pected anomaly was found: the very broad and strong absorption lies in the region of 400–1600 cm^{-1} with its maximum at 900 cm^{-1}.

Judging from the results so far available, which are consistent with other Type *A* acid salts, it seems probable that the $O(1)\cdots O(1^{i})$ bond is not only crystallographically, but also truly, of the symmetrical single-minimum type. The problem of the symmetrical OHO bond is interesting, since a model of order–disorder type is accepted in most hydrogen-bonded ferroelectrics. Structure analysis in the ferroelectric phase (at about 80°K) is now in progress. A more detailed discussion will be given on the basis of the structures of the para- and ferroelectric phases.

I am very grateful to all the staff in this laboratory for their valuable discussion and cooperation. I also wish to thank Professor K. Nakatsu of Kwansei Gakuin University for his valuable discussion and suggestion on the symmetrical hydrogen bond, and Professor Y. Matsunaga and Professor E. Osawa for their courtesy in the measurement of the infrared spectra. Thanks are also due to Dr T. Sakurai for kindly giving the information on '*UNICS*', and to the Computing Centre of the University of Tokyo and the Hokkaido University Computing Center for making the HITAC 5020E and the FACOM 230-60 computer available to me.

References

BACON, G. E. & CURRY, N. A. (1957). *Acta Cryst.* **10**, 524.
BACON, G. E. & CURRY, N. A. (1960). *Acta Cryst.* **13**, 717.
GOLIČ, L. & SPEAKMAN, J. C. (1965). *J. Chem. Soc.* p. 2530.
HAHN, T. (1957). *Z. Kristallogr.* **109**, 438.
ICHIKAWA, M. (1970). Unpublished work.
ICHIKAWA, M. & MITSUI, T. (1966). *Phys. Rev.* **152**, 495.
International Tables for X-ray Crystallography (1959). Vol. II, and (1962). Vol. III. Birmingham: Kynoch Press.
MANOJLOVIĆ, L. & SPEAKMAN, J. C. (1967). *J. Chem. Soc.* (*A*). p. 971.
MANOJLOVIĆ, L. & SPEAKMAN, J. C. (1968). *Acta Cryst.* B**24**, 323.
MANOJLOVIĆ, L. (1968). *Acta Cryst.* B**24**, 326.
MILLS, H. H. & SPEAKMAN, J. C. (1963). *J. Chem. Soc.* p. 4355.
PHILLIPS, D. C. (1956). *Acta Cryst.* **9**, 819.
ROLLETT, J. S. & SPARKS, R. A. (1960). *Acta Cryst.* **13**, 273.
SEQUEIRA, A., BERKEBILE, C. A. & HAMILTON, W. C. (1967). *J. Mol. Struc.* **1**, 283.
SHRIVASTAVA, H. N. & SPEAKMAN, J. C. (1961). *J. Chem. Soc.* p. 1151.
SKINNER, J. M. & SPEAKMAN, J. C. (1951). *J. Chem. Soc.* p. 185.
SPEAKMAN, J. C. (1949). *J. Chem. Soc.* p. 3357.
SPEAKMAN, J. C. (1967). *Chem. Commun.* p. 32.
SPEAKMAN, J. C. & MILLS, H. H. (1961). *J. Chem. Soc.* p. 1164.
SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions, Supplement.* London: The Chemical Society.
UNICS (1967). *Universal Crystallographic Computing System.* Editor T. SAKURAI, Crystallographic Society of Japan.
WILSON, A. J. C. (1949). *Acta Cryst.* **2**, 378.
YAMAMOTO, T., NAKAMURA, N. & CHIHARA, H. (1968). *J. Phys. Soc. Japan*, **25**, 291.
YAMAMOTO, T., NAKAMURA, N. & CHIHARA, H. (1970). *J. Phys. Soc. Japan*, **28**, Supplement, 112 (*Proc. Second Intern. Meeting Ferroelectricity*, Kyoto, 1969).

Acta Cryst. (1972). B**28**, 760

Barium Aluminate Hydrates. V.* The Crystal Structure of γ-$Ba[AlO(OH)_2]_2$

BY LESLEY S. DENT GLAASER AND R. GIOVANOLI†

Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, AB9 2UE, Scotland

(*Received* 30 *July* 1971)

γ-$BaO.Al_2O_3.2H_2O$ is orthorhombic, *Fdd*2, with $a=20{\cdot}70$, $b=8{\cdot}977$, $c=6{\cdot}416$ Å, $Z=8$. X-ray structural analysis shows that it contains chains of composition $[AlO(OH)_2^{-1}]_\infty$, made up of tetrahedra sharing corners. Its formula should therefore be written γ-$Ba[AlO(OH)_2]_2$.

