beta$  was determined as  $90.0^\circ$ ). Further refinements were made using the atomic parameters of Pb<sub>3</sub>GeAl<sub>10</sub>O<sub>20</sub> with reversed *z* parameters. Because the atomic scattering factors of Ga and Ge are almost the same, all Ge atoms were assumed to occupy the 2(*b*) positions and Ga atoms to occupy the other octahedral and tetrahedral sites of the structure. Because of the high isotropic temperature factor of Pb(1), 2.24 Å<sup>2</sup>, refinement was made in space group *I/m*, but the results did not improve. The final *R* factor is 0.031,  $wR = 0.032$ ,  $S = 1.74$ ,  $F(000) = 1496$ , maximum shift is 0.5 times its e.s.d. in the last cycle (0.07 for the position parameters), the mean parameter shift is 0.12 times its e.s.d. (0.024 for position parameters). In the difference Fourier map a maximum peak of  $5.0 \text{ e } \text{Å}^{-3}$  was observed, the noise level was  $1.6 \text{ e } \text{Å}^{-3}$ .

(b) Ba<sub>3</sub>SnFe<sub>10</sub>O<sub>20</sub>: prepared by solid-state reaction of BaCO<sub>3</sub>, SnO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> after thorough mixing, at 1470 K in air in a platinum crucible. The heating time was two weeks with repeated grinding. Neutron powder diffraction at 300 and 873 K on a sample of 40g Ba<sub>3</sub>SnFe<sub>10</sub>O<sub>20</sub> in a vanadium sample holder, powder diffractometer of the Petten High Flux Reactor of the 'Energie Centrum Nederland',  $\lambda = 2.8563(3) \text{ Å}$  from the (111) plane of a Cu monochromator, collimation 10', scanning steps 0.072°, angular range  $5.4^\circ < 2\theta < 138.6^\circ$ ; maximum absorption correction 1.0%,  $\mu R = 0.275$  (Weber, 1967), estimated background points at regions of the diffraction diagram where reflections were known to be absent. The diffraction pattern at 300 K showed strong magnetic reflections that can be indexed by changing the space lattice from body centred to primitive. The diffraction pattern at 873 K was used for the Rietveld refinement; magnetic reflections are absent because the antiferromagnetic ordering temperature is 760 K (Cadée & IJdo, 1981). For the calculations a set of programs written by Rietveld (1969) was used. The coherent scattering lengths assumed were: Ba 5.2, Sn 6.1, Fe 9.5, O 5.8 fm (Bacon, 1972). The Rietveld program minimizes the function  $X^2 = \sum_i w_i [y_i(\text{obs}) - (1/c)y_i(\text{calc})]^2$ ;  $y(\text{obs})$  and  $y(\text{calc})$  represent the observed and calculated profile data point,  $w$  is the statistical weight allotted to each data point and  $c$  the scale factor. The following *R* factors are calculated:

$$R_I = \frac{\sum |I(\text{obs}) - (1/c)I(\text{calc})|}{\sum I(\text{obs})}$$

$$R_p = \frac{\sum |y_i(\text{obs}) - (1/c)y_i(\text{calc})|}{\sum y_i(\text{obs})}$$

$$R_{wp} = \frac{[\sum w_i [y_i(\text{obs}) - (1/c)y_i(\text{calc})]^2]}{\sum w_i [y_i(\text{obs})]^2}^{\frac{1}{2}}$$

$I(\text{obs})$ ,  $I(\text{calc})$  = observed and calculated integrated intensity of each reflection. Starting parameters of the

