XVI. The Crystal Structure of Benitoite, $BaTiSi_3O_9$.

By

W. H. Zachariasen (Oslo — Manchester).

(With 2 figures.)

1. Introduction.

The mineral Benitoite from St. Benito in California has the composition $BaTiSi_3O_9$. From a crystallographical point of view this compound is especially interesting, being the only known member of the ditrigonal-bipyramidal symmetry class. The axial ratio is given as: 0.7319 (Palache[1]), 0.7344 (Louderback[2]), 0.7353 (Jezek[3]). The density is 3.64—3.67 (Louderback).

Some X-ray examinations of Benitoite have been made. Using the Laue-method F. Rinne[4]) was able to prove the ditrigonal-bipyramidal symmetry of the crystals. B. Gossner and F. Mussgnug[5]) found the dimensions of the unit cell to be: $a = 6.59$ Å, $c = 4.86$ Å, one molecule in the cell and space group D_{3h}^1. J. J. P. Valeton[6]) observed in rotation photographs weak layer lines incompatible with Gossner and Mussgnug's dimensions. Valeton's investigation gave: $a = 6.64$ Å, $c = 9.71$ Å. Two molecules in the cell and space group D_{3h}^2 or D_{3h}^4. He does not give any information about the atomic arrangement.

In the following I will give an account of a complete determination of the crystal structure of Benitoite.

2. Dimensions and Space Group.

I have worked with the Laue-, the oscillation- and the ionization methods.

In agreement with Valeton's results I found:

$$a = 6.60 \pm 0.01 \text{ Å},\ c = 9.71 \pm 0.01 \text{ Å},\ c/a = 2 \times 0.7356.$$

2 molecules in the cell. Calculated density 3.73.

No trace of odd order reflexions 0001 were observed, hence the space group is D_{3h}^2 or D_{3h}^4. As $(h\,0\,\bar{h}\,l)$ is absent if l is odd, the correct space croup is D_{3h}^2. There are thus $2\,Ba$, $2\,Ti$, $6\,Si$ and $18\,O$ atoms in the unit cell. The positions of this space group are:

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[1]) Z. Krist. **46**, 379. 1909.

[2]) Z. Krist **46**, 386. 1909; **50**, 184. 1912.

[3]) Z. Krist. **50**, 642. 1912.

[4]) C. Min. 193. 1919.

[5]) C. Min. A **1927**, 304.

[6]) C. Min. A **1927**, 387; Z. Krist. **66**, 496. 1927.

$2a$ $(0\,0\,0)$ $(0\,0\,\frac{1}{2})$ $2b$ $(0\,0\,\frac{1}{4})$ $(0\,0\,\frac{3}{4})$ $2c$ $(\frac{1}{3}\,\frac{2}{3}\,0)$ $(\frac{1}{3}\,\frac{2}{3}\,\frac{1}{2})$ $2d$ $(\frac{1}{3}\,\frac{2}{3}\,\frac{1}{4})$
$(\frac{1}{3}\,\frac{2}{3}\,\frac{3}{4})$ $2e$ $(\frac{2}{3}\,\frac{1}{3}\,0)$ $(\frac{2}{3}\,\frac{1}{3}\,\frac{1}{2})$ $2f$ $(\frac{2}{3}\,\frac{1}{3}\,\frac{1}{4})$ $(\frac{2}{3}\,\frac{1}{3}\,\frac{3}{4})$

$4g$ $(0\,0\,u)$ $(0\,0\,\bar{u})$ $(0\,0\,\frac{1}{2}-u)$ $(0\,0\,u+\frac{1}{2})$ $4h$ $(\frac{1}{3}\,\frac{2}{3}\,u)$ $(\frac{1}{3}\,\frac{2}{3}\,\bar{u})$ $(\frac{1}{3}\,\frac{2}{3}\,u+\frac{1}{2})$
$(\frac{1}{3}\,\frac{2}{3}\,\frac{1}{2}-u)$ $4i$ $(\frac{2}{3}\,\frac{1}{3}\,u)$ $(\frac{2}{3}\,\frac{1}{3}\,\bar{u})$ $(\frac{2}{3}\,\frac{1}{3}\,u+\frac{1}{2})$ $(\frac{2}{3}\,\frac{1}{3}\,\frac{1}{2}-u)$

