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The Structure of Barium Aluminate Hydrate, $2BaO.5Al_2O_3.H_2O$

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Abstract. $BaAl_5HO_9$, $M_r = 417{\cdot}2$, hexagonal, $P6_3/mmc$, $a = 5{\cdot}635\,(3)$, $c = 13{\cdot}489\,(8)$ Å, $V = 371{\cdot}0\,(3)$ Å^3, $Z = 2$, $D_m = 3{\cdot}93$, $D_x = 3{\cdot}733$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 5{\cdot}967$ mm^{-1}, $F(000) = 388$, $T = 298$ K, $R = 0{\cdot}0693$ for 225 independent reflections. This novel compound (obtained by the hydrothermal reaction of barium hydroxide and hydrated alumina, Al_2O_3: BaO ratio 2·5, at temperatures >528 K) exhibits a structure related to the well known β-alumina ($Na_2O.11Al_2O_3$) structure. The main difference is the absence of two of the oxygen layers from the spinel blocks.

Introduction. During an investigation of the system $BaO–Al_2O_3–H_2O$, an unidentified phase was obtained, crystallizing as fairly well formed hexagonal prisms. Chemical analysis of the new phase gave a formula of $BaO:2{\cdot}4Al_2O_3:2{\cdot}2H_2O$. The X-ray powder diffraction pattern did not correspond to any of the known barium aluminates. Magic-angle spinning ^{27}Al NMR showed that the aluminium was present in an approximately 1:1 ratio of tetrahedral coordination to octahedral coordination. Since this new phase did not correspond to any of the known barium aluminate hydrates, it was decided to carry out a full structure analysis.

Experimental. Well formed hexagonal prisms (suitable for intensity collection) were obtained by reacting $Ba(OH)_2.8H_2O$ and hydrated alumina (AlOOH), with Al_2O_3:BaO ratio 2·5, under hydrothermal conditions at 618 K for three weeks. The density was measured by water displacement, giving a value slightly higher than the X-ray density for the final formula ($2BaO$: $5Al_2O_3$:H_2O) from the structure analysis. This was thought to be due to the presence of non-essential water (the chemical analysis also indicated too high a water content). X-ray powder diffraction pattern obtained, using quartz as internal standard.† Crystals examined using polarizing microscope and showed parallel extinction, positive elongation and low birefringence. Crystal of width 0·05 mm, length 0·05 mm mounted on glass fibre. Precession photographs showed: hexagonal system, $a = 5{\cdot}63$ $c = 13{\cdot}4$ Å, possible space groups $P\bar{6}2c$, $P6_3mc$ or $P6_3/mmc$. Crystal transferred to automatic four-circle diffractometer (Nicolet *P*3) for data collection: graphite monochromator, unique reflections with $k \geq h \geq 0$, $l \geq 0$, $(\sin\theta/\lambda)_{\max} = 0{\cdot}6905$ Å^{-1}, θ–2θ scans, scan width automatically selected by diffractometer, scan speed $0{\cdot}0167°$ s^{-1}, background count measured on either side of each reflection, lattice parameters from least-squares fit to centred angles of 14 reflections with $2\theta \leq 15°$; two standard reflections (023 and 004) remeasured every 50 measurements, no systematic change observed, average variation of 1·5%; 225 unique reflections, 18 with $I < 2\sigma(I)$ classified as unobserved. No absorption correction (crystal very small). Most programs supplied by Ahmed, Hall, Pippy & Huber (1967). Survey of intensity distribution of reflections in principal zones and general reflections, using output from first part of *MULTAN*80 (*NORMAL*) (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), suggested that crystal structure was non-centrosymmetric. Positions for two barium atoms and eight oxygen atoms obtained from Patterson map, assuming space group $P6_3mc$. Remaining structure obtained from subsequent electron density map, giving overall cell contents $2BaO.5Al_2O_3.H_2O$. Block-diagonal least-squares refinement on *F*; scattering factors from *International Tables for X-ray Crystallography* (1962) for neutral atoms (except Ba^{2+}). Structure initially refined in $P6_3mc$ to $R = 0{\cdot}07$, with anisotropic temperature factors for barium atoms; some temperature factors negative. Coordinates of all atoms found (after change of origin) consistent with centrosymmetric space group $P6_3/mmc$. Refinement gave positive temperature factors. $w^{1/2} = \{1 + [(|F_o| - P_2)/P_1]^2\}^{-1/2}$ (with $P_1 = 26$ and $P_2 = 50$ by trial and error). Refinement converged giving $R = 0{\cdot}0693$, $wR = 0{\cdot}0695$ and $(\Delta/\sigma)_{\max} = 0{\cdot}015$.† Final difference Fourier map showed no significant features. Hydrogen atoms were not located.

