The Crystal Structure of Barium Orthotitanate, Ba$_2$TiO$_4$

By J. A. Bland*

Department of Mines and Technical Surveys, Ottawa, Canada

The crystal structure of Ba$_2$TiO$_4$ has been determined with moderate accuracy, using two-dimensional F_o and $F_o - F_c$ syntheses. The space group is $P2_1/n$ and the cell dimensions are:

$$a_0 = 6 \cdot 12 \pm 0 \cdot 03, \quad b_0 = 7 \cdot 70 \pm 0 \cdot 03, \quad c_0 = 10 \cdot 50 \pm 0 \cdot 03 \text{ Å}; \quad \beta = 93° \, 8' \pm 10'.$$

There are four units of Ba$_2$TiO$_4$ in the cell. The structure is of the β-K$_2$SO$_4$ type and is closely related to β-Ca$_2$SiO$_4$. The environment of the titanium atom is unusual; it is approximately tetrahedral and the structure is considered as an arrangement of discrete TiO$_4$ groups and Ba atoms. The relationship between Ba$_2$TiO$_4$ and ferro-electric BaTiO$_3$ is discussed.

1. Introduction

Barium orthotitanate, Ba$_2$TiO$_4$, was first examined crystallographically by Rooksby (1947) who showed that its X-ray powder pattern resembles that of Ba$_2$SiO$_4$, which has the β-K$_2$SO$_4$ type of structure (O'Daniel & Tscheischwili, 1942). Other workers (Rase & Roy, 1955; Murray, 1958; Jonker & Kwestroo, 1958) have prepared single-phase powders with composition Ba$_2$TiO$_4$ and have confirmed the observation of Rooksby.

The similarity between the powder patterns of the two compounds suggests that titanium in Ba$_2$TiO$_4$ may be compared with silicon in Ba$_2$SiO$_4$ and sulphur in β-K$_2$SO$_4$ and therefore may be tetrahedrally coordinated by four oxygen atoms. The present work was undertaken to determine the precise nature of the titanium coordination.

2. Experimental

(i) *Preparation of single crystals*

Single crystals of Ba$_2$TiO$_4$ were grown from a melt containing BaCl$_2$, BaCO$_3$ and TiO$_2$ in the ratio 5:5:1. This mixture was put in a platinum crucible and held at a temperature of 1340 °C. for 20 hr. and then cooled rapidly. The solidified flux was removed by solution in distilled water and the residue was quickly washed in alcohol. Approximately equal quantities of dark tan crystals and white crystals were found and these were separated by hand picking. The dark crystals were shown to be tetragonal BaTiO$_3$. A powder photograph of some of the white crystals agreed closely with one published by Rase & Roy (1955) for Ba$_2$TiO$_4$. A spectrographic analysis of the white crystals showed barium and titanium as major constituents with traces of silicon, aluminium and platinum. A small quantity of these crystals was examined by Messrs. Johnson,

Matthey and Co. Ltd., who found the composition to be:

Ba	Ti	O	
66·72	15·24	17·65	wt.%

It was assumed that this corresponds to 93·9% Ba$_2$TiO$_4$ and 6·1% TiO$_2$.

(ii) *Unit cell and symmetry*

A Buerger precession camera was used to determine the unit cell and symmetry of Ba$_2$TiO$_4$; the cell was found to be monoclinic but pseudo-orthorhombic and pseudo-trigonal. The dimensions of the unit cell are given in Table 1 together with the cells of the closely related structures Ba$_2$SiO$_4$ and β-Ca$_2$SiO$_4$ (Midgley, 1952). A careful scrutiny of precession and oscillation photographs was carried out to make quite sure that the axial lengths are not doubled, as it is for some of the polymorphic modifications of Ca$_2$SiO$_4$ (Douglas, 1952). Reflexions were observed in the $h0l$ zone only with $(h+l)$ even and in the $0k0$ zone only with k even, which are consistent with the space-group $P2_1/n$. The choice of axes is unconventional but is convenient for

Table 1. *Unit-cell constants of* Ba$_2$TiO$_4$, Ba$_2$SiO$_4$ *and* β-Ca$_2$SiO$_4$

