

*The magnesium aluminium borosilicates: kornerupine  
and grandidierite*

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*Summary.* A new occurrence of kornerupine in the skarn zone at Mautia Hill, Tanganyika, has yielded unit-cell dimensions  $a$  16.100,  $b$  13.767,  $c$  6.735 Å, density 3.297, and composition  $\text{Na}_{0.01}\text{Mn}_{0.01}\text{Ti}_{0.02}\text{Mg}_{3.69}\text{Fe}_{0.37}^{\text{III}}\text{Al}_{6.36}\text{Si}_{3.71}\text{B}_{0.41}\text{O}_{21.75}(\text{OH})_{0.25}$ . The unit-cell clearly contains 88 anions rather than the 86 proposed previously. Grandidierite from Sakatelo, Madagascar, has unit-cell dimensions  $a$  10.978,  $b$  10.335,  $c$  5.760 Å, space group  $Pna2_1$  or  $Pnam$ , density 2.976, and composition  $\text{Fe}_{0.12}^{\text{II}}\text{Ti}_{0.01}\text{Mg}_{0.88}\text{Fe}_{0.03}^{\text{III}}\text{Al}_{3.00}\text{Si}_{1.00}\text{B}_{0.97}\text{O}_{9.00}$ . The unit-cell contains 36 anions and the structure appears to involve  $\text{AlO}_6$  chains parallel to the  $c$ -axis.

**K**ORNERUPINE and grandidierite are the only two minerals known to have compositions lying essentially within the tetrahedron  $\text{MgO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$  and it is therefore convenient to present at once some new data that have recently been obtained for both minerals.

*Kornerupine*

In the course of examining a collection of specimens from Mautia Hill, Tanganyika, a pink nodular aggregate, some 10 ml in volume, was identified as kornerupine. So far a single nodule has been found in association with högbomite- and sapphirine-bearing assemblages at the junction of dolomite marble and quartz-yoderite-kyanite-talc-schist (McKie, 1959, 1963*a*, 1963*b*); these assemblages have not yet been studied in detail in the field and it is the purpose of the present communication merely to describe the mineralogy of the new occurrence and to make some emendations to the crystallography and crystal chemistry of kornerupine.

*Unit-cell dimensions and space group.* Measurement of zero layer  $a$ -axis and of zero, first, and second layer  $b$ -axis Weissenberg photographs taken on  $\text{CuK}\alpha$  radiation served to determine the unit-cell dimensions approximately as  $a$  16.02,  $b$  13.86,  $c$  6.78 Å. Refinement of the unit-cell dimensions was achieved by the back-reflection oscillation technique of Kelsey and McKie (1964) using an internal silicon standard. With the crystal set to oscillate about its  $b$ -axis the 20,0,0 reflection for  $\text{CuK}\alpha_2$

was observed to be exactly coincident with the silicon 642 ring for  $\text{CuK}\beta$  and the 008 reflections for  $\text{CuK}\alpha_1$  and  $\text{CuK}\alpha_2$  to lie on either side of the silicon 711, 551 ring for  $\text{CuK}\beta$  radiation. With the crystal remounted and set to oscillate about its  $a$ -axis the 0,16,0 reflections for  $\text{CuK}\alpha_1$  and  $\text{CuK}\alpha_2$  were observed to straddle the silicon 620 ring for  $\text{CuK}\alpha_1$  radiation. Measurement, with a travelling microscope, of films exposed at the oscillation ranges appropriate for recording the chosen reflection on either side of the centre of the film enabled accurate unit-cell dimensions to be determined for kornerupine from Mautia Hill as  $a$  16.100,  $b$  13.767,  $c$  6.735 Å (all to  $\pm 0.002$  Å).

Inspection of the four Weissenberg photographs led to the determination of the diffraction symbol as  $mmmC.c$ ; the zero layer  $b$ -axis photograph reveals the certain presence of the hitherto unrecognized  $c$ -glide normal to the  $b$ -axis. Three space groups are consistent with the observed diffraction symbol:  $Cmc2_1$ ,  $C2cm$  ( $Ama2$ ), and  $Cmcm$ . Uhlig (1910) found the symmetry of etch figures to be  $mmm$  and Girault (1952) found the symmetry of etch figures, produced in fused  $\text{Na}_2\text{CO}_3$ , to be consistent with the presence of a mirror plane perpendicular to the  $c$ -axis. Neither of these observations, however, provides a complete determination of the point group; kornerupine is probably holosymmetric, space group  $Cmcm$ , but may have the lower symmetry of space group  $Cmc2_1$  or  $C2cm$ .

The discovery of a glide plane has necessitated reorientation of the axes of kornerupine to bring the space group into the conventional form. The unit-cell defined by Gossner and Mussgnug (1928) and used by Hey, Anderson, and Payne (1941) and Girault (1952) has  $b > a > c$ ; it is related to the new unit-cell by interchange of  $a$  and  $b$ , indices based on the old cell being transformed to those for the new unit-cell by operation of the matrix  $010/100/001$ .<sup>1</sup>

*X-ray powder pattern.* The powder pattern, recorded on a diffractometer trace taken with  $\text{CuK}\alpha$  radiation at 2.6 cm per degree of  $2\theta$  over the range  $8^\circ < 2\theta < 68^\circ$ , is shown in the second and third columns of table I. The pattern was indexed by comparison with a list of sorted  $d$ -spacings calculated from the accurate unit-cell dimensions given above, account being taken of the relative intensities known from the four Weissenberg photographs, which give information about  $0kl$ ,  $h0l$ ,  $h1l$ , and  $h2l$  reflections; indexing has not been attempted for  $d$ -spacings less than 2 Å. The three strongest lines are 2.639 (1), 3.03 (2), 2.118 (3).

