KUNGLIGA SVENSKA

VETENSKAPSAKADEMIENS

HANDLINGAR

TREDJE SERIEN

NIONDE BANDET

STOCKHOLM
ALMQVIST & WIKSELLS BOKTRYCKERI-A.-B.
1931

II. Lattice Dimensions and Space-group of Braunite.

By

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With 4 figures in the text.

Literature on braunite from Långban:

1. 1888. G. FLINK, Mineralogiska notiser II. Stockholm. Bih. till K. Svenska Vet. Akad. Handl. Bd. 13, Avd. II, N:o 7, p. 34.
2. 1891. ——, Mineralogiska notiser III. Ibid. Bd. 16, Avd. II, N:o 4, p. 3.
3. 1910. ——, Bidrag till Sveriges mineralogi 2. Stockholm. Arkiv f. kemi, mineralogi etc. Bd. 3, N:o 35, p. 87.

Among the finds made during recent years at Långban are to be noticed well-formed crystals of braunite. These have been employed for the determination of the dimensions of the braunite lattice with the help of Laue photograph (Fig. 1), powder photograph (Fig. 2) and rotation photographs.

Rotation photographs were taken both round the *c*-axis and round two directions lying in [001], one corresponding to [010] and the other to $[1\bar{1}0]$ in the orientation of the braunite crystals which is used in GOLDSCHMIDT's angle-tables. Fe-radiation was employed.

Rotation axis = [001]

Layer line I	$c = 18{,}71$ Å
» » II	$= 18{,}55$
» » III	$= 18{,}74$
» » IV	$= 18{,}44$
» » V	$= 18{,}55$
» » VI	$= 18{,}44$
» » VII	$= 18{,}64$
	Mean value: $c = 18{,}58$ Å

Rotation axis = [010]

Layer line I	$a_1 = 13{,}37$ Å
» » II	$= 13{,}28$
» » III	$= 13{,}12$
» » IV	$= 13{,}42$
» » V	$= 13{,}22$
	Mean value: $a_1 = 13{,}28$ Å

Rotation axis = $[1\bar{1}0]$

Layer line I	$a_2 = 9{,}51$ Å
» » II	$= 9{,}39$
» » III	$= 9{,}28$
	Mean value: $a_2 = 9{,}39$ Å

As $9{,}39\sqrt{2} = 13{,}28$ the lattice whose c-edge = 18,58 Å and whose a-edge = 13,28 Å must be base-centred. As is shown below it is also centred on all three pinacoids.

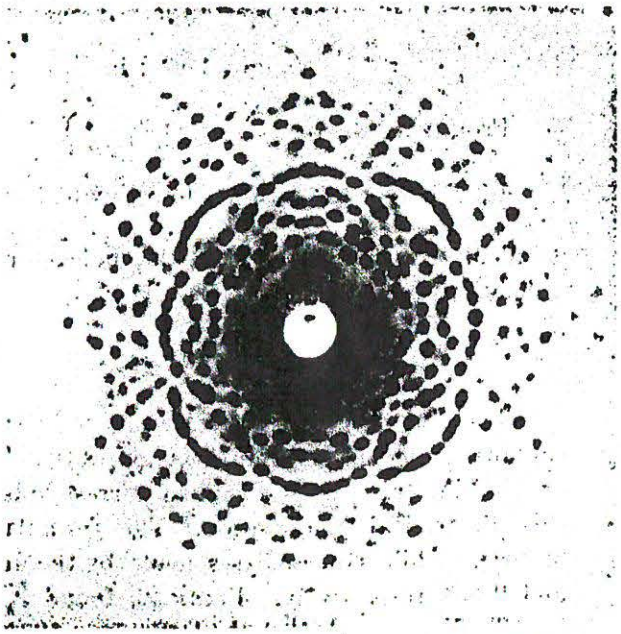


Fig. 1. Laue photograph of braunite on {001}.

