

References

- BOKHOVEN, C., SCHOONE, J. C. & BIJVOET, J. M. (1951). *Acta Cryst.* **4**, 275.
 HARGREAVES, A. (1957). *Acta Cryst.* **10**, 191.
 HARKER, D. (1956). *Acta Cryst.* **9**, 1.
International Tables for X-ray Crystallography (1952). Birmingham: Kynoch Press.
 LIPSON, H. & COCHRAN, W. (1953). *The Determination of Crystal Structures*. London: Bell.
 ROBERTSON, J. M. (1936). *J. Chem. Soc.* p. 1195.
 ROBERTSON, J. M. (1953). *Organic Crystals and Molecules*. Ithaca: Cornell University Press.
 WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 152.

Acta Cryst. (1957). **10**, 199

The Structure of BaBOF₃

By D. M. CHACKRABURTTY

Department of General Physics and X-rays, Indian Association for the Cultivation of Science, Calcutta 32, India

(Received 24 September 1956 and in revised form 5 November 1956)

With the help of Lipson's method, BaBOF₃ was shown to be orthorhombic with $a = 8.78 \pm 0.03$, $b = 5.41 \pm 0.02$, $c = 7.16 \pm 0.02$ Å. On the basis of the space group *Pnma*, the structure was worked out and is discussed in detail.

Introduction

The spacings and $\sin^2 \theta$ values of BaBOF₃, obtained in powder form by Roy (1955), were calculated from the powder patterns taken with Cu $K\alpha$ radiation. As the substance was found, by the application of the method of Hesse (1948), not to belong to the cubic, tetragonal or hexagonal systems, Lipson's method (1949) for orthorhombic systems was tried and used successfully.

For orthorhombic crystals $\sin^2 \theta = Ah^2 + Bk^2 + Cl^2$. It was shown by Lipson that if $\sin^2 \theta_{100} = A$, $\sin^2 \theta_{010} = B$ and $\sin^2 \theta_{001} = C$ then in general,

$$\sin^2 \theta_{1kl} - \sin^2 \theta_{0kl} = \sin^2 \theta_{100};$$

and similarly for the constants B and C . Here A occurs as differences between the $\sin^2 \theta$ values provided the h values differ by unity and the kl values for the two lines are the same.

To find such differences in BaBOF₃, the diagrammatic method described by Lipson (1949) was used. From the plot the possible values deduced were $A = 0.0077$, $B = 0.02031$ and $C = 0.0116$. Since $A = \lambda^2/4a^2$, $a = 8.78 \pm 0.03$ Å ($\lambda(\text{Cu } K\alpha) = 1.5418$ Å); similarly, $b = 5.41 \pm 0.02$ Å and $c = 7.16 \pm 0.02$ Å. The possible space group, after indexing of all lines, is *Pnma*. The calculated density, D_x , is 4.27 g.cm.^{-3} and the observed density, D_m , is 4.25 g.cm.^{-3} . The number of molecules per unit cell is 4.

Atomic coordinates

On the basis of the space group *Pnma*, and taking into consideration similar structures like BaSO₄ (James, 1925) and KMnO₄ (Mooney, 1931), and plac-

ing 8 F atoms in general positions, and 4 Ba, 4 B, 4 F, and 4 O atoms in special positions, the following atomic coordinates were derived after matching fairly the observed and calculated intensity of each line:

- 4 Ba in 4(c) with $x = 0.182$, $y = 0.25$, $z = 0.162$.
 4 B in 4(c) with $x = 0.069$, $y = 0.25$, $z = 0.695$.
 4 F_I in 4(c) with $x = -0.072$, $y = 0.25$, $z = 0.595$.
 4 O in 4(c) with $x = 0.191$, $y = 0.25$, $z = 0.562$.
 8 F_{II} in 8(d) with $x = 0.080$, $y = 0.042$, $z = 0.816$.

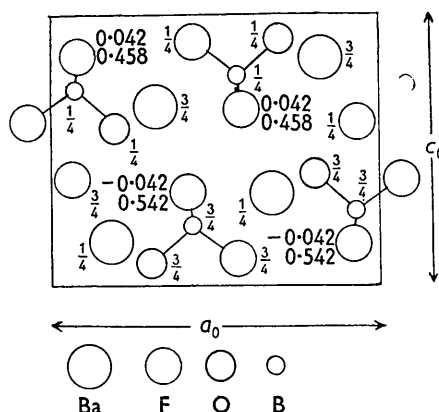
If the positions of F_I and O were interchanged, a fair discrepancy in the observed and calculated intensities of some important lines was observed. On the basis of the above coordinates the intensity of each line was calculated. For each calculated intensity, the polarization factor, multiplicity factor and absorption factor were taken into account. The absorption factor was calculated in the manner given in the *Internationale Tabellen* (1935). No correction was made, however, for the temperature factor. The values of $\sin^2 \theta_o$, $\sin^2 \theta_c$, I_o , I_c and the spacings are given in Table 1, in which some of the unobserved lines (such as 101, 121, 013, 200) are included to justify the correctness of the coordinates derived. Owing to heavy background scattering at low angles, the 101 and 200 reflexions, being very weak, were masked and could not be measured. The calculated d values of all the above unobserved lines are included in the table.

Discussion of the structure

The unit cell of the orthorhombic structure found for BaBOF₃, projected on its b face, is shown in Fig. 1.