Ba$_2$TiO$_4$
Monoclinic, $P2_1/n$

$a = 6 \cdot 12 \pm 0 \cdot 03, \quad b = 7 \cdot 70 \pm 0 \cdot 03, \quad c = 10 \cdot 50 \pm 0 \cdot 03 \text{ Å}$
$a:b = 0 \cdot 792, \quad b:c = 0 \cdot 733, \quad \beta = 93° \, 8' \pm 10'$

Ba$_2$SiO$_4$
(O'Daniel & Tscheischwili, 1942)

$a = 5 \cdot 77, \quad b = 7 \cdot 57, \quad c = 10 \cdot 19 \text{ Å}$
$a:b = 0 \cdot 762, \quad b:c = 0 \cdot 743$

β-Ca$_2$SiO$_4$ (Midgley, 1952)
Monoclinic, $P2_1/n$

$a = 5 \cdot 48 \pm 0 \cdot 02, \quad b = 6 \cdot 76 \pm 0 \cdot 02, \quad c = 9 \cdot 28 \pm 0 \cdot 02 \text{ Å}$
$a:b = 0 \cdot 810, \quad b:c = 0 \cdot 729, \quad \beta = 94° \, 33'$

* Present address: Imperial Chemical Industries Ltd., Plastics Division, Welwyn Garden City, Herts, England.

* Estimates of reasonable limits of experimental error are given.

comparison with the β-Ca_2SiO_4 structure. All crystals examined were twinned on (100) or (001).

The density calculated on the basis of four units of Ba_2TiO_4 per cell was found to be 5·16 g.cm.$^{-3}$, which may be compared with an observed value of 5·07 ± 0·15 g.cm.$^{-3}$, obtained by the displacement method.

(iii) X-ray intensities

Intensity data in the $hk0$, $0kl$ and $h0l$ zones were collected using a Weissenberg camera and Mo $K\alpha$ radiation; visual estimates of the intensities were made by comparison with a standard scale and corrections for Lorentz and polarization factors were made in the usual way. The crystal was roughly cubic in shape with edges of about 0·1 mm. and consisted of a twin with two components in the ratio 2·45:1. Reflexions from one component were absorbed in the other component but no correction was made for this effect. It was found, however, that there was an agreement factor of 7% between structure factors obtained independently from the two components.

3. Approximate structure

Patterson syntheses were prepared for the three axial projections using a sharpening function of the type advocated by Lipson & Cochran (1953). It was assumed that the strongest peaks in the syntheses correspond to Ba–Ba and Ba–Ti vectors and a self-consistent set of position coordinates was obtained for the two independent Ba atoms and the Ti atom. The coordinates are listed in Table 2 together with the coordinates of corresponding atoms in β-Ca_2SiO_4. It is evident that if the x-axis of β-Ca_2SiO_4 is reversed then the heavier atoms in the two structures occupy similar positions.

Table 2. *Atomic co-ordinates derived from Patterson syntheses, compared with the atomic co-ordinates in* β-Ca_2SiO_4

Ba_2TiO_4		x	y	z
	Ba_I	0·767	0·850	0·067
	Ba_{II}	0·227	0·492	0·195
	Ti	0·767	0·292	0·063
		x	y	z
β-Ca_2SiO_4	Ca_I	−0·760	0·838	0·071
	Ca_{II}	−0·216	0·502	0·201
	Si	−0·760	0·276	0·071

At this stage in the analysis it was possible to predict certain features of the arrangement of oxygen atoms by considering the coordinates in Table 2 and by noting that the normal Ti–O distance found in other structures is about 2·0 Å. The shortest distance between two Ti atoms is about 5·5 Å which means that one oxygen atom cannot be in contact with two titanium neighbours. It follows that the polyhedron of oxygen atoms surrounding one titanium atom will be isolated from that surrounding a neighbouring

titanium atom. Since there is only one titanium atom in the asymmetric unit, all polyhedra surrounding titanium will be identical, so that if the Ti:O ratio of 1:4 is to be preserved, the number of oxygen atoms in each polyhedron cannot exceed four. We may conclude that the titanium atom in Ba_2TiO_4 cannot be octahedrally coordinated by oxygen.