From $c = 18{,}58$ Å and $a = 13{,}28$ Å we get

$$c : a_1 = 1{,}399 : 1 .$$

This lattice then corresponds to the axial ratio 1,4032 : 1 given in GOLDSCHMIDT's tables.

With the guidance of the above, approximately correct, lattice dimensions, more exact values of the dimensions are calculated from the powder photograph (Radius of the camera = 40 mm, thickness of the preparate = 0,2 mm). From the lines whose indices were determined with complete certainty

	$\sin^2\frac{\vartheta}{2}$
515	0,200
880	0,663

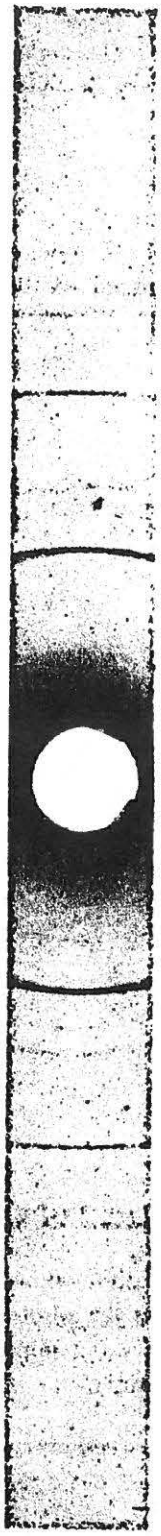


Fig. 2. Powder photograph of braunite. Fe-radiation.

are obtained:

$$\frac{\lambda^2}{4\,a_1^2} = 0{,}00518$$

$$\frac{\lambda^2}{4\,a_2^2} = 0{,}00261.$$

From these are calculated:

$$c = 18{,}93 \text{ Å}$$

$$a_1 = 13{,}43_5 \text{ »}$$

$$c : a_1 = 1{,}409 : 1.$$

From the identity:

$$10^{-24} \times a^2 c \times p = N \times \text{Mol. Weight} \times 1{,}65 \times 10^{-24}$$

is calculated, if $p = 4{,}72$[1] and the molecular weight $= 608{,}6$ (calculated for $3\,MnMnO_3 . MnSiO_3$):

$$N = 16{,}06.$$

The cell with $a = 13{,}43$ Å and $c = 18{,}93$ Å consequently contains 16 molecules $3\,MnMnO_3 . MnSiO_3$. The composition of the braunite from Långban corresponds very nearly to this theoretical composition. The formula requires 10,0 % of SiO_2, while two analyses made by the author gave 9,50 % and 9,49 % respectively. FLINK (2) found 9,89 %.

To discover whether the lattice $c = 18{,}93$ Å, $a = 13{,}43$ Å is centred on all three pinacoids the Laue photograph has been employed. The interference spots lying nearest to the central spot correspond to the form {911}.

From the formula

$$\lambda = \frac{2a^2 l}{c\left(h^2 + k^2 + \frac{a^2}{c^2} l^2\right)}$$

in calculated

$$\lambda_{911} = 0{,}23 \text{ Å}^2$$

which value fairly well corresponds to λ_{min} for the voltage employed. With the help of an index-field were construct-

[1] G. FLINK, (2), p. 8.

[2] For an exactly orientated crystal. Actually, the crystal being slightly inclined, wave-lengths down to 0,19 Å could be detected for {911}

ed all possible index combinations corresponding to reflections of the first order, *i.e.* with wave-lengths between 0,23 and 0,46 Å. Such a construction was made for index combinations with $l = 1$, 2 and 3.

$l = 1$:

Possible reflections between 0,23 Å and 0,46 Å (those italicized actually appear on the plate).

541	*551*				
631	641	651	661		
701	*711*	721	*731*	741	751
801	811	821	831	841	
901	*911*.				

No reflections occur from planes with mixed indices.