Introduction

Carlson & Wells (1948) were the first to produce monobarium aluminate dihydrate and their compound was designated 'α' by Thilo & Gessner (1965) when a second polymorph ('β') was found. Ahmed & Dent Glasser (1970) solved the structure of the α-polymorph and (1971) prepared a third compound of the same empirical formula which they called 'γ'. This present work deals with the γ modification. Crystal data from Ahmed & Dent Glasser (1971) are reproduced in Table 1. The compound crystallizes as plates lying on (100).

* Part IV: Dent Glasser & Giovanoli, *Acta Cryst.* (1972). B**28**, 519.

† Permanent address: Laboratorium für Elektronmikroskopie der Universität Bern, Freiestrasse 3, CH-3012 Berne, Switzerland.

Table 1. *Crystal data of* γ-$BaO.Al_2O_3.2H_2O$

a	$=20{\cdot}70 \pm 0{\cdot}02$ Å
b	$= 8{\cdot}977 \pm 0{\cdot}004$
c	$= 6{\cdot}416 \pm 0{\cdot}003$
D_{obs}	$= 3{\cdot}25$ g.cm^{-3}
D_x	$= 3{\cdot}35$ g.cm^{-3}

Space group *Fdd*2

Unit cell content $Ba_8Al_{16}O_{48}H_{32}$

Experimental

Intensity data were collected using a Hilger and Watts Y 190 automatic linear diffractometer with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). The rotation axis of the crystal was **c**, and reflexions throughout one half of reciprocal space up to $l = 8$ were measured. This gave a total of 1629 reflexions not systematically absent; agreement between equivalent reflexions was very good. After averaging equivalent reflexions a total of 529 reflexions remained, of which 71 were not considered to be significantly above background and were treated as 'unobserved'. Intensities were converted to structure factors in the usual way. No corrections were made for absorption or extinction. Data were processed on an ICL 4/50 computer, mainly using programs supplied by Dr F. R. Ahmed and collaborators of the National Research Council of Canada, and adapted for use on this machine by Mr J. S. Knowles of the Department of Computing, University of Aberdeen. Scattering factors for Ba^{2+} and Al^{3+} were taken from *International Tables for X-ray Crystallography* (1962). A curve for O^{2-} was constructed as described by Ahmed & Glasser (1970).

Structure determination

Approximate positions for the barium, aluminum and oxygen atoms were derived from the Patterson function and refined by the method of least squares (block-diagonal approximation). Reflexions were weighted according to $W = 1/\{1 + [(|F_o| - P_2)/P_1]^2\}$. P_1 and P_2 were chosen initially to give maximum weight to reflexions of moderate intensity; subsequently an error analysis showed that the scheme selected was reasonable.

The Patterson function could be satisfied by two solutions. One set of parameters refined readily to a final R value of 0·055, while the other stuck at 0·16. Moreover, the first set gave a chemically satisfactory set of bond lengths and angles, while the second did not. The first solution is thus assumed to be the correct one. The corresponding parameters are given in Table 2, and the observed and calculated structure factors in Table 3. In addition to the 'unobserved' reflexions, 8

