

The Crystal Structure of Pinnoite

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The space group of pinnoite has been determined unambiguously as $P4_2$ but the reflexions for $l = 0$, $h+k$ odd, are either absent or extremely weak showing that pseudo-symmetry is present, the space group conforming closely to $P4_2/n$. The structure, obtained by making use of this pseudo-symmetry and employing Patterson sections and projections, has been refined by successive two-dimensional syntheses and it is found that the B atoms are tetrahedrally surrounded by O atoms and that the Mg atom is at the centre of an octahedron of O atoms. This arrangement suggests that the chemical formula should no longer be written as $MgO \cdot B_2O_3 \cdot 3 H_2O$ but as $MgB_2O(OH)_6$. A surprising and noteworthy feature of the structure is the presence of long tubular voids running parallel to the c axis, an arrangement not normally found in borate compounds.

Introduction

Pinnoite is found associated with earthy boracite in the upper kainite layers at Stassfurt. The chemical formula is $MgO \cdot B_2O_3 \cdot 3 H_2O$ and the substance is classed by Groth (1908) as a hydrated metaborate. Stadler (1947) has cast doubt on this classification in an X-ray investigation which yielded the space group and cell dimensions. It was therefore felt worthwhile to determine the structure completely.

Experimental

The specimens used were kindly supplied by Dr G. F. Claringbull of the British Museum of Natural History. As had been found by previous investigators, it was impossible to isolate a crystal with developed faces, so firmly intergrown are the individual crystals. In fact even after careful examination under the microscope it was found impossible to obtain a crystal that did not exhibit at least slight twinning.

Using the best of the fragments, and employing $Cu K\alpha$ radiation, oscillation pictures and equi-inclination Weissenberg photographs of the zero layers and all obtainable c -axis upper layers were taken. Multiple-film techniques were employed and the relative intensities were estimated visually with the aid of a calibration strip produced with the X-ray set under carefully controlled conditions.

Unit cell and space group

The unit cell has the dimensions

$$a = 7.62 \pm 0.01, \quad c = 8.19 \pm 0.01 \text{ \AA}$$

and contains four molecules of $MgO \cdot B_2O_3 \cdot 3 H_2O$. The space group is $C_4^3-P4_2$ or $C_{4h}^2-P4_2/m$. This agrees with the results obtained by Stadler (1947), but the halving

of $h00$ which he observed is in fact not found if long exposures are taken. The calculated and experimentally obtained values of the density are both 2.29 g.cm.^{-3} .

Analysis

Because of the difficulty experienced in finding an untwinned single crystal, it was not found possible to differentiate experimentally between the two possible space groups. The use of intensity statistics (Wilson, 1949; Howells, Phillips & Rogers, 1950) yielded no positive result, showing that if the atomic arrangement was not in fact centrosymmetric it could not be far from it. Another approach to the problem had to be found.

If the space group is taken as $P4_2/m$, the presence of the mirror plane produces relationships between the coordinates of the atoms, reducing the number of independent coordinates. Because of this the z coordinates can be approximately determined using the method of Banerjee (1933). In addition, for $l = 0$, the $h+k$ odd spots are either absent or extremely weak, showing that the space group is almost $P4_2/n$. If the atomic arrangement in the c -axis projection is assumed to conform absolutely to this space group, an additional centre of symmetry is introduced at $x = \frac{1}{4}$, $y = \frac{1}{4}$, once again establishing relationships between the coordinates and reducing the number of independent variables. Using an extension of Banerjee's method to the special requirements of the space group, the x and y coordinates of the atoms can be approximately determined, allowing a rough test structure to be obtained. The above procedure was used but the structure it yielded refused to refine and it was therefore decided that the space group must be $P4_2$.

Since the required absences for $P4_2/n$ are so nearly satisfied, working in this space group with the origin taken at the centre of symmetry at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ from the fourfold axis eases the computational burden and