refinement were the atomic parameters found for Pb<sub>3</sub>GeGa<sub>10</sub>O<sub>20</sub>. The variables in the first refinements were: a scale factor, three half-width parameters defining the Gaussian line shape, the zero error of the counter, an overall temperature factor and the unit-cell dimensions. After the first runs the atomic position parameters and an asymmetry parameter below  $2\theta = 40^\circ$  were introduced. In the final stage of the refinement the occupation ratios of Fe and Sn in the octahedral sites were also variables within the overall formula and with the restriction that the two octahedral positions of the structure remained completely filled. Moreover, isotropic temperature factors for groups of atoms [Ba(1), Ba(2), the remaining cations and the O atoms] were introduced. The same procedure was followed in the structure determination of Ba<sub>3</sub>TiAl<sub>10</sub>O<sub>20</sub> (Cadée *et al.*, 1982). Individual temperature factors were not calculated because the number of parameters becomes too high in this case. The *R* factors obtained are:  $R_I = 0.051$ ,  $R_p = 0.115$ ,  $R_{wp} = 0.126$  ( $R_{wp}$  expected = 0.097). The maximum atomic parameter shift on the last cycle was 0.03 times its e.s.d.

**Discussion.** The atomic parameters of Pb<sub>3</sub>GeGa<sub>10</sub>O<sub>20</sub> are presented in Table 1; Table 2 contains the relevant distances and angles in the structure.\* The projection of the structure on the (100) plane is presented in Fig. 1; Fig. 2 shows the projection on the (001) plane.

The atomic parameters of Ba<sub>3</sub>SnFe<sub>10</sub>O<sub>20</sub> are reported in Table 3; the relatively high temperature factors can be explained by the temperature at which the diffraction data were collected (873 K). The agreement between the observed and calculated profile is shown in Fig. 3.\* Table 4 lists the relevant distances and angles in this structure. The unit-cell parameters determined from the neutron diffraction pattern at 873 K are given in the *Abstract*; the e.s.d.'s in the lattice parameters do not include errors in the neutron wavelength. The unit-cell dimensions at room temperature are  $a = 15.359(4)$ ,  $b = 11.875(3)$ ,  $c = 5.277(2) \text{ Å}$ ,  $\beta = 91.14(1)^\circ$  (Cadée & IJdo, 1981).

Ba<sub>3</sub>SnFe<sub>10</sub>O<sub>20</sub> is isostructural with Pb<sub>3</sub>GeGa<sub>10</sub>O<sub>20</sub>; there are some differences because of the different cations and these are discussed below.

The most striking feature in the structures of Pb<sub>3</sub>GeGa<sub>10</sub>O<sub>20</sub> and its isomorphs is the tetrahedra linkage that can be observed by projecting the structure on the (100) plane (Fig. 1). In this projection the six-membered rings of corner-sharing tetrahedra are

\* Lists of structure factors and anisotropic thermal parameters for Pb<sub>3</sub>GeGa<sub>10</sub>O<sub>20</sub>, and the numerical intensity of each measured point on the profile (shown in Fig. 3), as a function of angle, for Ba<sub>3</sub>SnFe<sub>10</sub>O<sub>20</sub>, together with tables of bond and coupling angles ( $^\circ$ ) for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38341 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

visible, enclosing a triangular inner space, comparable to that in  $\text{BaCaFe}_4\text{O}_8$  (Herrmann & Backmann, 1971) and  $\text{BaSrFe}_4\text{O}_8$  (Cadée, 1975). These rings are different from the six-membered rings in  $\beta$ -tridymite (Wyckoff, 1965), which enclose a hexagonal inner space.

Table 1. Atomic parameters of  $\text{Pb}_3\text{GeGa}_{10}\text{O}_{20}$  (space group  $I2/m$ )

	Position	$x$	$y$	$z$	$B_{\text{eq}}^\dagger$ ( $\text{\AA}^2$ )
Pb(1)	2(a)	0	0	0	2.27 (3)
Pb(2)	4(i)	0.2817 (3)	0	0.9512 (4)	0.88 (2)
Ge	2(b)	0	0.5	0	0.35 (5)
Ga(1)	4(h)	0	0.3665 (11)	0.5	0.26 (3)
Ga(2)	8(j)	0.3558 (6)	0.3634 (8)	0.0129 (7)	0.41 (2)
Ga(3)	8(j)	0.1356 (6)	0.2876 (8)	0.9744 (7)	0.36 (2)
O(1)	4(i)	0.432 (5)	0	0.822 (6)	0.05 (2)
O(2)	4(i)	0.903 (6)	0	0.410 (8)	1.0 (3)
O(3)	8(j)	0.240 (4)	0.365 (5)	0.889 (5)	0.8 (2)
O(4)	8(j)	0.417 (4)	0.246 (5)	0.850 (5)	0.6 (2)
O(5)	8(j)	0.861 (5)	0.147 (6)	0.867 (5)	1.3 (2)
O(6)	8(j)	0.930 (4)	0.384 (5)	0.821 (5)	0.6 (2)

$$\dagger B_{\text{eq}} = \frac{2}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Table 2. Relevant distances ( $\text{\AA}$ ) in  $\text{Pb}_3\text{GeGa}_{10}\text{O}_{20}$