$l = 2$:

Possible reflections between 0,23 and 0,46 Å:

762	772							
852	872							
902	912	922	932	942	952	962	972	982
								992

10·1·2 10·3·2 10·5·2 10·7·2

11·0·2 11·1·2 11·2·2 11·3·2 11·4·2 11·5·2 11·6·2

12·1·2 12·3·2.

None of these reflections, which all (of the first order) have mixed indices, appear on the plate.

$l = 3$:

Possible reflections between 0,23 and 0,46 Å:

883

973 983

10·5·3 10·6·3 10·7·3 10·8·3 10·9·3 10·10·3

11·0·3 *11·1·3* 11·2·3 *11·3·3* 11·4·3 11·5·3 11·6·3 11·7·3 11·8·3
11·9·3 11·10·3 *11·11·3*

12·0·3 12·1·3 12·2·3 12·3·3 12·4·3 12·5·3 12·7·3 12·8·3

13·0·3 *13·1·3* 13·2·3 13·4·3 13·5·3 13·6·3 *13·7·3* 13·8·3

14·0·3 14·1·3 14·2·3 14·3·3 14·4·3 14·5·3 14·6·3 14·7·3

15·0·3 15·1·3 15·2·3 15·4·3 *15·5·3*.

No reflections with mixed indices are found.

Within the investigated area of the index-field lie 80 index-combinations with mixed indices. None of these are visible on the plate. From this one

should be justified in drawing the conclusion that the lattice is face-centred. In the following consideration, therefore, we reckon with a body-centred lattice (Γ_i') whose a-edge is

$$a_2 = \frac{a_1}{\sqrt{2}} = \frac{13{,}43_5}{\sqrt{2}} = 9{,}50 \text{ Å}$$

and whose c-edge is the same as in the surface-centred lattice, or 18,93 Å.

The axial ratio is

$$c : a_2 = 1.996 : 1.$$

This cell contains 8 molecules of $3\,MnMnO_3 . MnSiO_3$, *i.e.* 32 Mn^{++}, 24 Mn^{++++}, 8 Si^{++++}, and 96 O^{--}, or together 160 ions.

The quadratic form for this lattice is (Fe_α-radiation):

$$\sin^2 \frac{\vartheta}{2} = 0{,}01036\,(H^2 + K^2) + 0{,}00261\,L^2.$$

With these constants, the powder film was deciphered (Table 1).

Table 1.

Line no.	Intensity	mm	$\sin^2$ meas.	$\sin^2$ calc.	HKL
1	w—	32 6	0,0420	0,0418	004
2	w	44,2	0,0755	0,0753	213
3	w—	52,1	0,108	0,104	310
4	str	57,5	$0{,}124_5$	0,124	224
5	w—	62,3	0,146	0,145	314
6	m	66,9	0,167	0,166 0,167	400 008
7	m	73,9	0,200	0,200	325
8	w	85,5	$0{,}260_5$	0,259	431
9	w	93,2	0,304	0,304 0,305	417 309
10	str	98,1	0,332	0,331 0,333	440 408
11	w	107,3	0,387	0,387 0,388	437 419
12	w	110,4	0,406	0,407	613
13	w	113,8	0,427	0,427	541
14	m+	118,2	0,455	0,456	624
15	m	119,2	0,460	0,459	2 · 2 · 12
16	w	123,7	0,488	0,490	633
17	w+	125,4	0,500	0,498	448
18	w—	137,2	0,572	0,573	723
19	w	152,5	0,663	0,663	800
20	m	154,2	0,673	0,676	741 811
21	w	158,2	0,697	0,697	655
22	m	176,4	0,808	0,808	754

The determination of the indices on the rotation films was greatly hampered by the large dimensions of the lattice. It was, however, possible to effect a determination of the indices on the rotation film round c and in the equator on the rotation film round the edge (101) : (001) (face centred lattice). In Table 2 the results of these determinations are given in symbols corresponding to body-centred lattice.

Table 2.

Rotation axis = c.