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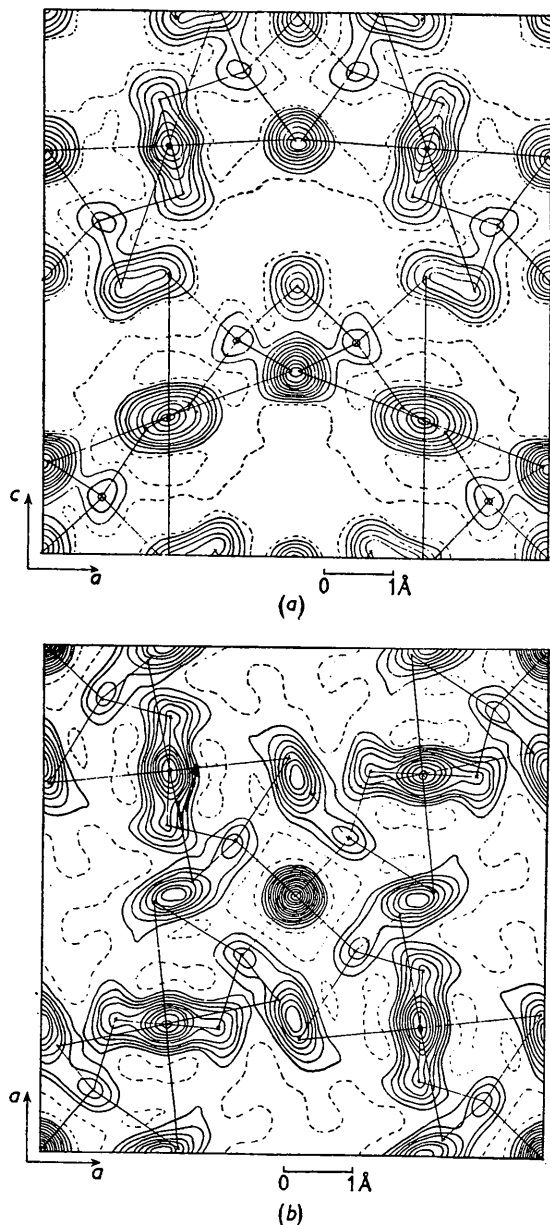


Fig. 1. Fourier projections of electron density (ρ) on (100), (b) on (001). Contours at intervals of $2 \text{ e.}\text{\AA}^{-2}$, the broken line being the $1 \text{ e.}\text{\AA}^{-2}$ contour.

should produce a structure different from the correct one in only minor respects. On this basis, and employing Patterson projections down the two principal axes and sections at $z = 0$ and $z = \frac{1}{2}$, a trial structure was obtained which located the magnesium atom at the origin with an octahedral arrangement of oxygen atoms round it. The boron atoms were found to be surrounded by tetrahedral arrangements of oxygens.

Optical transforms (Hughes & Taylor, 1953) were used in testing and improving the trial structure, which was then refined using successive Fourier and difference syntheses in both the a -axis and c -axis

projections. Fig. 1 shows the final two-dimensional electron-density projections obtained. The final reliability factors, R , defined as

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

for the $h = 0, l = 0$, and general reflexions were 0.19, 0.31 and 0.21 respectively. The overall reliability factor was 0.22.

The reflexions for $l = 0, h+k$ odd, have been ignored because of the assumption that the space group is $P4_2/n$; their calculated values are thus all zero. This explains why the value of R in the zone containing these reflexions is rather high. Furthermore, it complicates the problem of assessing the accuracy of the final atomic coordinates given in Table 1. Since

Table 1. Atomic coordinates

Origin on 4_2			
Atom	x/a	y/b	z/c
Mg	0.250	0.250	-0.250
B	0.393	0.383	-0.110
B'	0.107	0.117	-0.390
O ₁	0.000	0.000	0.010
O ₁	0.500	0.500	0.490
O ₂	0.339	0.238	0.013
O ₂	0.161	0.262	0.487
O ₃	0.488	0.302	-0.239
O ₃	0.012	0.198	-0.261
O ₄	0.228	0.488	-0.167
O ₄	0.272	0.012	-0.333

Denotes atom related by pseudo-centre of symmetry.

no estimate of the signs of these structure factors is possible, the conventional methods of determining accuracy (e.g. Cruickshank, 1949) break down and any figure quoted would be merely a guess. All the structure factors involved, however, are small so that their introduction into a Fourier synthesis should not alter the peak positions to any considerable extent.

Table 2 gives the F 's calculated from the final atomic coordinates compared with those experimentally observed, the latter having been put on an absolute basis initially by the method of Wilson (1942) and finally, for the zero-layer intensities, by multiplying by a factor $|F_c| \div |F_o|$. The absolute values for reflexions on upper layer lines were obtained by using reflexions common to these and to zero layer line photographs.