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† JCPDS Diffraction File No. 35-1495. See also deposition footnote.

† Lists of structure factors, anisotropic temperature factors for Ba, full tables of bond lengths and angles and the powder data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39730 (37 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Discussion. Table 1 lists the final parameters and isotropic temperature factors (or equivalent in the case of barium). Table 2 lists the important bond distances and angles.

Table 1. *Fractional atomic coordinates and isotropic temperature factors*

Figures in parentheses represent e.s.d.'s corresponding to the least significant digit(s).

	x	y	z	B_{iso}(Å^2)
Ba	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	0·797*
Al(1)	$\frac{1}{2}$	0	0	0·10 (3)
Al(2)	0	0	0·3799 (2)	0·19 (4)
O(1)	0	0	$\frac{1}{4}$	1·5 (2)
O(2)	0·173 (1)	0·345 (1)	0·4214 (3)	0·26 (5)
O(3)	$\frac{1}{3}$	$\frac{2}{3}$	0·5709 (4)	0·04 (8)

* Calculated from the anisotropic temperature factors of the form $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{23}kl + B_{13}hl + B_{12}hk) \times 10^{-5}]$. $B_{\text{iso}} = \frac{4}{3}\sum_i\sum_j B_{ij}\mathbf{a}_i.\mathbf{a}_j$.

Table 2. *Important interatomic distances* (Å) *and bond angles* (°)

E.s.d.'s in the least significant digits are given in parentheses.

Ba–O(1)	3·253 [×3]	Al(1)–O(2)	1·919 (6) [×4]
Ba–O(2)	2·796 (5) [×6]	Al(1)–O(3)	1·887 (3) [×2]
		Al(2)–O(1)	1·752 (3) [×1]
		Al(2)–O(2)	1·774 (5) [×3]

$O(2^{i})$–Al(1)–$O(2^{ii})$	180	$O(2^{iii})$–Al(1)–$O(2^{iv})$	180
$O(2^{iii})$	90·3 (2)	$O(3^{i})$	84·4 (2)
$O(2^{iv})$	89·7 (2)	$O(3^{ii})$	95·6 (2)
$O(3^{i})$	84·4 (2)	$O(2^{iv})$–Al(1)–$O(3^{i})$	95·6 (2)
$O(3^{ii})$	95·6 (2)	$O(3^{ii})$	84·4 (2)
$O(2^{ii})$–Al(1)–$O(2^{iii})$	89·7 (2)	$O(3^{i})$–Al(1)–$O(3^{ii})$	180
$O(2^{iv})$	90·3 (2)	O(1)–Al(2)–O(2)	108·4 (2) [×3]
$O(3^{i})$	95·6 (2)	O(2)–Al(2)–O(2)	110·5 (3) [×3]
$O(3^{ii})$	84·4 (2)		

Symmetry codes: O(2): (i) $2x, x, z-\frac{1}{2}$; (ii) $1-2x, \bar{x}, \frac{1}{2}-z$; (iii) $1-x, x, z-\frac{1}{2}$; (iv) $x, \bar{x}, \frac{1}{2}-z$. O(3): (i) $\frac{2}{3}, \frac{1}{3}, z-\frac{1}{2}$; (ii) $\frac{1}{3}, -\frac{1}{3}, \frac{1}{2}-z$.