4. Refinement of the structure

(i) Scattering curves

The scattering curves used in the refinement process were derived from the published values in the *Internationale Tabellen* (1935). It was assumed that barium is in the ionized state Ba^{2+} and the corresponding
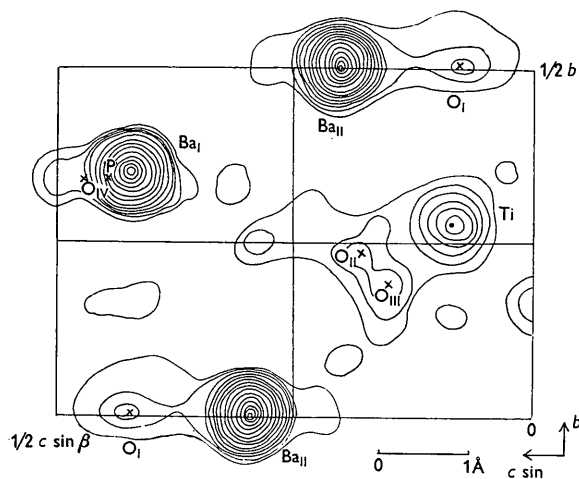

Fig. 1. Final F_o synthesis on (100). The contours are drawn at intervals approximately equal to 5 e.Å^{-2} for the heavy atoms and 2·5 e.Å^{-2} for the oxygen atoms. The point P marks an alternative position for O_{IV} suggested by packing considerations.
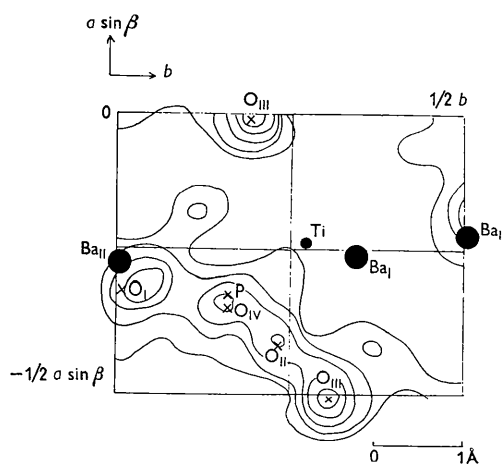

Fig. 2. Partial difference synthesis on (001) showing electron density due to oxygen atoms with contours drawn at intervals approximately equal to 2·5 e.Å^{-2}. The point P marks an alternative position for O_{IV} suggested by packing considerations.

Table 3(a). *Observed and calculated structure factors*

hkl	F_o	F_c	F_c'	hkl	F_o	F_c	F_c'	hkl	F_o	F_c	F_c'
002		5	0	035	55	−62	−51	066	73	−66	−72
004	60	−28	−41	036	<30	15	15	067	<37	−12	−10
006	128	−134	−149	037	180	220	231	068	136	−145	−150
008	220	−244	−255	038	<34	−18	−22	069	<41	−7	−2
0,0,10	124	117	111	039	<34	10	18	0,6,10	85	87	84
0,0,12	<40	29	30	0,3,10	53	−48	−52				
0,0,14	128	151	140	0,3,11	56	−59	−57	071	80	66	66
				0,3,12	<40	−12	−17	072	85	67	67
011	<20	27	27					073	106	120	117
012	45	46	51	040	150	112	112	074	80	93	93
013	136	159	154	041	76	−42	−43	075	176	−186	−193
014	111	139	145	042	183	−179	−176	076	<39	19	19
015	153	−201	−209	043	144	−148	−151	077	<40	−7	−14
016	37	36	37	044	66	54	61	078	30	−47	−47
017	58	71	63	045	110	−108	−110	079	46	−63	−69
018	45	−47	−52	046	88	79	88	0,7,10	65	−73	−73
019	68	−73	−78	047	45	33	35				
0,1,10	50	−49	−58	048	70	−61	−53	080	118	109	109
0,1,11	<38	4	3	049	98	90	94	081	53	53	54
0,1,12	45	−32	−42	0,4,10	104	107	111	082	108	−83	−84
0,1,13	113	111	110	0,4,11	83	72	77	083	55	68	70
				0,4,12	99	−105	−106	084	55	45	43
020	<18	28	28					085	30	51	52
021	93	80	84	051	55	−37	−37	086	<42	22	19
022	168	−203	−202	052	133	−145	−148	087	<43	6	4
023	133	185	192	053	103	85	86	088	88	−71	−75
024	108	111	113	054	136	−133	−137	089	65	−61	−66
025	121	132	136	055	118	−120	−118				
026	116	96	99	056	48	−56	−56	091	153	−140	−139
027	<30	−21	−26	057	100	106	108	092	58	34	36
028	45	−31	−30	058	90	78	83	093	58	53	54
029	95	−103	−114	059	38	−54	−53	094	<40	51	53
0,2,10	98	102	104	0,5,10	113	110	119	095	<43	−4	−3
0,2,11	95	−74	−85					096	<44	2	2
0,2,12	118	−148	−148	060	257	250	250	097	150	177	179
				061	<32	−10	−12				
031	200	−240	−240	062	<33	−28	−30	0,10,0	<44	18	18
032	90	85	88	063	<34	−19	−22	0,10,1	<44	−3	−3
033	121	114	119	064	<34	12	8	0,10,2	125	−118	−117
034	63	51	53	065	<35	−2	−4	0,10,3	<41	−30	−29