Description of the structure

The structure of pinnoite is illustrated in Fig. 2. It exhibits no marked layer or chain structure, a fact which was expected since no features characteristic of these types of arrangement (Kenyon & Taylor, 1953) were observed in weighted reciprocal lattice drawings. For convenience of description we may single out the $\text{H}_6\text{B}_2\text{O}_7$ group, which is linked as shown:

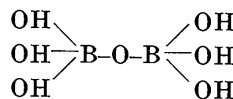


Table 2. *Measured and calculated values of the structure factors*

hkl	F _o	F _c	hkl	F _o	F _c	hkl	F _o	F _c	hkl	F _o	F _c	hkl	F _o	F _c	hkl	F _o	F _c
000	-	312	002	35	35	091	7	9	214	27	-28	414	21	-19	614	8	-4
010	3	-	004	74	87	092	11	13	224	43	47	424	20	14	624	22	25
020	40	40	006	6	-3	093	7	9	234	14	8	434	9	-5	634	12	4
030	4	-	008	48	55	094	7	-8	244	15	15	444	13	7	644	12	-10
040	74	93	00,10	11	9				254	18	16	454	<3	0	654	7	-4
050	2	-				111	21	-29	264	29	33	464	11	7	664	13	17
060	12	1	011	5	-3	121	34	-38	274	7	5	474	3	3			
070	3	-	012	38	43	131	62	-81	284	17	20	484	13	18	655	<2	-1
080	40	51	013	40	35	141	6	-2									
090	3	-	014	8	13	151	30	-35	255	10	4	455	9	14	616	8	10
			015	3	-3	161	11	9							626	20	25
110	43	-54	016	<3	-	171	36	-41	266	14	21	466	16	25	636	<3	1
120	2	-	017	5	-4	181	11	13							646	17	29
130	33	33	018	4	4	191	10	-13	277	3	-6	511	4	-4	656	3	5
140	3	-	019	15	-16							521	14	-15			
150	14	14	01,10	2	10	112	16	-13	311	21	-14	531	32	-46	711	15	-9
160	2	-				122	23	22	321	36	-41	541	6	-4	721	20	-21
170	27	28	021	9	2	132	38	44	331	35	-33	551	12	-14	731	33	-35
180	4	-	022	22	22	142	2	2	341	28	-26	561	8	-6	741	4	5
190	9	-5	023	38	37	152	33	38	351	13	13	571	32	-44	751	6	2
			024	38	36	162	18	13	361	22	-21	581	8	12	761	5	6
210	2	-	025	43	43	172	25	25	371	27	-27						
220	9	-1	026	20	18	182	9	4	381	3	6	512	23	-21	712	7	1
230	2	-	027	34	-36	192	4	-2	391	4	6	522	18	22	722	4	2
240	12	14	028	24	19							532	8	7	732	16	-16
250	5	-	029	15	9	113	24	-29	312	21	13	542	17	14	742	10	-11
260	16	14	02,10	10	13	123	28	28	322	11	-11	552	3	3	752	2	1
270	4	-				133	34	-40	332	31	-28	562	9	4	762	<2	-2
280	18	25	031	33	-28	143	34	35	342	33	-30	572	10	8			
290	<2	-	032	21	-20	153	24	-26	352	26	25	582	6	-8	713	21	-21
			033	16	17	163	8	4	362	<3	2				723	14	-17
310	10	-7	034	16	-14	173	35	-41	372	14	-10	513	8	-11	733	15	-13
320	2	-	035	21	-11	183	7	8	382	10	-6	523	23	17	743	2	4
330	6	0	036	19	-14	193	10	-9	392	5	10	533	36	-46	753	8	-8
340	4	-	037	19	20							543	24	28	763	11	-18