$6j$ $(u\,\bar{u}\,0)$ $(2\bar{u}\,\bar{u}\,0)$ $(u\,2u\,0)$ $(u\,\bar{u}\,\frac{1}{2})$ $(2\bar{u}\,\bar{u}\,\frac{1}{2})$ $(u\,2u\,\frac{1}{2})$ $6k$ $(u\,v\,\frac{1}{4})$
$(v-u\,\bar{u}\,\frac{1}{4})$ $(\bar{v}\,u-v\,\frac{1}{4})$ $(u\,u-v\,\frac{3}{4})$ $(\bar{v}\,\bar{u}\,\frac{3}{4})$ $(v-u\,v\,\frac{3}{4})$

$12b$ $(x\,y\,z)$ $(y-x\,\bar{x}\,z)$ $(\bar{y}\,x-y\,z)$ $(x\,x-y\,\bar{z})$ $(\bar{y}\,\bar{x}\,\bar{z})$ $(y-x\,y\,\bar{z})$ $(x\,y\,\frac{1}{2}-z$
$(y-x\,\bar{x}\,\frac{1}{2}-z)$ $(\bar{y}\,x-y\,\frac{1}{2}-z)$ $(x\,x-y\,z+\frac{1}{2})$ $(\bar{y}\,\bar{x}\,z+\frac{1}{2})$
$(y-x\,y\,z+\frac{1}{2})$.

3. Observations.

In the following tables I have listed the most important observations. With regard to measurements of absolute intensities reference must be made to previous papers in this journal by Professor W. L. Bragg and his co-workers.

Table 1. Absolute Measurements of the 000l Reflexions.

$0\,0\,0\,l$	$\sin\theta$	$\varrho' \times 10^6$	$\pm F'$	$\pm F$ corr.	F calc.
0002	0.0729	15.0	37.5	38	33
0004	1458	74.5	122	143	141
0006	2187	0.6	14	14	16
0008	2915	41.0	136	148	164
00010	3645	0.9	23	23	41
00012	4374	5.1	62	63	87
00014	5100	0.4	20	20	28
00016	5830	1.8	45	45	75
00018	6560	0	0	0	34
00020	7290	0.7	31	31	54

Table 2. Absolute Measurements of Reflexions $10\bar{1}2$.

$h\,0\,\bar{h}\,2h$	$\sin\theta$	$\varrho' \times 10^6$	F'	F corr.	F calc.
$10\bar{1}2$	0.0954	75.1	90	116	124
$20\bar{2}4$	1908	25.0	82	86	103
$30\bar{3}6$	2862	9.5	64	65	79
$40\bar{4}8$	3827	0.5	18	18	31
$50\bar{5}10$	4782	0.4	19	19	38
$60\bar{6}12$	5724	0.6	26	26	47

$$\varrho' = \frac{Q}{2\mu}, \qquad Q = \left(\frac{Ne^2}{mc^2}|F|\right)^2 \lambda^3 \frac{1+\cos^2 2\theta}{2\sin 2\theta}, \qquad \mu = \mu_o + gQ,$$

$$N = \frac{1}{V} = \frac{1}{370 \times 10^{-24}}, \qquad \frac{e^2}{mc^2} = 2.816 \times 10^{-13}, \qquad \lambda = 0.7095 \times 10^{-8},$$

$$\mu_o = 69.3 \qquad g = 1.85 \times 10^{-3}.$$

Table 3. Observations from Oscillation Photographs[1]).

$h0\bar{h}l$	sin θ	Int. obs.	F calc.	$h0\bar{h}l$	sin θ	Int. obs.	F calc.
$10\bar{1}0$	0.0621	m.	50	$40\bar{4}2$	0.2598	s.	83
$10\bar{1}2$	0959	vs.	124	$30\bar{3}6$	2877	m.	79
$20\bar{2}0$	1242	vs.	114	$40\bar{4}4$	2880	m.	60
$20\bar{2}2$	1440	w.	42	$50\bar{5}0$	3105	w.	47
$10\bar{1}4$	1588	m.	63	$50\bar{5}2$	3190	vw.	50
$30\bar{3}0$	1863	vs.	125	$40\bar{4}6$	3312	w—m.	68
$20\bar{2}4$	1918	vs.	103	$50\bar{5}4$	3431	m.	56
$30\bar{3}2$	2001	vs.	99	$60\bar{6}0$	3725	w.	54
$30\bar{3}4$	2367	s.	88	$60\bar{6}2$	3796	s.	78
$40\bar{4}0$	2484	w.	38	$50\bar{5}6$	3799	vw.	39
$20\bar{2}6$	2520	w.	34	$60\bar{6}4$	4002	m.	60

Table 4. F-Curves.