Pb(1)—O(2)	2.54 (6) 2x	Ga(2)—O(2)	1.82 (4) 1x
Pb(1)—O(5)	2.76 (7) 4x	Ga(2)—O(3)	1.82 (5) 1x
		Ga(2)—O(4)	1.85 (6) 1x
		Ga(2)—O(5)	1.81 (3) 1x
Pb(2)—O(1)	2.32 (7) 1x		
Pb(2)—O(2)	3.28 (8) 1x		
Pb(2)—O(3)	2.37 (5) 2x	Ga(3)—O(3)	1.83 (6) 1x
Pb(2)—O(5)	2.88 (7) 2x	Ga(3)—O(4)	1.87 (4) 1x
Pb(2)—O(6)	3.19 (5) 2x	Ga(3)—O(5)	1.83 (6) 1x
		Ga(3)—O(6)	1.82 (5) 1x
Ge—O(1)	1.93 (5) 2x		
Ge—O(6)	1.93 (5) 4x	Ge—Ga(1)	2.99 (1)
		Ge—Ga(3)	3.19 (1)
Ga(1)—O(1)	2.06 (4) 2x	Ga(1)—Ga(1)	3.12 (3)
Ga(1)—O(4)	1.95 (6) 2x	Ga(1)—Ga(2)	3.43 (1)
Ga(1)—O(6)	1.95 (4) 2x	Ga(1)—Ga(3)	3.27 (1)
		Ga(2)—Ga(2)	3.20 (2)
		Ga(2)—Ga(3)	3.05 (1)

Table 3. Atomic parameters and isotropic temperature factors of  $\text{Ba}_3\text{SnFe}_{10}\text{O}_{20}$  (space group  $I2/m$ )

	Position	$x$	$y$	$z$	$B(\text{\AA}^2)$
Ba(1)	2(a)	0	0	0	3.3 (6)
Ba(2)	4(i)	0.2842 (10)	0	0.0192 (32)	3.9 (5)
Oc(1)*	2(b)	0	0.5	0	1.02 (7)
Oc(2)†	4(h)	0	0.3640 (7)	0.5	1.02 (7)
Fe(1)	8(j)	0.3542 (3)	0.3619 (4)	0.0129 (10)	1.02 (7)
Fe(2)	8(j)	0.1370 (4)	0.2841 (4)	0.9756 (11)	1.02 (7)
O(1)	4(i)	0.4344 (9)	0	0.8233 (22)	2.1 (1)
O(2)	4(i)	0.8988 (9)	0	0.4093 (23)	2.1 (1)
O(3)	8(j)	0.2385 (6)	0.3587 (8)	0.9093 (16)	2.1 (1)
O(4)	8(j)	0.4168 (6)	0.2456 (9)	0.8423 (18)	2.1 (1)
O(5)	8(j)	0.8590 (6)	0.1424 (8)	0.8649 (16)	2.1 (1)
O(6)	8(j)	0.9277 (6)	0.3753 (9)	0.8170 (16)	2.1 (1)

\* Sn 42 (4)%, Fe 58 (4)%.

† Sn 29 (2)%, Fe 71 (2)%.