The F_c' values are based on the structure which has O_{IV} in the alternative position O_{IV}'.

The < sign indicates an unobserved reflexion; the corresponding value of F_o is the minimum observable F_o in that region of the photograph.

curve was obtained by drawing a smooth line from the curve for Ba at $\sin\theta/\lambda = 0.3$ to the value 54 at $\sin\theta/\lambda = 0$. The curve Ti^{+4} was used for titanium and the curve O^{-2} was used for oxygen. In the final stages of the structure determination, temperature factors of the form $\exp(-B\sin^2\theta/\lambda^2)$ were applied to scattering curves with $B = 0.25$ Å², 0.40 Å² and 0.40 Å² for barium, titanium and oxygen respectively.

(ii) *The* (100) *and* (001) *projections*

Refinement was carried out using the 0kl and hk0 intensity data; reflexions with $\sin\theta/\lambda < 0.4$ were considered first and higher angle reflexions included at later stages. The signs of the F_c values, obtained by considering heavy atoms only, were applied to the observed structure factors and the corresponding F_o and $F_o - F_c$ syntheses were calculated. After a few cycles, peaks corresponding to oxygen atoms were detected and their contribution was included in subsequent structure factor calculations.

The final F_o synthesis on (100) is shown in Fig. 1 with a converging factor $\exp[-1.8\sin^2\theta/\lambda^2]$ applied to the Fourier coefficients. In this projection, O_I is well resolved, O_{II} and O_{IV} overlap slightly with each other and O_{IV} is partly obscured by Ba_I. On the (001) projection, however, the oxygen atoms are well separated from each other and are shown in the partial difference synthesis obtained after the heavy atoms had been removed (Fig. 2). On completion of the refinement, an R-factor of approximately 14% was obtained on each projection; F_o values were scaled for comparison with F_c and unobserved reflexions were included when F_c exceeded the minimum observable level. Values of F_o and F_c for the 0kl an hk0 reflexions are given in Tables 3(a) and 3(b) respectively. The corresponding atomic coordinates are given in Table 4. The standard deviations quoted in Table 4 were obtained by assuming that the standard deviation in the F_o values is 15% of F_o (Lipson & Cochran, 1953). The corresponding standard deviations in the interatomic distances are then approximately 0.17 Å for