L = 0:									
400 m	440 str	800 m	820 w	840 str					
L = 1:									
431 w+	521 w—	541 m	741, 811 m	831 m					
L = 2:									
332 w	512 w—	642 w—	822 m	752 m—					
L = 3:									
213 w	323 w	523 w	613 m	633 m	723 m	653 w			
L = 4:									
224 str	314 w—	624 str	714, 554 w	644 w	734 m	754 str			
L = 5:									
325 str	615 w	635 w—	725? w—	655 str					

Rotation axis = (101) : (001).

H ± K = 0:									
224 str	008 m	332 w	336 w	440 m+	$2\cdot2\cdot12_\beta$ w—	448_β w—	$2\cdot2\cdot12$ str	448 str—	$1\cdot1\cdot14$ w
							$0\cdot0\cdot16$ str	$3\cdot3\cdot14$ w	664 str

No observations are made that indicate that braunite has a lower symmetry than tetragonal holohedral (D_{4h}). The Laue photograph also shows full tetragonal symmetry. When the lattice is surface-centred, therefore, the only groups that can come into question are:

$$D_{4h}^{17},\ D_{4h}^{18},\ D_{4h}^{19} \text{ and } D_{4h}^{20}.$$

No reflections have been observed with complete certainty which exclude any of these space-groups. Therefore, if one wishes to try to determine the space-group, it is necessary to employ the criteria afforded by the *absence* of reflections, a method which will be justifiable in this case, where atoms reasonably occur in the most general positions.

The space-groups D_{4h}^{17-20} vary chiefly in respect to reflections of the type HHL. While D_{4h}^{17} and D_{4h}^{18} do not systematically exclude any kind of such reflections, in D_{4h}^{19} and D_{4h}^{20} HHL-reflections can only appear where

$$2H+L=4p \qquad (1)$$

Within the areas photographed a large number of reflections of the type HHL may occur:

H = 0:

Occurring:	004	008	0·0·16	(0·0·12 coincides with $2\cdot2\cdot12_{/3}$)
Absent :	006	0·0·10	0·0·14	

The reflections which occur satisfy the equation (1), while those which are absent do not.

H = 1:

On one rotation film occurs 1·1·14, which satisfies the equation (1), while on the other hand 118, 1·1·12 and 1·1·16, which do not satisfy the equation, are absent.

H = 2:

224 and 2·2·12 occur and satisfy the equation (1). 226, 228, 2·2·10, 2·2·14 and 2·2·16 are absent. Of these 228 and 2·2·16 satisfy the equation (1).

H = 3:

332, 336 and 3·3·14 occur. These satisfy the equation (1). 334, 338, 3·3·10 and 3·3·12 are absent. Of these 3·3·10 satisfies the equation (1).

H = 4:

440 and 448, which both satisfy the equation (1), occur. 442, 444, 446, 4·4·10 and 4·4·12 are absent. Of these 444 and 4·4·12 satisfy the equation (1).

H = 5:

No reflection observed with certainty.

H = 6:

664, which satisfies the equation (1), occurs. 660 and 662 are absent. Of these 660 satisfies the equation (1).

Thus all the observed reflections of type HHL satisfy the equation (1), *i.e.* are the only kind of HHL reflections which are permissible in D_{4h}^{19} and D_{4h}^{20}.

D_{4h}^{19} and D_{4h}^{20} are further distinguished from D_{4h}^{17} and D_{4h}^{18} in that they do not permit of other reflections of type HKO than such in which H and K are even numbers. Nor has any reflection HKO, where H and K are odd

numbers, been observed with certainty. A very faint reflection can be identified as 510, but it coincides with 440_β, for which reason it cannot be regarded as certain.

Conditions with regard to reflections of types HHL and HKO thus speak strongly in favour of one of the groups D_{4h}^{19} or D_{4h}^{20}.