350	40	39	038	21	21	114	19	22	313	12	-5	553	21	-25			
360	4	-	039	3	6	124	30	22	323	17	12	563	3	-3	714	21	18
370	12	5	03,10	4	3	134	35	-31	333	38	-41	573	21	-25	724	10	-11
380	3	-				144	6	5	343	18	17	583	8	15	734	5	0
390	5	-4	041	17	-13	154	22	21	353	11	-7				744	11	-15
			042	42	45	164	18	10	363	15	-16	514	39	48	754	7	-11
410	3	-	043	5	-4	174	19	-19	373	13	-2	524	17	15			
420	30	30	044	50	58	184	5	-3	383	2	4	534	14	-10	755	2	-6
430	5	-	045	13	-15	194	7	11				544	4	0			
440	56	62	046	6	-4				314	10	5	554	16	17	717	5	10
450	7	-	047	6	1	155	21	-21	324	17	-15	564	18	18	727	5	3
460	9	-2	048	21	20				334	20	-20	574	8	-7			
470	3	-	049	10	-12	166	5	-11	344	7	-7				811	11	-13
480	17	16							354	13	-13	515	15	-17	821	11	12
			051	3	3	177	8	-6	364	7	-3	525	20	-23	831	18	+20
510	34	-30	052	4	-4				374	17	-19	535	25	-23	841	11	-9
520	3	-	053	25	28	211	27	29	384	8	-2	545	<3	2	851	5	-4
530	13	8	054	10	10	221	19	15				555	14	-16			
540	4	-	055	4	1	231	25	-25	355	6	-11	565	7	1	812	19	-14
550	27	-24	056	18	20	241	12	-10				575	8	-12	822	29	48
560	3	-	057	5	-1	251	6	3	366	<3	-8				832	4	-3
570	8	1	058	12	-5	261	13	-14				566	<2	-5	842	21	23
580	2	-	059	8	-14	271	19	15	411	7	5				852	2	7
						281	10	-7	421	5	4	611	9	-10			
610	3	-	061	14	-13	291	9	9	431	8	-2	621	8	4	813	14	16
620	3	-1	062	25	19				441	9	-3	631	3	-3	823	5	-5
630	3	-	063	13	12	212	11	-10	451	15	16	641	8	-6	833	3	5
640	25	-28	064	<3	-5	222	49	-55	461	15	15	651	7	4	843	11	-11
650	4	-	065	14	11	232	16	16	471	14	16	661	12	8	853	2	8
660	6	8	066	18	21	242	40	45	481	2	4	671	1	-2			
670	4	-	067	17	20	252	10	-10							814	3	2
			068	6	4	262	4	4	412	11	0	612	3	-5	824	17	20
710	4	4				272	<3	0	422	47	60	622	9	10	834	2	-3
720	4	-	071	5	1	282	19	27	432	22	19	632	9	3	844	10	13
730	9	-8	072	16	-16	292	6	-10	442	38	40	642	26	32	854	1	-1
740	3	-	073	6	-1				452	20	15	652	3	2			
750	14	14	074	7	-12	213	23	23	462	40	43	662	18	22	911	4	-2
760	4	-	075	8	8	223	15	-11	472	4	6	672	2	-3	921	3	-2
			076	<3	3	233	18	-21	482	13	7				931	13	-22
			077	5	5	243	18	13				613	21	17			
810	3	-				253	6	-8	413	4	6	623	21	26	912	12	-13
820	19	22	081	12	-11	263	8	1	423	14	-19	633	8	7	922	6	10
830	3	-				273	17	-19	433	13	-4	643	3	-4	932	10	19
840	15	11	082	11	8	283	9	-12	443	12	-9	653	8	0			
850	2	-	083	10	-12	293	7	-13	453	3	3	663	2	-1	913	6	-11
			084	14	14				463	<3	0	673	11	-21	923	3	-3
910	16	-14	085	10	-18				473	14	-13						
920	-	-	086	4	-1				483	<2	3						
930	3	-2															

