Table 2. *Bond distances* (Å) *and angles* (°) *for the water network in* $MoO_3.2D_2O$ *at* 298 K

E.s.d.'s are in parentheses. The atom labelling corresponds to that used in Fig. 3.

(*a*) Originating from the coordinated D_2O groups

	*c*1	O(*c*) – D(*c*1)		*m*	O(*c*) – O(*m*)	D(*c*1) – O(*m*)	O(*c*) – D(*c*1) – O(*m*)
c			D(*c*1) – O(*c*) – D(*c*2)				
	*c*2	O(*c*) – D(*c*2)		*m'*	O(*c*) – O(*m'*)	D(*c*2) – O(*m'*)	O(*c*) – D(*c*2) – O(*m'*)
	1	0·95 (3)		18^{i}	2·73 (1)	1·79 (3)	170·4 (15)
13			102·5 (15)				
	2	0·93		18^{ii}	2·79	1·86	174·1
	3	0·91		19^{ii}	2·75	1·85	174·1
14			98·4				
	4	0·93		20^{ii}	2·70	1·77	172·2
	5	0·97		19	2·74	1·80	163·3
15			106·6				
	6	0·97		20	2·78	1·82	169·6
	7	0·95		17^{ii}	2·76	1·82	175·9
16			106·2				
	8	0·99		17^{iii}	2·75	1·77	166·7

(*b*) Originating from the interlayer D_2O molecules

	*m*1	O(*m*) – D(*m*1)		*t*	O(*m*) – O(*t*)	D(*m*1) – O(*t*)	O(*m*) – D(*m*1) – O(*t*)
m			D(*m*1) – O(*m*) – D(*m*2)				
	*m*2	O(*m*) – D(*m*2)		*c''*	O(*m*) – O(*c''*)	D(*m*2) – O(*c''*)	O(*m*) – D(*m*2) – O(*c''*)
				b	O(*m*) – O(*b*)	D(*m*2) – O(*b*)	O(*m*) – D(*m*2) – O(*b*)
	9	0·97 (3)		9	2·85 (1)	1·89 (3)	175·6 (15)
17			112·4 (15)				
	10	0·94		13^{iv}	3·06	2·47	121·3
				2^{iv}	3·23	2·32	166·2
	11	0·98		12	2·82	1·84	174·0
18			102·4				
	12	0·95		16^{v}	3·12	2·22	158·9
				7^{vi}	3·08	2·42	125·6
	13	0·91		10	2·77	1·87	171·3
19			104·5				
	14	0·93		15^{vi}	3·10	2·20	163·6
				3^{iv}	3·20	2·60	122·2
	15	1·03		11^{vii}	2·85	1·82	175·0
20			106·8				
	16	0·88		14^{i}	3·15	2·46	136·5
				6^{i}	3·15	2·35	150·8

Roman numerals attached to atom labels refer to the following transformations of the coordinates given in Table 1. (i) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (ii) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (iii) $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (v) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (vi) $-x, 1-y, 1-z$; (vii) $-\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

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The Structure of Barium Aluminate, $Ba_{0\cdot75}Al_{11}O_{17\cdot25}$

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Abstract. $M_r = 675\cdot8$, $P6_3/mmc$, $a = 5\cdot582$ (2), $c = 22\cdot715$ (3) Å, $V = 612\cdot9$ (1) Å^3, $Z = 2$, $D_x = 3\cdot662$ (1) g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71073$ Å, $\mu = 42\cdot14$ cm^{-1}, $F(000) = 646\cdot45$, $T = 293$ K, $R = 0\cdot025$ for 317 observed reflections. The compound almost has the sodium aluminate structure. Instead of BaO layers, layers are found in which one of every four Ba's is replaced by an O to obtain, in combination with the

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$[Al_{11}O_{16}]^+$ spinel slices, a charge neutrality, yielding $Ba_{0.75}O_{1.25}$ layers. This replacement is found to be randomly distributed.

Introduction. Because of a research program on the immobilization of radioactive wastes in stable host lattices (for instance the hollandite structure), we were interested in the structure of $BaTiAl_6O_{12}$. In an attempt to grow single crystals of this compound another phase was obtained. This phase was found to be barium hexaaluminate. Since this type of structure is also a possible host lattice for radioactive waste disposal the structure was investigated.