Table 3(b). *Observed and calculated structure factors*

hkl	F_o	F_c	F'_c	hkl	F_o	F_c	F'_c	hkl	F_o	F_c	F'_c
200	360	−416	−428	930	122	−137	−137	670	<43	−35	−36
400	260	299	313					770	<44	14	23
600	198	−191	−194	040	128	112	112				
800	154	129	121	140	147	146	145	080	96	109	109
				240	96	−79	−72	180	78	−61	−60
110	<18	−30	−26	340	146	−139	−134	280	103	−105	−107
210	64	−62	−56	440	87	68	58	380	71	54	49
310	72	72	71	540	103	98	94	480	60	67	71
410	56	36	40	640	55	−44	−41	580	63	−59	−54
510	46	−52	−59	740	62	−76	−77	680	<43	−56	−57
610	51	−46	−56								
710	57	51	58	150	<28	−13	−14	190	<39	−30	−31
810	<40	46	53	250	<29	25	21	290	<40	−21	−19
				350	72	57	57	390	<41	60	60
020	<18	28	28	450	<32	−51	−55	490	<41	21	23
120	163	−164	−161	550	53	−53	−51	590	65	−90	−89
220	93	−90	−87	650	<41	40	50	690	<48	20	18
320	148	−156	−143	750	<43	72	71				
420	<27	25	21					0,10,0	<43	18	18
520	115	−114	−106	060	235	250	250	1,10,0	<45	41	42
620	<37	−7	−6	160	<32	16	15	2,10,0	<47	−11	−9
720	92	82	85	260	213	−223	−227	3,10,0	<48	−27	−28
820	<45	−10	−8	360	<33	−7	−4	4,10,0	<50	16	11
920	<48	−49	−58	460	180	178	183				
				560	<39	19	15	1,11,0	<45	0	−1
130	62	−46	−51	660	114	−107	−113	2,11,0	<48	14	13
230	<22	−5	−2	760	<44	−2	−4	3,11,0	<50	41	
330	96	83	84	860	52	80	76	4,11,0	<52	22	
430	25	27	29								
530	137	−143	−134	170	<33	−13	−10	0,12,0	135	139	
630	<37	−11	−15	270	<35	−15	−15	1,12,0	72	−72	
730	137	134	124	370	<37	29	28	2,12,0	103	−129	
830	<45	11	14	470	<39	39	39	3,12,0	52	72	
				570	<41	−34	−41	4,12,0	75	99	

The F'_c values are based on the structure which has O_{IV} in the alternative position O'_{IV}.

The < sign indicates an unobserved reflexion; the corresponding value of F_o is the minimum observable F_o in that region of the photograph.

the metal–oxygen distances and 0·22 Å for the oxygen–oxygen distances. It is estimated that the standard deviation for interbond angles is of the order of 5°.

Table 4. *Final atomic co-ordinates and standard deviations in Ba_2TiO_4*

	x	y	z
Ba_I	0·765	0·841	0·076
Ba_{II}	0·229	0·498	0·202
Ti	0·754	0·276	0·079
O_I	0·693	0·008	0·430
O_{II}	0·567	0·230	0·180
O_{III}	0·993	0·190	0·153
O_{IV}	0·650	0·145	0·970
O'_{IV}	(0·695)	(0·145)	(0·945)

$\sigma(x)$ for Ba = 0·01 Å
$\sigma(x)$ for Ti = 0·05
$\sigma(x)$ for O = 0·16

These coordinates were obtained by Fourier methods except for O'_{IV} which is an alternative position for O_{IV} obtained by packing considerations.

5. Description of the structure

The results of the structure analysis show that Rooksby's (1947) suggestion is correct and that

Ba_2TiO_4 has the β-K_2SO_4 type of structure and the titanium atom is surrounded by a distorted tetrahedron of oxygen atoms (Fig. 5). The structure may be regarded as a sequence of TiO_4 groups which alternate with the Ba_I atoms in the y-direction. These strings of barium atoms and tetrahedra are linked through the Ba_{II} atoms which are located between the tetrahedra. There is a pseudo-trigonal arrangement of tetrahedra about the Ba_{II} atoms. The structure is not strictly isomorphous with β-Ca_2SiO_4 but there is a close correspondence between the atomic positions. This is illustrated in Figs. 3 and 4 which represent projections of the two structures on (100) and (001) respectively; corresponding SiO_4 and TiO_4 tetrahedra are outlined.