Each H_3BO_4 group is tetrahedrally arranged and the OH groups link on to magnesium atoms.

Taking the magnesium atom as the reference point of the structure, we find that each magnesium is surrounded by an octahedral arrangement of OH groups, each of which link to boron atoms. The structure, in fact, appears to bear out the arguments presented by

Stadler (1947), who suggested, on the basis of the behaviour exhibited under dehydration, that the water must be present in the form of OH groups. The chemical formula would appear to be more suitably given in the form $MgB_2O(OH)_6$ rather than in the usual manner as $MgO \cdot B_2O_3 \cdot 3H_2O$.

One unusual and interesting feature of the structure

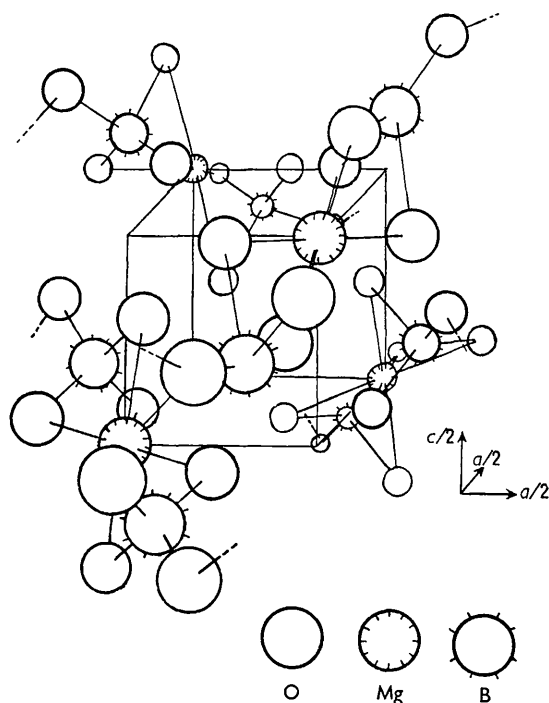


Fig. 2. The structure of pinnoite with bonds shown. The relative sizes of the atoms give an indication of the magnitudes of their y co-ordinates.

is the presence of long tubular voids parallel to the c axis. Close packing might well have been expected since the borate ions are not cross-linked. As far as the present authors can discover, such a feature has

Table 3. *Interatomic distances*

Octahedron		Tetrahedron		Other distances	
Mg-O ₂	2.06 Å	B-O ₁	1.46 Å	O ₁ -O ₂ *	3.15 Å
-O ₃	2.04	-O ₂	1.54	-O ₃ *	2.68
-O ₄	2.12	-O ₃	1.42	-O ₆ *	3.50
O ₂ -O ₃	2.93	-O ₄	1.56	O ₂ -O ₂ *	3.11
-O ₃	2.87	O ₁ -O ₂	2.35	-O ₃ *	3.50
-O ₄	2.95	-O ₃	2.41	-O ₄ *	3.36
-O ₄	2.96	-O ₄	2.44	O ₃ -O ₄ *	2.85
O ₃ -O ₄	2.76	O ₂ -O ₃	2.40	O ₄ -O ₄ *	3.67
-O ₄	3.11	-O ₄	2.53		
		O ₃ -O ₄	2.50		

Denoted atom related by pseudo-centre of symmetry.

* Denotes atom in neighbouring molecule.

not been reported before in borates, and the reason for it is not clear.

The interatomic distances and bond angles are listed in Tables 3 and 4. From these it will be seen that the

Table 4. *Bond angles*

O ₂ -Mg-O ₃	91°	O ₁ -B-O ₂	103°
O ₂ -Mg-O ₃	89	O ₁ -B-O ₃	113
O ₂ -Mg-O ₄	89	O ₁ -B-O ₄	108
O ₂ -Mg-O ₄	90	O ₂ -B-O ₃	108
O ₃ -Mg-O ₄	83	O ₂ -B-O ₄	110
O ₃ -Mg-O ₄	97	O ₃ -B-O ₄	113

magnesium groups are very close to the perfect octahedron, the Mg-O distances being in agreement with those already given in the literature. The bond angles of the tetrahedral group are as expected, but the B-O distances are not all the same. The B-O₂H and B-O₄H distances agree with the values given for this bond in datolite (Ito & Mori, 1953) and the other two agree with the B-O distances in BO₄ tetrahedra. This fact, together with the short O₁-O₃* distance, may indicate that the hydrogen is not directly associated with the O₃* atom but takes part in hydrogen bonding between O₁ and O₃*.

We wish to express our thanks to Dr Claringbull for supplying the material for this investigation. One of us (F. P.) is also indebted to The Caird Trust for the award of a scholarship which made the carrying out of this research possible.

References

- BANERJEE, K. (1933). *Proc. Roy. Soc. A*, **141**, 188.
 CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
 GROTH, P. (1908). *Chemische Krystallographie*, vol. 2. Leipzig: Engelmann.
 HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.
 HUGHES, W. & TAYLOR, C. A. (1953). *J. Sci. Instrum.* **30**, 105.
 ITO, T. & MORI, H. (1953). *Acta Cryst.* **6**, 24.
 KENYON, P. A. & TAYLOR, C. A. (1953). *Acta Cryst.* **6**, 745.
 STADLER, H. P. (1947). *Miner. Mag.* **28**, 26.
 WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 152.
 WILSON, A. J. C. (1949). *Acta Cryst.* **2**, 318.