The barium hexaaluminates have been investigated intensively in the last decade. However, there have been no publications on the structure of these compounds. Many possible compositions have been given in the literature. The following compositions have been proposed in the literature of the last six years. Haberey, Oehlschlegel & Sahl (1977) reported the existence of two independent phases: $1{\cdot}30BaO.6Al_2O_3$ and $0{\cdot}9BaO.6Al_2O_3$. Stevels (1978) reported the composition of barium hexaaluminate as a solid solution with bounding compositions $1{\cdot}30BaO.6Al_2O_3$ and $0{\cdot}91BaO.6Al_2O_3$. Mateika & Lauden (1979) grew single crystals with composition $0{\cdot}84$ $BaO.6Al_2O_3$. On these crystals they grew layers of barium hexaaluminate with composition ranging between $0{\cdot}9BaO.6Al_2O_3$ and $0{\cdot}8BaO.6Al_2O_3$. Kimura, Bannai & Shindo (1982) reported the existence of only two phases of barium hexaaluminate *i.e.* $1{\cdot}32BaO.6Al_2O_3$ and $0{\cdot}82BaO.6Al_2O_3$, both with hexagonal symmetry: $a = 5{\cdot}6003\ (2)$, $c = 22{\cdot}910\ (1)$ and $a = 5{\cdot}5881\ (2)$, $c = 22{\cdot}723\ (1)$ Å, respectively. Recently, Iyi, Takekawa, Bando & Kimura (1983) reported an electron microscopic study of barium hexaaluminate. They report the existence of two phases, $Ba_{0\cdot79}Al_{10\cdot9}O_{17\cdot14}$ ($=0{\cdot}87BaO.6Al_2O_3$), for which the sodium aluminate-type structure with space group $P6_3/mmc$ is proposed, and $Ba_{2\cdot34}Al_{21\cdot0}O_{33\cdot84}$ ($=1{\cdot}34BaO.6Al_2O_3$) with $\sqrt{3}a \times \sqrt{3}a$ superstructure. Morgan & Shaw (1983) suggested that the compositions of the phases were $0{\cdot}82BaO.6Al_2O_3$, with a $[Ba_{0\cdot82}AlO_{2\cdot82}]^-$ layer and an $[Al_{11}O_{16}]^+$ spinel slice, and $1{\cdot}30BaO.6Al_2O_3$, with a $[Ba_{1\cdot19}O_{1\cdot69}]^-$ layer stacked with an $[Al_{11}O_{16}]^+$ spinel slice.

Experimental. Single crystals were obtained during attempts to prepare single crystals of $BaTiAl_6O_{12}$ (Cadée & IJdo, 1982). $BaCO_3$, TiO_2 and Al_2O_3 were heated at 1470 K, the $BaTiAl_6O_{12}$ powder obtained was heated with a CH_4/O_2 flame. This resulted in colorless single crystals characterized with Weissenberg photographs of the zero and first level, suggesting hexagonal symmetry with systematic absences $h\,h\,l$: $l = 2n$ and axes $a = 5{\cdot}60$ and $b = 22{\cdot}30$ Å. From these observations it was concluded that the single crystal under consideration was a barium hexaaluminate containing perhaps some Ti and a unit cell closely resembling the barium hexaaluminate given by Kimura *et al.* (1982).

Electron diffraction data obtained from a Siemens Elmiskop 102 electron microscope, fitted with a double tilt and a lift cartridge operating at 100 kV.

Colorless plates, $0{\cdot}25 \times 0{\cdot}07 \times 0{\cdot}002$ mm, Enraf–Nonius four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation, 25 reflections used for determination of unit-cell dimensions, space group $P6_3/mmc$, 3906 reflections measured, $2 < \theta < 30°$, 449 independent, 317 significant $[I > 2\sigma(I)]$, h 0 to 7, k −7 to 7 and l −32 to 32, 3 standard reflections ($\bar{2}$,2,14, $30\bar{4}$, $2\bar{4}0$), intensity variation 6·14%, observed reflections corrected for this variation; e.s.d. of standard reflections 2·5%; Lp correction, absorption correction (de Graaff, 1973), min. and max. transmission 0·6063 and 0·8772; scattering factors from *International Tables for X-ray Crystallography* (1974) with correction for real and imaginary parts of anomalous dispersion. Function minimized during least squares refinement $w[\,|F(\text{obs})| - |F(\text{calc})|\,]^2$, $w = 1/\sigma(F)^2$, $\sigma(F)$ e.s.d. calculated from counting statistics and errors in various correction factors. For all calculations computer programs written or modified by Rutten-Keulemans and de Graaff were used on the Leiden University Amdahl V7B computer.