The interatomic distances are listed in Table 5(a). Although the standard deviations indicate a large range of uncertainty in any one distance, it does appear that the Ti–O bonds are abnormally short when compared with 1·86 Å, which is the sum of the Goldschmidt radii corrected for the reduction of the coordination number from six to four (Pauling, 1940). The Ti–O bond in Ba_2TiO_4 must therefore have a considerable covalent character. The angles between the bonds, (Table 5(b)), range from 94° to 129°, which
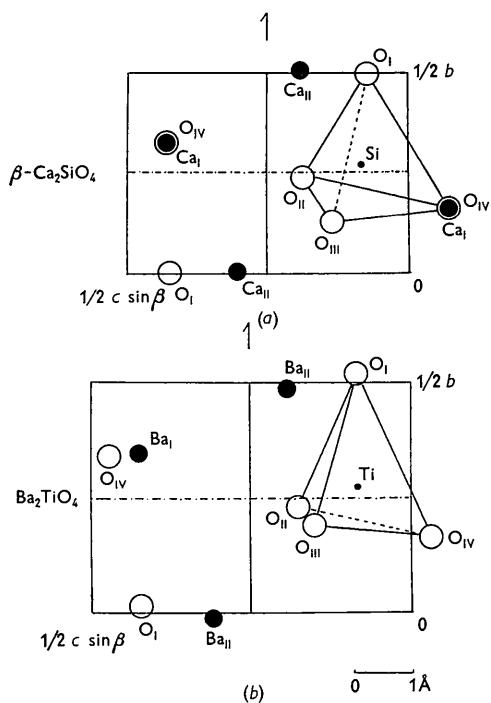
Fig. 3. Diagrammatic projections of (a) β-Ca$_2$SiO$_4$ and (b) Ba$_2$TiO$_4$ on (100) showing the close similarity between the structures. Corresponding oxygen tetrahedra are outlined.
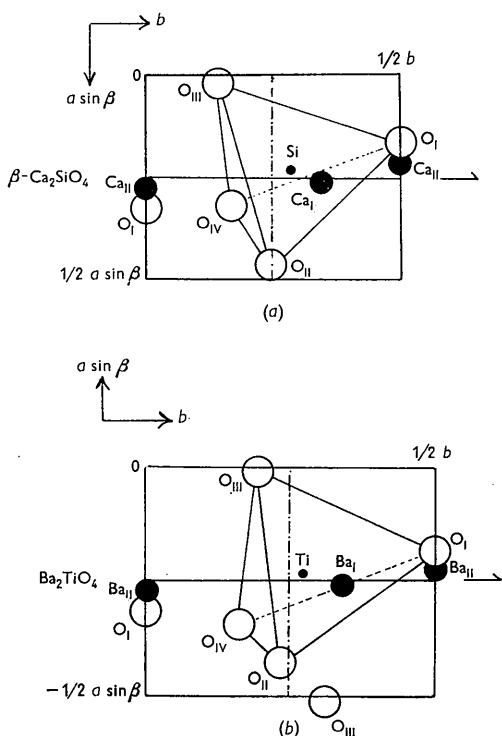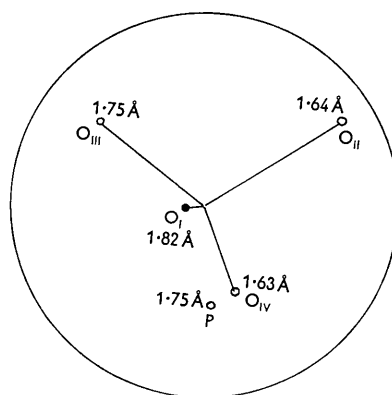

Fig. 4. Diagrammatic projections of (a) β-Ca$_2$SiO$_4$ and (b) Ba$_2$TiO$_4$ on (001) showing the close similarity between structures. Corresponding oxygen tetrahedra are outlined.

Fig. 5. A stereogram showing the approximately tetrahedral arrangement of oxygen atoms round the titanium atom. The point P marks an alternative position for O_{IV} suggested by packing considerations.

deviate from the normal tetrahedral angle of 109° 28'; a stereogram of the distorted tetrahedron is shown in Fig. 5. The oxygen–oxygen distances within the tetrahedron lie reasonably close to the normal value of 2·8 Å with the exception of the short distance of 2·38 Å between O_{II} and O_{IV}. It was found that when

Table 5(a). *Interatomic distances in* Ba$_2$TiO$_4$

Atom	No. of neighbours	Neighbour	Distance
Ti*	4	O_{IV}	1·63 Å
		O_{II}	1·64
		O_{III}	1·75
		O_{I}	1·82
O_{I}		O_{III}	2·82
		O_{I}	2·85
		O_{IV}	3·12
		O_{II}	2·87
O_{II}		O_{IV}	2·38
		O_{III}	2·66
O_{III}		O_{IV}	2·79
O_{IV}		O_{IV}	2·98
Ba$_{I}$	9 or 10	O_{IV}	2·56
		O_{I}	2·58
		O_{IV}	2·67
		O_{II}	2·84
		O_{III}	2·90
		O_{III}	3·11
		O_{III}	3·32
		O_{II}	3·43
		O_{III}	3·52
		O_{IV}	3·64
Ba$_{II}$	8	O_{III}	2·67
		O_{III}	2·81
		O_{I}	2·85
		O_{I}	2·87
		O_{II}	2·87
		O_{II}	2·94
		O_{IV}	3·08
		O_{IV}	3·39

Standard deviations of bond lengths

Metal–oxygen 0·17 Å   Oxygen–oxygen 0·22 Å

* The next greatest Ti–O distance is 3,59 Å to O_{I} in a neighbouring tetrahedron.