Table 1

<i>d</i> (Å)	sin ² θ_o	sin ² θ_c	<i>hkl</i>	<i>I</i> _o	<i>I</i> _c
5.546	—	0.0193	101	—	12
4.296	—	0.0308	200	—	11
4.271	0.0326	0.0319	011	<i>m</i>	132
3.856	0.0399	0.0396	111	<i>mw*</i>	80
3.553	0.0470	0.0464	002	<i>vw</i>	3
3.392	0.0517	0.0511	210	<i>s*</i>	200
3.308	0.0546	0.0541	102	<i>ms</i>	145
3.067	0.0632	0.0627	211	<i>s</i>	183
2.810	0.0753	0.0744	112	<i>ms</i>	171
2.702	0.0815	0.0813	020	<i>m</i>	118
2.460	0.0983	0.0975	212	<i>w*</i>	36
2.431	—	0.1005	121	—	< 1
2.300	0.1124	0.1121	220	—	95
—	—	0.1121	103	<i>mw*</i>	69
2.192	0.1238	0.1232	400	<i>w</i>	11
2.183	—	0.1247	013	—	< 1
2.158	—	0.1276	022	—	< 1
2.100	0.1347	0.1348	401	<i>vs</i>	216
2.037	0.1432	0.1435	410	<i>mw</i>	100
1.914	0.1622	0.1622	321	<i>vw</i>	5
1.848	0.1740	0.1737	303	<i>m</i>	122
1.752	0.1936	0.1944	031	<i>mw</i>	82
1.721	0.2008	0.2021	131	<i>w</i>	9
1.667	0.2136	0.2136	114	<i>mw</i>	10
1.629	0.2240	0.2244	511	<i>w*</i>	29
1.588	0.2358	0.2367	214	<i>mw</i>	51
1.531	0.2538	0.2549	304	<i>mw*</i>	42
1.489	0.2681	0.2669	024	<i>mw</i>	40
1.472	0.2744	0.2746	124	<i>m</i>	106
1.462	0.2782	0.2772	600	<i>w</i>	10
1.421	0.2942	0.2949	133	<i>m</i>	116
1.411	0.2984	0.2977	105	<i>w</i>	14
1.382	0.3111	0.3103	015	<i>mw</i>	84
1.361	0.3207	0.3208	205	<i>w*</i>	16
1.352	0.3253	0.3250	040	<i>mw</i>	67
—	—	0.3236	602	—	5
1.320	0.3409	0.3411	215	<i>mw</i>	51
1.288	0.3580	0.3584	620	<i>mw</i>	59
1.266	0.3710	0.3714	042	<i>mw</i>	14
1.217	0.3992	0.3984	514	<i>w*</i>	23
1.199	0.4139	0.4132	405	<i>mw</i>	70
1.166	0.4332	0.4335	415	<i>w*</i>	61
1.150	0.4490	0.4484	206	<i>mw</i>	17
1.127	0.4681	0.4687	216	<i>mw</i>	50
1.100	0.4911	0.4916	434	—	32
—	—	0.4928	800	<i>mw</i>	48
1.081	0.5084	0.5072	316	<i>w*</i>	51
1.064	0.5255	0.5247	811	<i>mw</i>	47
1.052	0.5375	0.5392	802	—	14
—	—	0.5387	250	<i>w*</i>	60
1.031	0.5585	0.5609	534	<i>w*</i>	25.5
1.019	0.5725	0.5717	731	<i>w</i>	20
1.004	0.5895	0.5887	017	<i>w</i>	26
0.9137	0.7121	0.7120	551	<i>w</i>	11
0.9028	0.7293	0.7281	903	<i>w*</i>	28
0.8826	0.7626	0.7628	354	<i>mw</i>	75
0.8632	0.7979	0.7979	055	<i>w*</i>	70
0.8494	0.8239	0.8237	028	<i>vw</i>	5.6

Fig. 1. The unit cell of the orthorhombic structure of BaBOF₃ projected on the *b* face.

In this structure each boron atom is surrounded by three fluorine atoms (one F_I and two F_{II}) and one oxygen atom, forming a nearly regular tetrahedron. The tetrahedral angle is $110 \pm 15^\circ$. For each BOF₃ tetrahedron the B-F_I distance is 1.43 Å, and the B-F_{II} distance is 1.434 Å; the average B-F_I distance is 1.432 Å. This value agrees with that obtained by Hoard & Blair (1935) in the structure of RbBF₄ and NH₄BF₄, where the B-F distance is 1.43 Å. Similarly, the B-O distance is 1.435 Å, which is slightly lower than the value (1.44 Å) obtained by Schulze (1933) in the structure BaSO₄. The nearest Ba-O distance is 2.86 Å, the Ba-F_I distance is 2.84 Å and the Ba-F_{II} distance is 2.84 Å.

The author records his thanks to Prof. K. Banerjee and Prof. B. N. Srivastava for their keen interest in the work, and to Dr G. Mitra for encouragement and for supplying the sample for analysis.

References

- HESSE, R. (1948). *Acta Cryst.* **1**, 200.
 HOARD, J. L. & BLAIR, V. (1935). *J. Amer. Chem. Soc.* **57**, 1985.
Internationale Tabellen zur Bestimmung von Kristallstrukturen (1935), p. 576. Berlin: Borntraeger.
 JAMES, R. W. (1925). *Proc. Roy. Soc. A*, **109**, 598.
 LIPSON, H. (1949). *Acta Cryst.* **2**, 43.
 MOONEY, R. C. L. (1931). *Phys. Rev.* **37**, 1306.
 ROY, A. (1955). *Thesis*, Calcutta University.
 SCHULZE, E. R. (1933). *Naturwissenschaften*, **21**, 562.