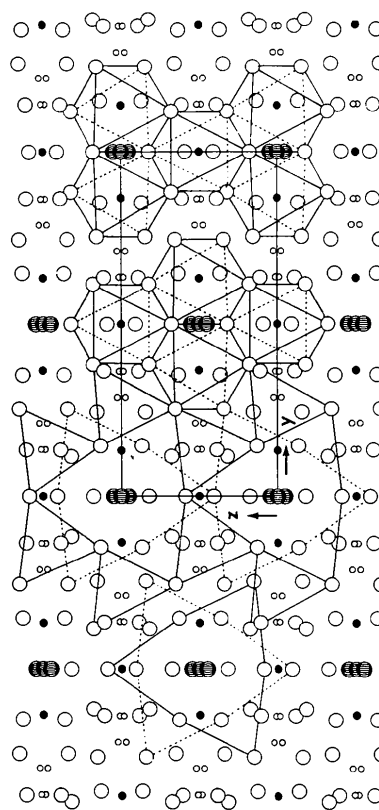


Fig. 1. Projection of the structure of  $\text{Pb}_3\text{GeGa}_{10}\text{O}_{20}$  on the (100) plane, showing six-membered rings of corner-sharing tetrahedra and strings of edge-sharing octahedra. From the tetrahedra only the basic plane or the edges that bound the inner space of the six-membered rings are drawn.

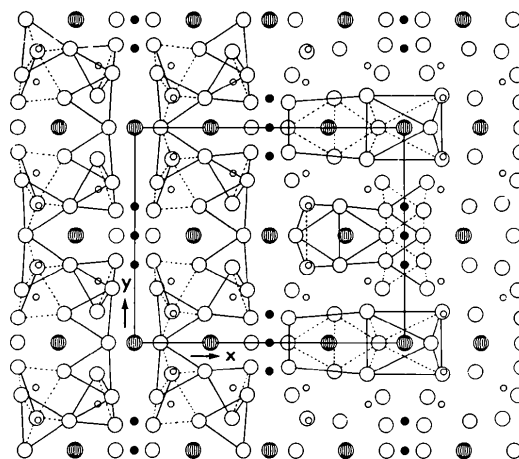


Fig. 2. Projection of the structure of  $\text{Pb}_3\text{GeGa}_{10}\text{O}_{20}$  on the (001) plane, showing the ribbed planes of corner-sharing tetrahedra in cross section. The string of octahedra and the Pb(1) coordination are drawn; from the Pb(2) coordination only some planes are visible. For both figures: shaded circles: Pb; open circles: O; small black circles: octahedral positions (Ga or Ge); small open circles: Ga in tetrahedral coordination. The projections were generated using the crystallographic plotting program FIGATOM (Langlet, 1972).

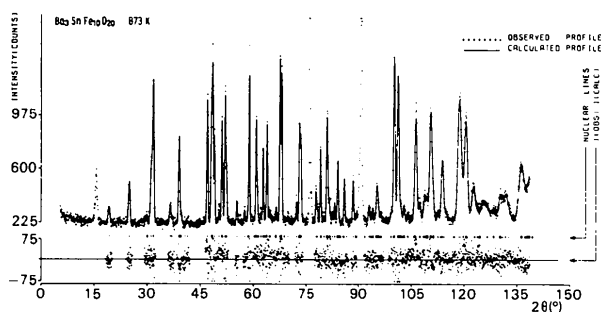


Fig. 3. Observed (dots) and calculated (full line) neutron diffraction profile of Ba<sub>3</sub>SnFe<sub>10</sub>O<sub>20</sub> at 873 K, a difference (observed—calculated) curve appears at the bottom of the figure. Tick marks below the profile indicate the positions of the Bragg reflections included in the calculation.