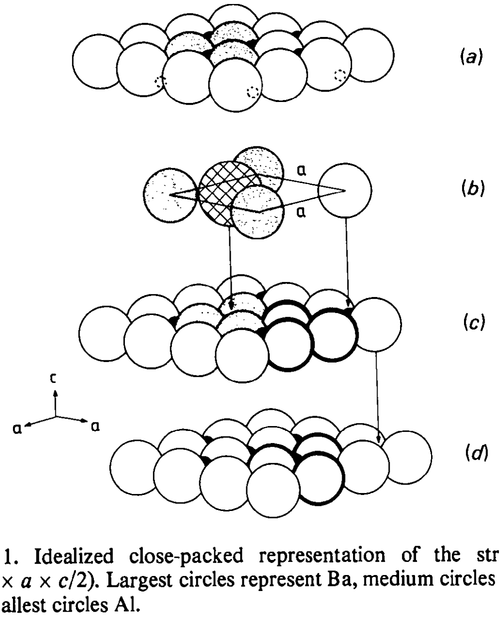

Fig. 1. Idealized close-packed representation of the structure ($a \times a \times c/2$). Largest circles represent Ba, medium circles O and smallest circles Al.

An idealized structure based on layers of close-packed oxygens is shown in Fig. 1 (the layers have been separated for clarity). The barium atoms are nine-coordinate with respect to oxygen: six forming a regular triangular prism with the barium at the centre, with the remaining three lying just outside the three vertical edges of the prism. Nine coordination also occurs in other barium aluminates, *e.g.* in $Ba[AlO(OH)_2]_2$ (Ahmed & Dent Glasser, 1970) the BaO_9 polyhedron is a distorted triangular prism, but with extra oxygen atoms lying just outside the centres of the faces.

Aluminium atoms occupy octahedral and tetrahedral sites as shown in the diagram. Each tetrahedral aluminium shares three of its oxygens with octahedral aluminium atoms and one with another tetrahedral aluminium atom. This is reflected in the bond lengths (three equal at 1·774, one shorter at 1·752 Å). The tetrahedral angles all lie fairly close to the ideal of 109·47°. The AlO_6 octahedron is slightly distorted, with four Al–O bond lengths equal at 1·919 Å, while the remaining two are slightly shorter at 1·887 Å. This is also reflected in the bond angles, with some deviating from the ideal (90°) by up to ±5·6°.

It is not easy to apply satisfactory electrostatic valence calculations to this compound, but if the shorter Ba–O(2) bonds are assumed to have a strength of 0·25 e and the longer Ba–O(1) bonds to be 0·167 e, then, as can be seen in Table 3, all oxygens are

Table 3. *Coordination and total electrostatic bond strength* (*EBS*) (e) *for each atom*

1 e ≡ $1{\cdot}60 \times 10^{-19}$ C.

Atom	Coordination Atom	Number (n)	EBS	$n \times$ EBS	Total EBS
Ba	O(1)	3	0·167	0·50	2·0
	O(2)	6	0·25	1·50	
Al(1)	O(2)	4	0·50	2·00	3·00
	O(3)	2	0·50	1·00	
Al(2)	O(1)	1	0·75	0·75	3·00
	O(2)	3	0·75	2·25	
O(1)	Ba	3	0·167	0·50	2·00
	Al(2)	2	0·75	1·50	
O(2)	Ba	1	0·25	0·25	2·00
	Al(1)	2	0·50	1·00	
	Al(2)	1	0·75	0·75	
O(3)	Al(1)	3	0·50	1·50	1·50

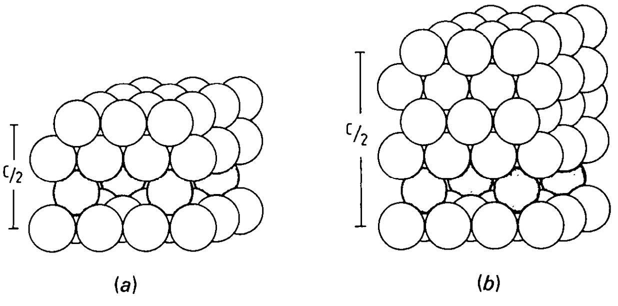

Fig. 2. Comparison of the close-packed oxygen layers in (*a*) $BaO{:}5Al_2O_3{:}H_2O$, (*b*) β-alumina.