A refinement with the atomic parameters of $BaFe_{12}O_{19}$ as starting parameters did not meet with complete success. The isotropic refinement showed large thermal parameters for Al on $z = 0{\cdot}25$. Therefore, this Al was omitted. Furthermore, it was found that BaO and not BaO_3 layers occur on $z = 0{\cdot}25$. A difference Fourier analysis showed extra electron density in this layer, which can be accounted for by the partial replacement of a Ba by an O. Refinement with these alterations in the model and occupation parameters for Ba, Al(3), Al(5) and O(6) with a ratio in their shifts 1:2:−2:−1 resulted in the formula $Ba_{0\cdot753\,(3)}Al_{11}O_{17\cdot247\,(3)}$ and $wR = 0{\cdot}0252$.* This composition is in very good agreement with the phase study of Kimura, Bannai & Shindo (1982), who reported $0{\cdot}82BaO.6Al_2O_3$ ($=Ba_{0\cdot75}Al_{11}O_{17\cdot25}$) for the Ba-poor phase, using X-ray powder diffraction. Furthermore, the phase diagram they reported suggests that only the Ba-poor phase is formed from a melt. To obtain charge neutrality (see *Discussion*) $Ba_{0\cdot75}Al_{11}O_{17\cdot25}$ is expected. Fixing the occupation parameters at the proper values for this composition, refinement leads to exactly the same wR value. Because of this, further refinements were carried out assuming the composition to be $Ba_{0\cdot75}Al_{11}O_{17\cdot25}$. Refinement including extinction correction led to convergence at $R = 0{\cdot}0250$ and wR

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* With the scattering factors Ba^{2+}, Al^{3+} and O^-, the composition was refined to $Ba_{0\cdot746\,(3)}Al_{11}O_{17\cdot254\,(3)}$.

Table 1. *Positional, equivalent thermal and occupational* (*n*) *parameters of* $Ba_{0.75}Al_{11}O_{17.25}$

	x	y	z	B(Å²)*	(n)
Ba 2(d)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$	1·12 (2)	1·5
Al(1) 2(a)	0	0	0	0·44 (5)	2
Al(2) 4(f)	$\frac{1}{3}$	$\frac{2}{3}$	0·0235 (1)	0·47 (3)	4
Al(3)12(k)	0·1676 (1)	0·3351 (3)	−0·1046 (1)	0·51 (3)	11
Al(4) 4(f)	$\frac{1}{3}$	$\frac{2}{3}$	0·1756 (1)	0·77 (3)	4
Al(5)12(k)	0·8453 (2)	0·6906 (3)	0·1780 (5)	0·50 (30)	1
O(1) 4(e)	0	0	0·1413 (2)	0·50 (7)	4
O(2) 4(f)	$\frac{1}{3}$	$\frac{2}{3}$	−0·0554 (2)	0·27 (7)	4
O(3) 2(c)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	5·15 (27)	2
O(4)12(k)	0·1582 (2)	0·3164 (5)	0·0495 (1)	0·59 (6)	12
O(5)12(k)	0·5036 (2)	0·0073 (5)	0·1474 (1)	0·67 (6)	12
O(6) 6(h)	0·8855 (49)	0·7710 (94)	$\frac{1}{4}$	1·3 (1·3)	0·5

$* B = \sum_i \sum_j U_{ij} a^*_i a^*_j \mathbf{a}_i . \mathbf{a}_j$.

Table 2. *Relevant distances* (Å) *in* $Ba_{0\cdot75}Al_{11}O_{17\cdot25}$

Ba—O(3)	3·223 (1)	3×	Al(3)—O(4)	2·012 (2)	1×
Ba—O(5)	2·814 (2)	6×	Al(3)—O(5)	1·864 (2)	2×
Al(1)—O(4)	1·908 (3)	6×	Al(4)—O(3)	1·700 (2)	1×
Al(2)—O(2)	1·792 (4)	1×	Al(4)—O(5)	1·767 (3)	3×
Al(2)—O(4)	1·794 (3)	3×	Al(5)—O(1)	1·71 (1)	1×
Al(3)—O(1)	1·823 (2)	1×	Al(5)—O(5)	1·79 (1)	2×
Al(3)—O(2)	1·954 (2)	1×	Al(5)—O(6)	1·68 (2)	1×