Table 4. Relevant distances (Å) in Ba<sub>3</sub>SnFe<sub>10</sub>O<sub>20</sub>

Ba(1)—O(2)	2.68 (1) 2×	Fe(1)—O(4)	1.92 (1) 1×
Ba(1)—O(5)	2.84 (1) 4×	Fe(1)—O(5)	1.85 (1) 1×
Ba(2)—O(1)	2.55 (2) 1×	Fe(2)—O(3)	1.82 (1) 1×
Ba(2)—O(3)	2.90 (2) 2×	Fe(2)—O(4)	1.89 (1) 1×
Ba(2)—O(5)	2.86 (2) 2×	Fe(2)—O(5)	1.90 (1) 1×
Ba(2)—O(6)	3.07 (2) 2×	Fe(2)—O(6)	1.84 (1) 1×
Oc(1)—O(1)	1.99 (1) 2×	Oc(1)—Oc(2)	3.09 (1)
Oc(1)—O(6)	2.08 (1) 4×	Oc(1)—Fe(2)	3.32 (1)
Oc(2)—O(1)	2.12 (1) 2×	Oc(2)—Oc(2)	3.24 (2)
Oc(2)—O(4)	2.00 (1) 2×	Oc(2)—Fe(1)	3.51 (1)
Oc(2)—O(6)	2.08 (1) 2×	Oc(2)—Fe(2)	3.38 (1)
Fe(1)—O(2)	1.87 (1) 1×	Fe(1)—Fe(1)	3.29 (1)
Fe(1)—O(3)	1.84 (1) 1×	Fe(1)—Fe(2)	3.11 (1)

The ribbed planes of tetrahedra can be observed by projecting the structure on the (001) plane (Fig. 2). The ribbed planes of tetrahedra are connected by a string of octahedra, with the octahedra sharing corners with the tetrahedra of the ribbed planes. In these strings the octahedra share edges; a string consists of one octahedron and two octahedra alternating (Fig. 1). The Pb(1) atom is situated at the inversion centre between two six-membered rings with the basic planes in near opposition. This Pb(1) atom has an octahedral coordination (Fig. 2) comparable to the Ca atom in BaCaFe<sub>4</sub>O<sub>8</sub> and the Sr atom in BaSrFe<sub>4</sub>O<sub>8</sub>, which both also have an octahedral coordination.

The inner side of the ribs of the ribbed plane forms channels, bounded by the tetrahedra of the plane and the octahedra that connect the planes. In these channels are situated the Pb(2) atoms which have an irregular eight-coordination. This coordination is best described as a bicapped trigonal prism.

The Pb(2) atom has three short Pb—O distances, but this is not unusual in Pb-containing structures (Vinek *et al.*, 1970). The 6s<sup>2</sup> lone pair of the Pb atom favours the irregular eight-coordination. The difference between the isotropic temperature factors of Pb(1) and Pb(2),

2.22 (4) and 0.84 (2) Å<sup>2</sup> respectively, is probably caused by the lone pair of the Pb(1) atom. The anisotropic temperature factors also show this difference, especially  $U_{11}$ , 0.0494 (4) and 0.0119 (1) Å<sup>2</sup> respectively. The Pb(1) coordination is regular but Pb favours an irregular coordination, thus the Pb(1) atom shows a more important thermal vibration. The same difference in temperature factors was reported for Pb<sub>3</sub>GeAl<sub>10</sub>O<sub>20</sub> (Vinek *et al.*, 1970).

The tetrahedra framework is the most important part of the structure; all O atoms except O(1) join in this framework. A change in this framework, *e.g.* substituting Ga<sup>3+</sup> (radius 0.47 Å) by Al<sup>3+</sup> (radius 0.39 Å) (Shannon & Prewitt, 1969), also influences the Pb(1)—O distances; these are shorter in Pb<sub>3</sub>GeAl<sub>10</sub>O<sub>20</sub>. The mean Pb(2)—O distances have not changed (Table 5). The mean Ga—O distances of the distorted tetrahedra are in good agreement with the value found in β-Ga<sub>2</sub>O<sub>3</sub>, 1.83 Å. Mean cation—O distances of oxides were calculated using the atomic parameters reported by Wyckoff (1965).

The mean Ge—O distance of the regular coordinated Ge atom in Pb<sub>3</sub>GeGa<sub>10</sub>O<sub>20</sub> is somewhat longer than the observed mean distance in GeO<sub>2</sub> (rutile form), 1.88 Å. The mean Ga—O distance for the more distorted Ga(1) octahedron is in good agreement with the value observed in β-Ga<sub>2</sub>O<sub>3</sub>, 2.01 Å. The mean distances found for the Ge and Ga(1) octahedra indicate that the assumption made for the distribution of Ge and Ga over the octahedral sites is a realistic one. Both octahedra are smaller in Pb<sub>3</sub>GeAl<sub>10</sub>O<sub>20</sub> (Table 5).