sin θ	0.1	0.2	0.3	0.4	0.5	0.6	0.7
Ba^{+2}	48	38	29.5	22	16	10	8
Ti^{+4}	17	12.8	10.0	7.8	6.2	4.5	3.3
Si^{+4}	10.6	8.3	6.3	4.7	3.3	2.0	1.1
O^{-2}	7.1	4.0	2.3	1.3	0.8	0.4	0.2

4. Determination of the Structure.

The $2\,Ba$ and the $2\,Ti$ atoms must lie in twofold positions. In order to get a tetrahedral arrangement of 4 oxygens about each silicon, the 6 silicon atoms must be equivalent and lie either on the reflexion planes or halfway between. Of the 18 oxygen atoms in the cell 12 must be in general positions while the remaining 6 oxygens are equivalent and lie either on the reflexion planes or halfway between them. The silicon: oxygen ratio is 1 : 3, so the SiO_4-tetrahedra are not independent. From considerations of the symmetry of the space group we can take it as granted that every oxygen atom must belong to at least one SiO_4-tetrahedron. The $6\,Si$ atoms and the $6\,O$ atoms must therefore lie either all on the reflexion planes or all halfway between.

In every structure containing Ti and O, Ti is found to be surrounded octahedrally by 6 oxygen atoms. If Ti in the present structure is lying in the twofold positions on the reflexion planes, the 6 oxygens around Ti will form a trigonal prism. Such a configuration would not be stable as the oxygen — oxygen distance must be rather small in order to give the correct Ti — O distance 1.96 Å, found in all other structures. It

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1) s = strong, m = medium, w = weak.

is therefore far more plausible that the 2 *Ti* atoms are situated on the trigonal axes halfway between the reflexion planes. In order to obtain almost regular tetrahedra around silicon we must further put the 6 silicon and the 6 oxygen atoms on the reflexion planes. These assumptions can be most readily tested by means of the length of the *c*-axis. If we take the *O—O* distance in the tetrahedra as 2.64 Å and the *Ti—O* distance equal to 1.96 Å, and assume the octahedron about *Ti* to be regular, the length of the *c*-axis should be:

$$4 \times \left(1.32 + 1.96\frac{\sqrt{3}}{3}\right) = 9.81 \text{ Å},$$

the observed value is 9.71 Å, so the agreement is really very good.

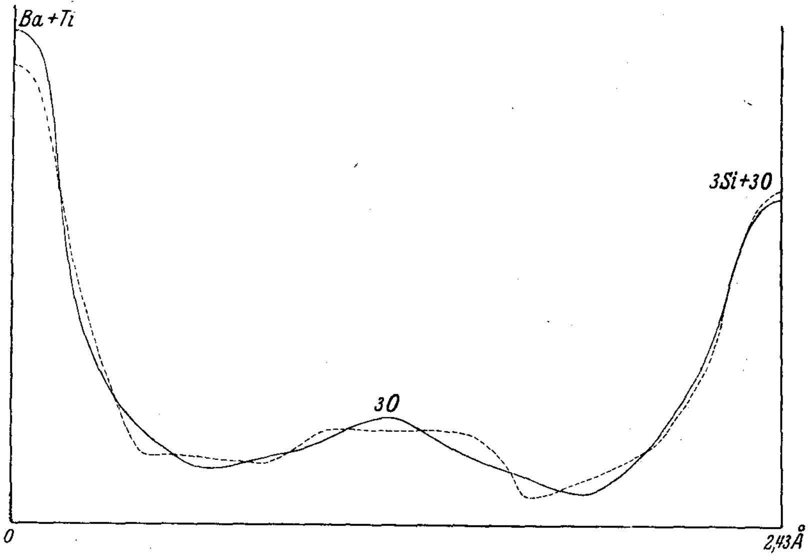

Fig. 1. The distribution of electron density between planes 0001.

In order to explain the very faint reflexions 0002, 0006, 000.10, 000.14 and 000.18 we must put the 2*Ba* on the trigonal axes halfway between the reflexion planes.

The positions of the different atoms are thus:

2*Ba* in 2*e* 2 *Ti* in 2*c*
6*Si* in 6*k* with parameters u_1 and v_1
$6\,O_{\mathrm{I}}$ in 6*k* » » u_2 » v_2
$12\,O_{\mathrm{II}}$ in 12*l* » » x, y and z.