Groups D_{4h}^{19} and D_{4h}^{20} are distinguished from each other as regards reflections of type HOL in that D_{4h}^{20} does not permit of reflections of this type in odd orders. No reflection HOL in odd orders has been observed, although a large number of such reflections may occur within the areas photographed. This regularity also speaks in favour of D_{4h}^{20}. To the extent that it has been possible to investigate it, therefore, the intensity distribution indicates D_{4h}^{20} as the most probable space group for braunite.

In group D_{4h}^{20} there are two kinds of eight-fold positions, four kinds of sixteen-fold positions, and one kind of twenty-four-fold positions. It would hardly be possible to deduce the arrangement of the 160 atoms that braunite contains. A certain interest attaches, however, to a comparison between the structure of synthetic Mn_2O_3 deduced by ZACHARIASEN[1] and the braunite cell. For Mn_2O_3 ZACHARIASEN found: Space group T^5, $z=16$, $a=9{,}41 \pm 0{,}01$ Å. The dimensions of braunite are: $a=9{,}50$ Å, $c=18{,}98$ Å, $z=32$ molecules $(^3/_4\,Mn + {}^1/_4\,Si)_2O_3$. The cell of braunite is thus very nearly double as high as that of manganic oxide and has an a-edge which only differs from that of manganic oxide by 0,09 Å. Geometrically the braunite cell is obtained by joining two manganic oxide cubes.[2]

The braunite cell contains double as many molecules R_2O_3 as Manganic oxide, in braunite however $^7/_8$ of the R atoms are Mn atoms, while $^1/_8$ are silicon atoms. Attempts have been made to utilise the atom parameters of manganic oxide with the object of finding the atom arrangement of braunite, but no certain results have been obtained.

* * *

The angles which have been measured on the crystals employed for X-ray investigations differ so slightly from those given in GOLDSCHMIDT's tables that it has not been considered necessary to calculate a new axial ratio. The following forms were observed for these crystals[3] (face-centred lattice):

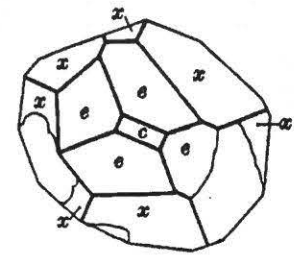
m	a	e	x	y	c
{100}	{110}	{101}	{311}	{313}	{001}

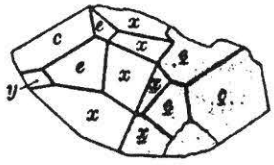
FLINK (2) had previously found the following forms for braunite crystals from Långban:

[1] Zeitschr. f. Krist. 67 (1928), p. 455.

[2] Compare »trirutiles». V. M. GOLDSCHMIDT, Geochem. Verteilungsgesetze der Elemente VI (1926), p. 18.

[3] Two of the crystals measured are reproduced in Figs. 3 and 4.





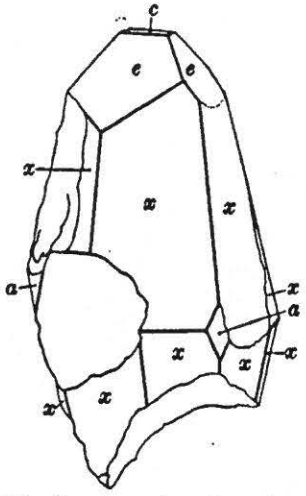


Fig. 3. Crystal of braunite.

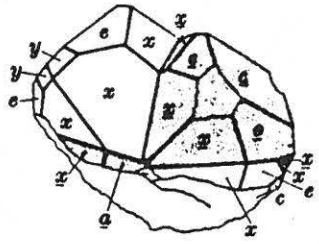


Fig. 4. Twin crystal of braunite.

l	*o*	*i*	*s*	*t*
{221}	{338}	{134}	{155}	{378}

Twinned crystals from Långban are mentioned and reproduced by FLINK (3). The symbol for the twinning plane is:

face-centred lattice	{112}
body-centred lattice	{102}