Most differences between the structures of Ba<sub>3</sub>SnFe<sub>10</sub>O<sub>20</sub> and Pb<sub>3</sub>GeGa<sub>10</sub>O<sub>20</sub> are caused by the substitution of Pb by Ba. Because of the larger radius of Ba<sup>2+</sup> (1.36 Å) in six-coordination [1.18 Å for Pb<sup>2+</sup> (Shannon & Prewitt, 1969)] the mean Ba—O distances are about 0.1 Å longer than the Pb—O distances. The Ba(2) coordination has reduced to seven and is still irregular. Of course, it is a problem where to stop regarding an O atom as coordinating the Ba(2) atom, but the next short Ba—O distance is Ba(2)—O(6) at 3.42 Å, while Ba(2)—O(2) is 3.66 Å. The coordination of Ba(2) can be described as a monocapped trigonal prism.

From the refinement a slight preference of Sn<sup>4+</sup> for the Oc(1) site is observed (Table 3). As the mean Sn—O distances in SnO<sub>2</sub> and the mean Fe—O distances in Fe<sub>2</sub>O<sub>3</sub> are almost the same, 2.05 and 2.03 Å respectively, it is not possible also to observe the preference of Sn<sup>4+</sup> for the Oc(1) site from the mean distances (Table 5). The mean Fe—O distances of the distorted Fe(1) and Fe(2) tetrahedra are in good agreement with the mean Fe—O distances observed in BaSrFe<sub>4</sub>O<sub>8</sub>, 1.86 Å (Cadée, 1975).

Compared to the structure of Ba<sub>3</sub>TiAl<sub>10</sub>O<sub>20</sub> (Cadée *et al.*, 1982), the Ba(1)—O distances have increased in Ba<sub>3</sub>SnFe<sub>10</sub>O<sub>20</sub> whereas the Ba(2)—O distances remain unchanged, analogous to the substitution of Al by Ga in the Pb isomorphs (Table 5).

Table 5. Mean cation—oxygen distances (Å) in four isostructural compounds of the type  $A^{II}_3B^{IV}C^{III}_{10}O_{20}$ 

Pb <sub>3</sub> GeGa <sub>10</sub> O <sub>20</sub>		Pb <sub>3</sub> GeAl <sub>10</sub> O <sub>20</sub> *		Ba <sub>3</sub> SnFe <sub>10</sub> O <sub>20</sub>		Ba <sub>3</sub> TiAl <sub>10</sub> O <sub>20</sub> †	
Pb(1)	2.69	Pb(1)	2.59	Ba(1)	2.79	Ba(1)	2.72
Pb(2)	2.82	Pb(2)	2.81	Ba(2)	2.89	Ba(2)	2.90
Ge	1.93	Al(1)	1.86	Oc(1)	2.05	TiAl(1)	1.90
Ga(1)	1.99	Al(2)	1.94	Oc(2)	2.07	TiAl(2)	1.95
Ga(2)	1.83	Al(3)	1.79	Fe(1)	1.87	Al(3)	1.77
Ga(3)	1.83	Al(4)	1.77	Fe(2)	1.86	Al(4)	1.76

\* Vinek *et al.* (1970).† Cadée *et al.* (1982).

The isotropic temperature factor of Ba(2) in Ba<sub>3</sub>TiAl<sub>10</sub>O<sub>20</sub>, which has an irregular nine-coordination, is high (1.62 Å<sup>2</sup>) compared to Ba(1) (0.12 Å<sup>2</sup>). This can be explained by the fact that Ba<sup>2+</sup> favours a more regular coordination. In Ba<sub>3</sub>SnFe<sub>10</sub>O<sub>20</sub> these differences are not large, probably due to the high temperature of the diffraction measurement, 873 K.

In Ba<sub>3</sub>TiAl<sub>10</sub>O<sub>20</sub> a slight preference of Ti for the Oc(2) site can be observed from the mean cation—O distances of the octahedral sites (Table 5), opposite to the preference of Sn in Ba<sub>3</sub>SnFe<sub>10</sub>O<sub>20</sub>.