= 0·0251. Max. shift in last cycle 0·13σ (0·014σ for positional parameters); in difference Fourier map max. peak 2·2 e Å^{-3} observed, with noise level 0·4 e Å^{-3}.*

Discussion. The atomic parameters of $Ba_{0\cdot75}Al_{11}O_{17\cdot25}$ are presented in Table 1. Table 2 contains the relevant distances in the structure. The (110) plane, showing the structure with a BaO(3) unit and an O(6)O(3) unit, is depicted in Fig. 1. The structure of $Ba_{0\cdot75}Al_{11}O_{17\cdot25}$ is very similar to that of sodium aluminate ($NaAl_{11}O_{17}$), which consists of spinel $[Al_{11}O_{16}]^+$ slices stacked alternately with NaO layers.

In the case of $BaAl_{11}O_{17}$, Na is replaced by Ba, causing too much positive charge. This is prevented by replacement of one of every four Ba by an O, O(6), yielding $Ba_{0\cdot75}Al_{11}O_{17\cdot25}$. In fact, the Ba ions are replaced by Al_2O groups $[Al(5)_2O(6)]$, whereby the Al_2O group is shifted from the threefold axis, and the Al(4) ions, which are very close to the Al(5) ions of the Al_2O group, are omitted. The O(6), and with it Al(5), are not generated into two others by the threefold axis because this would lead to Al(5)—A(5) distances which are too short. The macroscopic hexagonal symmetry is maintained because these other positions are occupied partly and randomly in other unit cells.

Since electron diffraction images show no diffuse scattering in any direction it must be concluded that no ordered planes of BaO(3) or O(6)O(3) exist in the structure. The very low R values suggest the same. This is to be expected because of the electroneutrality required. In the case of an ordering of the O(6) ions in the plane, a 2a,2a,c unit cell is obtained. No indications for such a unit-cell enlargement were found. Therefore, it is concluded that the structure consists of spinel slices, which are separated by layers which contain, besides O(3) ions, randomly distributed Ba ions and O(6) ions in the ratio 3:1.

Whereas $BaFe_{12}O_{19}$ and $SrAl_{12}O_{19}$ both adopt the magnetoplumbite structure in which $[BaAlO_3]^-$ layers occur between spinel-like $[Al_{11}O_{16}]^+$ slices, this is not observed for $BaAl_{12}O_{19}$. An obvious reason for this is the size of Al^{3+} which is much smaller than Fe^{3+}. In a $[BaAlO_3]^-$ layer embedded in an $[Al_{11}O_{16}]^+$ matrix the Ba—O distances in this layer are too small. Contrary to $BaAl_{12}O_{19}$, $SrAl_{12}O_{19}$ can adopt the magnetoplumbite structure because of the smaller size of Sr^{2+}. Since the Ba—O distance in a BaO layer is considerably larger, this type of layer is expected for barium hexaaluminate. This results in the sodium aluminate-type structure.

The large anisotropic parameters of O(3) are caused by the shift from the threefold axis, because there is not enough space between the two Al(4) atoms. The same will occur for O(6). The negative anisotropic thermal parameter U_{33} [being −0·0075 (149) Å²] is probably caused by this effect.

Probably no or very little Ti is present in the investigated compound since (i) there are no indications from the refinements (introduction of a mixture of Ti and Al of which the ratio was refined did not result in lower R values) and (ii) no Ti^{3+} is present in the single