Table 5(b). *Angles in the* TiO_4 *tetrahedron*

O_I–Ti–O_{IV}	129°
O_{II}–Ti–O_{IV}	94
O_{III}–Ti–O_{II}	103
O_{III}–Ti–O_I	104
O_I–Ti–O_{II}	112
O_{III}–Ti–O_{IV}	111

O_{IV} was shifted from position (0·650, 0·145, 0·970) to (0·695, 0·145, 0·945), shown as position P in Figs. 1, 2 and 5, then O_{II}–O_{IV} became 2·71 Å and other distances involving O_{IV} moved closer to normal values (Table 6(a)); the mean deviation from the tetrahedral

Table 6(a). *Changes in interatomic distances by altering position of* O_{IV} *from*
(0·650, 0·145, 0·970) *to* (0·695, 0·145, 0·945)

	Distances obtained from Fourier maps	Distances obtained with new parameters
Ba_I–O_{IV}	2·56 Å	2·81 Å
Ba_I–O_{IV}	2·67	2·74
Ba_I–O_{IV}	3·64	3·33
Ba_{II}–O_{IV}	3·08	2·80
Ba_{II}–O_{IV}	3·39	3·20
Ti–O_{IV}	1·63	1·75
O_I–O_{IV}	3·12	3·15
O_{II}–O_{IV}	2·38	2·71
O_{II}–O_{IV}	3·51	3·52
O_{II}–O_{IV}	>4·00	3·81
O_{III}–O_{IV}	2·79	2·79
O_{IV}–O_{IV}	2·98	3·51

Table 6(b). *Changes in angles in* TiO_4 *tetrahedron*

	Angles obtained from Fourier maps	Angles obtained with new parameters
O_I–Ti–O_{IV}	129°	124°
O_{II}–Ti–O_{IV}	94	106
O_{III}–Ti–O_{IV}	111	106

angle changed from 8·5° to 6·0° (Table 6(b)). There is no evidence for such an atomic shift on the (100) projection while on the (001) projection, (Fig. 2), the two alternative positions for O_{IV} are equally acceptable. Similarly, the corresponding sets of structure factors F_c and F'_c in Tables 3(a) and 3(b) have R-factors which are not significantly different. It is evident that the estimated standard deviations of interatomic distances involving O_{IV} do not allow for inaccuracies resulting from serious overlap in projection.

The Ba–O distances may be arbitrarily divided into two classes: oxygen atoms at distances less than 2·95 Å are classed as nearest neighbours in contact with barium, and oxygen atoms at distances between 2·95 Å and 3·55 Å are classed as second-nearest neighbours. In making this division, it was noted that the sum of the Goldschmidt radii of Ba and O atoms is 2·75 Å and the average Ba–O distance in BaTiO₃ is 2·84 Å. In Ba_2TiO_4, Ba_I is coordinated by ten oxygen atoms, five of which are nearest neighbours. The second barium, Ba_{II}, is coordinated by eight oxygen atoms and is in contact with six of them;

when the revised position of O_{IV} is considered, Ba_{II} is in contact with seven oxygen atoms. For comparison, barium both in paracelsian, $BaAl_2Si_2O_8$ (Smith, 1953) and in sanbornite, $Ba_2Si_2O_5$ (Douglass, 1958) has nine oxygen neighbours, seven of which are in contact with the central barium atom.

6. Discussion

An important feature of the structure is that the atoms are loosely packed; in fact there is room for eight more oxygen atoms in the unit cell. In contrast to this, phases at the oxygen-rich end of the BaO–TiO_2 systems have structures derived from the close packing of oxygen atoms and the slightly larger barium atoms (Harrison, 1956a, 1956b); only octahedral intersticies between oxygen atoms are then available for the titanium atoms. Ferroelectric $BaTiO_3$, however, has a distorted perovskite structure and is not perfectly close packed. Megaw (1957) has suggested that, even in this structure, the Ti atom shows some evidence of covalent bonding; the O–Ti–O angles in the oxygen octahedron differ from 180° and there is a short Ti–O distance of 1·87 Å (Frazer, Danner & Pepinsky, 1955).