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## A Neutron Diffraction Determination of the Structure of Deuterated Aluminium Nitrate Nonahydrate, Al(NO<sub>3</sub>)<sub>3</sub>·9D<sub>2</sub>O

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**Abstract.**  $M_r = 393.26$ , monoclinic,  $P2_1/c$ ,  $a = 13.8937$  (14),  $b = 9.6258$  (7),  $c = 10.9127$  (7) Å,  $\beta = 95.66$  (1)°,  $V = 1452.3$  (2) Å<sup>3</sup>,  $T = 295$  K [the cell parameters were determined from the refinement of 39  $\theta$  values from a Guinier–Hägg X-ray powder film (Cr  $K\alpha$  radiation,  $\lambda = 2.28975$  Å, using a CoP<sub>3</sub> standard:  $a = 7.70778$  Å)],  $Z = 4$ ,  $D_x = 1.80$  Mg m<sup>-3</sup>, final  $R_w(F^2) = 0.069$  for all 4480 independent reflections collected out to  $\sin\theta/\lambda = 0.69$  Å<sup>-1</sup>. The crystal structure of Al(NO<sub>3</sub>)<sub>3</sub>·9D<sub>2</sub>O has been studied by three-dimensional neutron diffraction data collected at 295 K. The asymmetric unit contains Al(D<sub>2</sub>O)<sub>6</sub><sup>3+</sup> octahedra, NO<sub>3</sub><sup>-</sup> ions and three D<sub>2</sub>O molecules which are not coordinated to Al<sup>3+</sup> ions. All nine water molecules in the formula unit are crystallographically independent and the 19 hydrogen bonds donated have O...O distances in the range 2.650 (2)–3.054 (2) Å. The hydrogen bonds donated by the D<sub>2</sub>O molecules which

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### References

- BACON, G. E. (1972). *Acta Cryst.* A28, 357–358.  
 CADÉE, M. C. (1975). *Acta Cryst.* B31, 2012–2015.  
 CADÉE, M. C. & IJDO, D. J. W. (1981). *J. Solid State Chem.* 36, 314–323.  
 CADÉE, M. C., IJDO, D. J. W. & BLASSE, G. (1982). *J. Solid State Chem.* 41, 39–43.  
 GRAAFF, R. A. G. DE (1973). *Acta Cryst.* A29, 298–301.  
 GUHA, J. P., KOLAR, D. & VOLAVSEK, B. (1976). *J. Solid State Chem.* 16, 49–54.  
 HERRMANN, D. & BACKMANN, M. (1971). *Mater. Res. Bull.* 6, 725–736.  
*International Tables for X-ray Crystallography* (1974). Vol IV. Birmingham: Kynoch Press.  
 LANGLET, G. A. (1972). *J. Appl. Cryst.* 5, 66–71.  
 RIETVELD, H. M. (1969). *J. Appl. Cryst.* 2, 65–71.  
 SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* B25, 925–946.  
 VINEK, H., VÖLLENKE, H. & NOWOTNY, H. (1970). *Monatsh. Chem.* 101, 275–284.  
 WEBER, K. (1967). *Acta Cryst.* 23, 720–725.  
 WYCKOFF, R. W. G. (1965). *Crystal Structures*, 2nd ed. New York: Interscience.

are coordinated to Al<sup>3+</sup> ions are shorter than the other hydrogen bonds. A distinct correlation exists between the O—D and D...O distances.

**Introduction.** The present room-temperature study was undertaken to obtain a detailed picture of the hydrogen bonding in Al(NO<sub>3</sub>)<sub>3</sub>·9D<sub>2</sub>O prior to a low-temperature electron density study. An earlier determination of the structure of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O from film data (Herpin & Sudarsanan, 1965) roused interest in the compound, since the nine H<sub>2</sub>O molecules were crystallographically independent and donated hydrogen bonds spanning a wide range of O...O lengths. Errors in the earlier structure determination made it impossible to fit the structure to the neutron diffraction data. A redetermination of the structure was therefore essential, and could most readily be achieved from X-ray data. A low-accuracy X-ray data set was collected and the