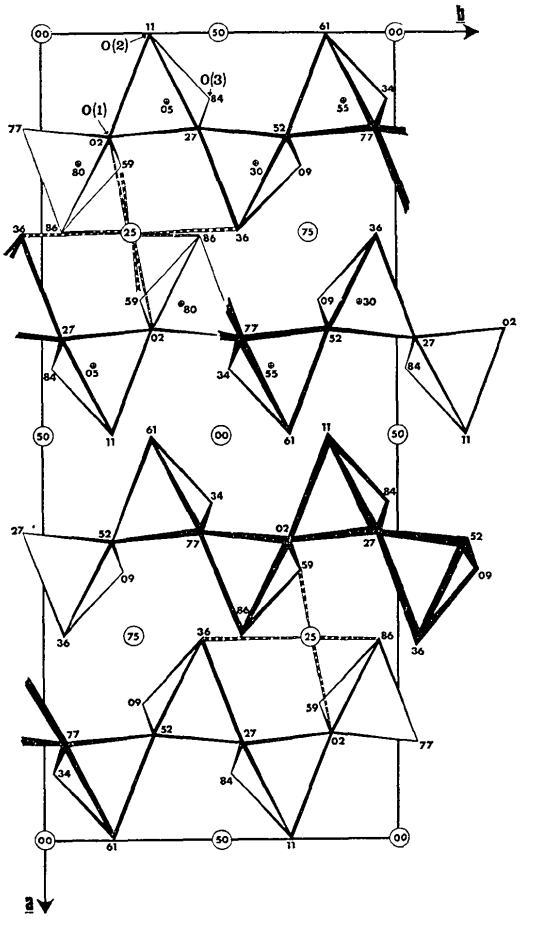


Fig. 1. The structure of γ-$Ba[AlO(OH)_2]_2$ projected down **c**; heights are in $c/100$. Oxygen atoms are at the corners of the tetrahedra, and the heights of the corresponding aluminium atoms (small circles containing crosses) are shown in the upper half of the diagram. Large open circles indicate barium atoms. The upper half of the cell is drawn to emphasize the twofold axes on which the barium atoms lie; the lower emphasizes the perspective of the criss-crossing chains.

Table 2. *Final parameters for* γ-$Ba[AlO(OH)_2]_2$

Figures in brackets represent the estimated standard deviation corresponding to the least significant digit.

	Positional parameter			Isotropic temperature factor
	x/a	y/b	z/c	B_{iso}
Ba	0	0	0	1·05 (1)
Al	0·0860 (2)	0·3556 (3)	0·0519 (8)	0·46 (4)
O(1)	0·1307 (4)	0·194 (1)	0·017 (1)	0·3 (1)
O(2) (hydroxyl)	0·0022 (4)	0·305 (2)	0·114 (3)	1·1 (2)
O(3) (hydroxyl)	0·0831 (7)	0·474 (1)	0·835 (2)	1·0 (2)

reflexions where the agreement between F_o and F_c was poor were omitted from the final cycles of refinement. These corresponded mainly either to very weak reflexions at high angles, or to reflexions very close to **c*** which the mechanical construction of the Y190 makes it difficult to measure accurately.

Description of the structure

Fig. 1 shows the structure viewed along **c**. Each aluminum atom is surrounded tetrahedrally by four oxygen atoms. These tetrahedra share corners [O(1)] to form chains, and it is assumed that the two unshared corners [O(2) and O(3)] correspond to hydroxyl groups. The temperature factors (Table 2) are in accordance with this assumption.

The barium atoms lie on the twofold axes, and the chains lie along the *d*-glide planes perpendicular to **a**. This means that the chains run diagonally across the cell, with alternate chains running in opposite directions (Figs. 1 and 2). We believe that this is the first chain structure in which the chains do not run parallel to one another. There is no hydrogen bonding between the chains.

Details of the coordination polyhedra about Al and Ba are given in Table 4. The barium atom is surrounded by eight oxygen atoms which form a very distorted cube (Fig. 1). The four independent distances [Table

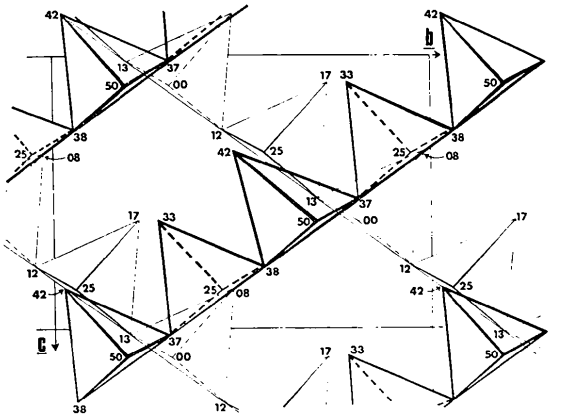


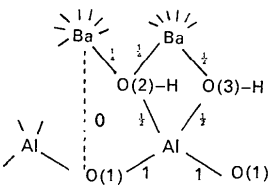
Fig. 2. The structure of γ-Ba[AlO(OH)$_2$]$_2$ viewed along **a**, showing how the anion chains criss-cross. For simplicity only one half the unit cell, from 0 to $a/2$, is shown. Heights of oxygen atoms are expressed in $a/100$.