From the considerations given above we have got a rather accurate knowledge of the distribution of atoms in the *c*-direction. The only parameter in this direction is the parameter z for oxygen in the general position. The probable value of z we can get from the O—O distance in the SiO_4-group. This knowledge enables us to tell the sign of the amplitude of all reflexions $0\,0\,0\,l$. The accurate value of z can then be fixed by means of a Fourier sheet analysis. The distribution of electron density between planes 0001 is shown in Fig. 1. For the parameter z we get 42°. In a later section the results of the Fourier analysis will be discussed more thoroughly.

The remaining parameters represent the displacement of the atoms in horizontal directions.

We know that the silicons are tetrahedrally surrounded by 4 oxygens. Considerations of the symmetry elements of the space group show that the SiO_4-tetrahedra must necessarily be linked up so as to form rings of composition Si_3O_9. From a large number of silicate structures we have gathered so much information about the SiO_4-group, that we with the greatest accuracy are able to predict the dimensions of these Si_3O_9-groups. Trigonal rotation axes are passing through the centres of these rings. As a matter of fact, the problem of determining 6 parameters (2 for Si, 2 for O_{I} and 2 for O_{II}) is now reduced to the determination of one parameter only, namely the angle of rotation of the Si_3O_9-group about the trigonal axis. This angle of rotation can be fixed in different ways. We can make use of 1) the distance Ti—$O = 1.96$ Å, 2) theformation of a regular octahedron of 6 oxygens around Ti, 3) the distance Ba—$O = 2.75$ Å, 4) the requirement, which is accurately or approximately fullfilled in all silicate structures hitherto known, that an oxygen atom which is attached to three cations is lying in the plane formed by the three cations.

An inspection now shows that if we rotate the Si_3O_9-group so as to make one of these 4 requirements fullfilled, the remaining three requirements will be simultaneously satisfied. The structure for Benitoite obtained in this way is the only one which is in accordance with the empirical rules of silicate structures. However, in order to make a yet more thorough test of the structure, the intensities of reflexions must be considered. The tables 1, 2 and 3 show that the agreement between calculated and observed intensities is very good, so the correctness of the structure cannot be doubted.

The parameter values are:

$2\,Ba$ in $(\frac{2}{3}\,\frac{1}{3}\,0)$			
$2\,Ti$ in $(\frac{1}{3}\,\frac{2}{3}\,0)$			
$6\,Si$ in $u_1\,v_1\,\frac{1}{4}$	$u_1 = 80^\circ$	$v_1 = -20^\circ$	
$6\,O_{\mathrm{I}}$ in $u_2\,v_2\,\frac{1}{4}$	$u_2 = 80^\circ$	$v_2 = 70^\circ$	
$12\,O_{\mathrm{II}}$ in $x\,y\,z$	$x = 125^\circ$	$y = -30^\circ$	$z = 42^\circ$

5. Discussion of the Structure.

Fig. 2 shows a projection of the structure on 0001. The silicon atoms are surrounded by $2\,O_{\mathrm{I}}$ atoms at a distance 1.65 Å and of $2\,O_{\mathrm{II}}$ atoms at a distance of 1.59 Å. The O—O distances in the tetrahedra are:

$$O_{\mathrm{I}}\text{—}O_{\mathrm{I}} = 2.40\ \text{Å},\quad O_{\mathrm{I}}\text{—}O_{\mathrm{II}} = 2.69\ \text{Å},\quad O_{\mathrm{II}}\text{—}O_{\mathrm{II}} = 2.59\ \text{Å}$$

6 oxygen atoms form an almost regular octahedron around *Ti*, the *Ti*—*O* distance being 1.965 Å.

Ba is surrounded by 6 oxygen atoms at a distance 2.74 Å, forming a distorted octahedron. 6 other oxygen atoms have a distance of about 3.4 Å from *Ba*, but we cannot consider them as belonging to the first sphere of coordination around *Ba*.

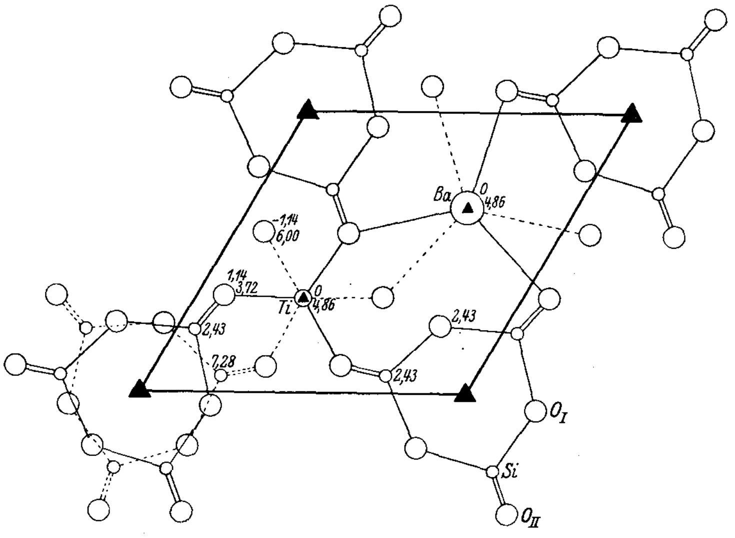

Fig. 2. Projection of the structure on the plane 0001.