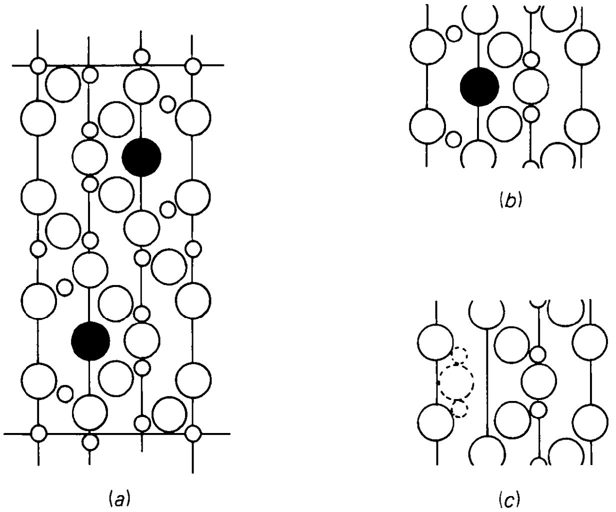

Fig. 1. The structure of $Ba_{0\cdot75}Al_{11}O_{17\cdot25}$ related to the structure of $NaAl_{11}O_{17}$ of which the (110) plane is depicted in (*a*) (Na: large filled circles; O: large open circles; Al: small circles). In $Ba_{0\cdot75}Al_{11}O_{17\cdot25}$ $\frac{1}{4}$ of the Ba's are replaced randomly by an O leading to 75% BaO(3) units (*b*) and 25% O(6)O(3) units (*c*).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39350 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

crystal, since the crystal is colorless. Heating experiments above 1670 K with compounds containing Ti^{4+} always make the compounds become more or less black–blue because of the reduction of Ti^{4+} to Ti^{3+}.

Iyi *et al.* (1983) prepared a single crystal with the same lattice parameters (within three times the e.s.d.) as the crystal investigated above, but they found another composition. Morgan & Shaw (1983), however, have shown that intergrowth of the Ba-poor and Ba-rich phases can occur. This makes the determination of the composition of both pure phases very difficult, especially when bulk methods such as electron probe microanalysis and density measurements (Iyi *et al.*, 1983) are used. The method of determining the composition by X-ray diffraction, used by Kimura *et al.* (1982), is in this respect more reliable. Their results for the composition of the Ba-poor phase is in agreement with our results.

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Hexagonal $Y_{13}Pd_{40}Sn_{31}$, a New Structure Type Containing Intergrown $CaCu_5$- and $MnCu_2Al$-Type Derived Structure Segments

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Abstract. $M_r = 9091{\cdot}2$, hexagonal, $hP168$, $P6/mmm$, $a = 19{\cdot}891\ (7)$, $c = 9{\cdot}246\ (6)$ Å, $V = 3168{\cdot}1$ Å^3, $Z = 2$, $D_x = 9{\cdot}529$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 34{\cdot}9$ mm^{-1}, $F(000) = 7794$, $T = 293$ K, $R_w = 0{\cdot}067$ for 975 independent reflections. The $Y_{13}Pd_{40}Sn_{31}$ structure can be interpreted as an intergrowth of three kinds of structure segments: one is a ternary ordering variant of the $CaCu_5$ type; the second has an atom arrangement similar to that of YPd_2Sn with $MnCu_2Al$ (Heusler phase) type, a W-type derivative; and the third segment is a column of Pd-centered Sn prisms and Sn-centered Pd prisms. It is further shown that another stannide structure, $CeNi_5Sn$, can be interpreted as an intergrowth of binary $CaCu_5$-type and ternary Heusler-type slabs.

Introduction. There are only limited data available on the formation of ternary rare-earth–transition-element stannides and their crystal structures. In a recent crystal-chemical study of ternary rare-earth alloy structures (Parthé & Chabot, 1984) only eight ternary structure types are listed for stannides, to which has to be added the newly reported structure type of cubic $Gd_9Ni_{24}Sn_{49}$ (Akselrud, Komarovska & Skolozdra, 1983). However, the interest in ternary stannides has grown since the discovery of superconducting phases belonging to the $R_3T_4Sn_{13}$ family of compounds (Vandenberg, 1980; Hodeau, Chenavas, Marezio & Remeika, 1980; Remeika *et al.*, 1980; Espinosa, Cooper & Barz, 1982). In an effort to find new superconducting ternary stannides, Jorda (1984) investigated part of the Y–Pd–Sn phase diagram and found four intermetallic compounds. Among these a phase with composition YPd_2Sn was identified by Ishikawa, Jorda & Junod (1982) as having the cubic $MnCu_2Al$ (Heusler phase) type ($L2_1$ type according to *Strukturbericht,* **1**, 488), a face-centered superstructure of the W type. This paper reports on the structure determination of another of the phases found by Jorda with approximate composition YPd_3Sn_2.

Experimental. Sample of nominal composition $Y_{15.5}Pd_{50}Sn_{34.5}$ prepared by levitation melting (starting materials Y 99·99%, Pd 99·9%, Sn 99·999%). As no

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