Table 3. *Observed and calculated F values* ($\times 10$)

Unobserved reflexions are marked with an asterisk.

4(*b*)] vary from 2·77 to 3·03 Å. There are no other barium oxygen contacts below 3·2 Å, and for the purpose of applying Pauling's rules (see below) these longer contacts are assumed not to represent bonds. The Al–O tetrahedron is somewhat irregular, with the Al–O(2) bond significantly longer than the rest. A possible explanation of this is that this oxygen atom forms bonds to two barium atoms, and that this weakens the Al–O linkage. This can be illustrated by considering the different ways in which Pauling's rules can be applied to the structure:

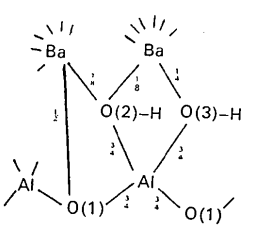
(*a*) Assume that Al–O has bond order 1, and Al–OH bond order $\frac{1}{2}$. This leads to the following picture:



I

which is unsatisfactory on several counts, although it does explain why Ba–O(3) is shorter than either of the Ba–O(2) distances. However the enormous variation in bond order for the variuos Ba–O contacts is not supported by the distances listed in Table 4.

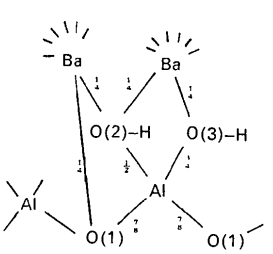
(*b*) Assume that all Al–O bonds are of equal order *i.e.* $\frac{3}{4}$. The picture is then:



II

This is again unsatisfactory, since it would suggest that Ba–O(1) should be the shortest contact.

(*c*) Assume that all Ba–O bonds are equal, *i.e.* of order $\frac{1}{4}$. This leads to:



III

and this is in many ways the most satisfactory picture. It explains the variation of Al–O bond lengths very neatly, although it does not account for the variations in Ba–O contacts.

Table 4. *Coordination polyhedra in* γ-$Ba[AlO(OH)_2]_2$

Figures in brackets give estimated standard deviations corresponding to the least significant digit.

(*a*) Al–O tetrahedron

	Bond distances
Al–O(1) (bridge)	1·74 (1) Å
Al–O(1′) (bridge)	1·73 (1)
Al–O(2) (hydroxyl)	1·84 (1)
Al–O(3) (hydroxyl)	1·75 (1)

	Bond angles		Bond angles
O(1)–Al–O(1′)	105·8 (5)°	O(1′)–Al–O(2)	108·3 (6)°
O(1)–Al–O(2)	108·9 (6)	O(1′)–Al–O(3)	111·8 (5)
O(1)–Al–O(3)	115·1 (6)	O(2)–Al–O(3)	106·8 (6)

(*b*) Ba–O coordination

Since the barium atoms lie on twofold axes, each contact occurs twice.

Ba–O(1′)	2·930 (9) Å
Ba–O(2)	2·84 (2)
Ba–O(2′)	3·03 (2)
Ba–O(3′)	2·77 (1)

All of the above represent over-simplifications in one way or another, and the true situation presumably lies somewhere between these three assignments.

It is interesting to compare this structure with that of α-$Ba[AlO(OH)_2]_2$ (Ahmed & Dent Glasser, 1970), which also contains $[AlO(OH)_2^-]_\infty$ chains. In the α-modification the chains are kinked into an almost helical configuration, they run parallel to one another, and there is hydrogen bonding between the chains. It may well be that the γ-modification is difficult to prepare because the arrangement of chains in a criss-cross pattern is inherently less favoured than arrangement in a parallel one; the absence of hydrogen bonding and distortion of the Al–O tetrahedra may also betoken strain in the structure.

We are grateful to the Royal Society for providing a grant for one of us (RG).

References

AHMED, A. H. M. & DENT GLASSER, L. S. (1970). *Acta Cryst.* B**26**, (6), 867.

AHMED, A. H. M. & DENT GLASSER, L. S. (1971). *J. Appl. Chem. Biotechnol.* **21**, 109.

CARLSON, E. T. & WELLS, L. S. (1948). *J. Res. Nat. Bur. Stand.* **41**, 103.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

THILO, E. & GESSNER, W. (1965). *Z. anorg. allg. Chem.* **337** (5–6), 238.