Paulings rule of the electrostatic valency bonds is satisfied: an O_{I}-ion is connected to two silicons only, while an O_{II}-ion is connected to one silicon + one titanium + one barium.

The SiO_4-tetrahedra share only corners with other polyhedra. The TiO_6-octahedra share three edges with BaO_6-polyhedra, and the reverse.

The most interesting feature of the structure is the way in which the tetrahedra are linked together. Rings of composition Si_3O_9 are formed.

6. Fourier Sheet Analysis.

The Fourier analysis of the distribution of electron density between planes 0001 was carried out in order to get the accurate value of the parameter z. In fig. 1 the results of the analysis are given. The dotted curve represents the distribution obtained when using only the observed amplitudes of table 1. The fully drawn curve is the distribution obtained when additional amplitudes were taken into consideration. I calculated the amplitudes of the reflexions 000.18, 000.22 and 000.24 (introducing correction for the too high values of the F-curves at these glancing angles) and inserted the values in the Fourier series. It will be seen from Fig. 1 that the form of the curve depends considerably on the number of members of the series, which have been taken into consideration, although the value of the parameter does not seem to be so much affected.

I have tried to count up the number of electrons attached to the different ions. I do not wish, however, to give any accurate figures here, as I do not consider the results to be so unique, that we can draw any conclusions from them. I found for Si about 11 electrons, for oxygen a little more than 9 and for $Ba + Ti$ a little more than the number of electrons in the ionic state. A trial showed that it would not be impossible to draw the curves of the electron density so as to give the correct number of electrons in the ionic state.

7. Summary.

Benitoite, $BaTiSi_3O_9$, crystallizes ditrigonal-bipyramidal. The unit cell containing 2 molecules has the dimensions:

$$a = 6.60 \pm 0.01\ \text{Å}, \quad c = 9.71 \pm 0.01\ \text{Å}, \quad c/a = 1.4712 = 2 \times 0.7356.$$

The space group is D_{3h}^2. The calculated density is 3.73.

The Laue-, the oscillation- and the ionization methods were used.

The structure is given by the following information:

$2\,Ba$ in positions $2e$ $(\frac{2}{3}\,\frac{1}{3}\,0)$, $2\,Ti$ in positions $2c$ $(\frac{1}{3}\,\frac{2}{3}\,0)$
$6\,Si$ in $6k$ $(u_1\,v_1\,\frac{1}{4})$ $u_1 = 80^\circ$ $v_1 = -20^\circ$
$6\,O_{\mathrm{I}}$ in $6k$ $(u_2\,v_2\,\frac{1}{4})$ $u_2 = 80^\circ$ $v_2 = 70^\circ$
$12\,O_{\mathrm{II}}$ in $12l$ $(x\,y\,z)$ $x = 125^\circ$ $y = -30^\circ$ $z = 42^\circ$.

Si is surrounded by $2\,O_{\mathrm{I}} + 2\,O_{\mathrm{II}}$ forming a nearly regular tetrahedron: $Si—O_{\mathrm{I}} = 1.65$ Å, $Si—O_{\mathrm{II}} = 1.59$ Å. The silicon tetrahedra grouped three together form rings of composition Si_3O_9.

Ti is surrounded by $6\,O_{\mathrm{II}}$ in an almost regular octahedron, the distance $Ti—O$ being 1.96 Å. Ba is also surrounded by six oxygens at a distance 2.74 Å. The six oxygens around *Ba* form a distorted octahedron.

The empirical rules of complex coordination structures are satisfied.

Most of the experimental work was done in the Physical Laboratories of Victoria University, Manchester. I wish to express my most sincere thanks to Professor W. L. Bragg, F. R. S. Manchester for the interest he always showed my work while I stayed in his laboratories, and for his kind help and advice.

Professor Ch. Palache of Harvard University supplied me with crystals of Benitoite. I am very much indebted to him for his kindness.

Oslo, Mineralogical Institute of the University,
February 20th 1930.

Received March 17th, 1930.