It is evident that for Ba_2TiO_4 and $BaTiO_3$ the ratio of the number of oxygen atoms to barium atoms is not sufficient to allow a close packed framework, the effect being much more important in Ba_2TiO_4 than in $BaTiO_3$. In Ba_2TiO_4, the Ti–O bond becomes the predominant factor which produces a tetrahedral environment around titanium, and the result is a loosely packed structure of barium atoms and TiO_4 groups.

The atomic arrangement in Sr_2TiO_4 provides an example of the type of structure Ba_2TiO_4 might have if the barium atoms were slightly smaller. The radii of the strontium and oxygen atoms are nearly equal, with the result that Sr_2TiO_4 has a K_2NiF_4 type structure (Ruddlesden & Popper, 1957), an arrangement of atoms derived from a cubic close-packed array of strontium and oxygen atoms. The structure is closely related to $SrTiO_3$ and the titanium atom is octahedrally coordinated. At very low temperatures, however, the close-packing factor ceases to be overwhelming and some distortion is allowed; evidence for this is provided by the presence of an induced ferroelectric effect in $SrTiO_3$ at 4 °K. (Gränicher, 1956).

7. Thermal behaviour of Ba_2TiO_4

Since the crystallographic features of Ba_2TiO_4 and β-Ca_2SiO_4 are similar, it is natural to expect that Ba_2TiO_4 may show polymorphic modifications similar to those observed in Ca_2SiO_4 (Bredig, 1950). Some support for this suggestion comes from the work of Todd & Lorenson (1952). They showed that, as the temperature is increased, the heat capacity of Ba_2TiO_4 approaches a peak in the region of room temperature while the heat capacity of Sr_2TiO_4 shows no unusual type of variation with temperature. This could mean

that Ba_2TiO_4 undergoes at least one phase change above room temperature.

Midgley (1952) has suggested that the structures of the high-temperature modifications of Ca_2SiO_4 may be derived from the β-phase by rotating the SiO_4 tetrahedra. This may not happen with Ba_2TiO_4 for it is not possible to predict the effect of a temperature change on the Ti–O bond. If it ceases to be stronger than the other bonds then it is more likely that there will be a reconstructive change to a more close packed arrangement such as the Sr_2TiO_4 structure.

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The Crystal Structure of Barbituric Acid Dihydrate

By G. A. JEFFREY, SUBRATA GHOSE AND J. O. WARWICKER*

The Crystallography Laboratory, The University of Pittsburgh, U.S.A., and The Chemistry Department, The University of Leeds, England

Barbituric acid dihydrate, $C_4H_4N_2O_3 . 2H_2O$, forms crystals which have a hydrogen-bonded layer structure in which the barbituric acid and water molecules lie on the mirror planes of the space group Pnma. The barbituric acid is in the tri-keto form and, within the accuracy of the analysis, has *mm* symmetry. The water molecules are hydrogen-bonded in pairs and their hydrogen-bond coordination is unusual in that it is planar and approximately trigonal. The structure analysis was refined by isotropic and anisotropic least squares methods.

Introduction

Barbituric acid, $C_4H_4N_2O_3$, is the parent compound for a wide variety of derivatives famous for their drug action. A recent compilation (Blicke & Cox, 1959) listed several hundred such compounds, under the general classification as 'barbiturates', which had been synthesized and examined with respect to their pharmacological activity.

The structural interest in the molecule of barbituric acid itself, I, lies in its behaviour as a carboxylic acid comparable in strength with formic and benzoic acids. This acidity ($K_a = 1\cdot0 \times 10^{-4}$) is apparently associated with the particular combination of the active methylene group of the malonyl system with the potential imino carboxylic configuration of urea, since comparable acidity is not shown either by the malonyl esters or urea derivatives separately or by related cyclic compounds such as isobarbituric acid, II, ($K_a = 2\cdot5 \times 10^{-9}$), alloxan, III, ($K_a = 2\cdot3 \times 10^{-7}$), and diketopiperazine, IV.

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* Present address, The British Cotton Industry Research Association.