satisfactorily bonded except for O(3), which has a net charge of $-\frac{1}{2}$. It seems probable, therefore, that the hydrogen atoms are statistically distributed over the O(3) atoms. This would also account for the very low temperature factor obtained for O(3). If the occupancy for O(3) is increased to 1·06 (to take the $\frac{1}{2}$ proton into account) and the structure refined, R decreases marginally and the temperature factor increases up to a similar value to that obtained for O(2). Clearly, this supports the statistical distribution of protons over the O(3) atoms.

Fig. 2 compares this new structure with that of the well known β-alumina ($Na_2O.11Al_2O_3$) structure (Beevers & Ross, 1937). The major difference lies within the close-packed part of the structure. In β-alumina, four close-packed layers form the so-called spinel block; this new structure has only two such layers.

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Structure of Ca-Rich Agardite, $(Ca_{0.40}Y_{0.31}Fe_{0.09}Ce_{0.06}La_{0.04}Nd_{0.01})Cu_{6.19}[(AsO_4)_{2.42}(HAsO_4)_{0.49}](OH)_{6.38}.3H_2O$

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Abstract. $M_r = 1023{\cdot}8$, hexagonal, $P6_3/m$, $a = 13{\cdot}583$ (2), $c = 5{\cdot}895$ (1) Å, $V = 941{\cdot}9$ (2) Å^3, $Z = 2$, $D_x = 3{\cdot}61$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 14·0 mm^{-1}, $F(000) = 484{\cdot}9$, room temperature, final $R = 0{\cdot}077$, $R_w = 0{\cdot}056$ for 1087 reflections. The specimen is from Setoda, Hiroshima, Japan. The structure consists of infinite CuO_4 chains running along the c axis, which are alternately connected to MO_9 polyhedra (M = Ca, Y, *etc.*) and AsO_4 tetrahedra. In the mixite group, the charge compensation on the substitution of a divalent cation (*e.g.* Ca^{2+}) for a trivalent cation (*e.g.* Y^{3+}) is accomplished by the concomitant substitution of OH^- for O^{2-}.

Introduction. There exist copper minerals having the general formula $MCu_6(XO_4)_3(OH)_6.3H_2O$ where M = Bi, Y, rare-earth element, Ca, Al; X = As, P, known as the mixite-group minerals. So far four minerals are known to belong to this group: agardite (M = Y, Ca; X = As; Dietrich, Orliac & Permingeat, 1969), goudeyite (M = Al, Y; X = As; Wise, 1978), mixite (M = Bi; X = As; Walenta, 1960), and petersite (M = Y, rare-earth element, Ca; X = P; Peacor & Dunn, 1982). All these minerals crystallize in the hexagonal space group $P6_3/m$ or $P6_3$ with similar lattice constants of $a = 13{\cdot}29$–$13{\cdot}88$ and $c = 5{\cdot}87$–$5{\cdot}96$ Å. Therefore, they are presumed to be isostructural. None of their crystal structures, however, has yet been reported probably because only small crystals have been found. In these minerals, isomorphous substitution of a trivalent. cation by a divalent cation (*e.g.* Ca^{2+}) is frequently observed in the M site. The mechanism of the charge compensation has, for many years, posed a problem in the understanding of this mineral group. This work has been performed to elucidate the crystal structure and the substitution mechanism of mixite-group minerals.

The specimens used in the study are Ca-rich agardite from Setoda, Hiroshima prefecture, Japan. They were collected by Dr K. Masutomi and members of the Kyoto Kobutsu Kenkyukai.

Experimental. Electron microprobe analyses gave Cu, 48·97; As, 32·22; Y, 3·42; Ca, 2·57; Ce, 1·01; Fe, 0·73; La, 0·70; Nd, 0·13 wt%; Gd, trace. The corresponding unit-cell composition, normalized to 21

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