<sup>1</sup> Weissenberg photographs of kornerupine from Waldheim (Min. Mus. Camb. 19356) confirm the diffraction symbol  $mmmC.c$ .

TABLE I. X-ray powder data for kornerupine

Quebec		Mautia		<i>hkl</i>
<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>	
10.4	8	10.5	w	110
7.94	4	8.06	vw	200
6.83	7	6.86	w	020
4.06	1	4.14	vw	221
3.99	6	4.03	vw	400
		3.70	vw	131
3.42	7	3.45	w	040
3.34	9	3.37	s	002
3.00	10	3.03	vs	022
2.87	4	2.85	vw	511, 222
		2.79	vw	312
2.69	5	2.716	w	150
2.61	10	2.639	vvs	530
2.387	6	2.410	w	042
2.273	5	2.299	vw	512, 060
2.117	5	2.137	w	023
2.095	8	2.118	s	640
		2.096	mw	550
2.069	6	2.079	vw	532
		2.017	vw	800
1.976	5	2.000	vw	
1.854	4	1.883	vw	
1.795	4			
		1.774	vw	
		1.720	vw	
		1.711	vw	
1.670	8	1.685	mw	
		1.672	vw	
1.590	6	1.610	vw	
1.533	7	1.549	w	
1.488	9	1.503	m	
1.436	6	1.456	vw	
1.406	8	1.420	w	

The photographic data for Quebec kornerupine are quoted from Girault (1952), who reported visually measured intensities on a scale 10–1. The data for Mautia kornerupine are derived from measurement of a diffractometer trace; intensities, from peak-height measurements, are reported on a decreasing scale, vvs, vs, s, ms, m, mw, w, vw.

The powder pattern reported by Girault (1952) for yellow kornerupine from Lac Ste-Marie, Quebec, is correlated with the pattern of the Mautia material in table I; intensities show general correspondence, but the Quebec *d*-spacings are consistently smaller in conformity with the smaller unit-cell determined by Girault from single crystal data. Revision of the diffraction symbol, the availability of highly accurate unit-cell dimensions, and greater knowledge of relative intensities from

single crystal photographs have enabled some modifications to be made to Girault's indexing.

*Optics.* Kornerupine from Mautia Hill has refractive indices close to the upper end of the range given by Girault (1952),  $\alpha$  1.675,  $\beta$  1.695, and  $\alpha$  1.710 (all  $\pm 0.003$ ), with  $-2V \simeq 50^\circ$ .

*Unit-cell contents.* The chemical composition of Mautia kornerupine, determined by Mr. J. H. Scoon, is set down in table II. Boron was

TABLE II. Chemical composition of kornerupine from Mautia Hill, Tanganyika

SiO <sub>2</sub>	29.91	Be	35
TiO <sub>2</sub>	0.16	Ga	22
Al <sub>2</sub> O <sub>3</sub>	43.45	Cr	5
Fe <sub>2</sub> O <sub>3</sub>	3.98	V	—
FeO	nil	Sn	22
MnO	0.05	Li	120
MgO	19.96	Ni	2
CaO	nil	Co	—
Na <sub>2</sub> O	0.03	Se	—
K <sub>2</sub> O	0.02	Zr	—
H <sub>2</sub> O <sup>+</sup>	0.30	Cu	100
H <sub>2</sub> O <sup>-</sup>	0.02	Y	—
B <sub>2</sub> O <sub>3</sub>	1.92	Sr	—
	<u>99.80</u>	Ba	—
		Rb	—

Analyst: J. H. Scoon. Trace elements (quoted in ppm) determined spectrographically by Dr. S. R. Nockolds and Mr. R. Allen. A dash indicates concentration below the limit of sensitivity.

determined by distillation of methyl borate, followed by titration of boric acid with NaOH (Chapin's method). FeO was determined in this material, which proved to be more readily soluble than kornerupine is usually reported to be, by solution in HF in the presence of NH<sub>4</sub>VO<sub>3</sub>, followed by titration of excess VO<sub>3</sub><sup>-</sup>; no Fe<sup>2+</sup> was found on titration and it was observed that the solution did not go blue as it normally does in the presence of even very low concentrations of Fe<sup>2+</sup>. For showing that the content of fluorine is below the limit of spectrographic detection and for the trace element analysis shown on table II, I have to thank Dr. S. R. Nockolds.

Estimation of the specific gravity as 3.29<sub>7</sub>, by measurement of the loss in weight of a mercury-in-glass mass immersed in Clerici's solution in which some grains of the mineral remained in suspension after being centrifuged for 10 minutes, taken together with the unit-cell dimensions and chemical composition led to an oxygen content of 87.6 atoms per

unit-cell for Mautia kornerupine, a value that is unlikely to be inaccurate by more than  $\pm 0.5$  and forces the conclusion that the true anion content of the unit-cell is 88 atoms. That the number of oxygen atoms in the unit-cell should be a multiple of four is supported by the space-group determination: the minimum multiplicity of special positions in each of

TABLE III. Contents of a quarter of the unit-cell in kornerupine, calculated to  $\sum (\text{O,OH}) = 22$

	1	2	3	4	5	6	7	8	9
B <sup>3+</sup>	0.411	0.757	0.709	0.611	0.778	0.550	0.666	0.771	0.777
Si <sup>4+</sup>	3.714	3.791	3.792	3.857	3.770	3.732	3.922	3.867	3.801
P <sup>5+</sup>	—	0.010	0.009	—	—	—	—	—	0.013
Al <sup>3+</sup>	6.359	6.038	6.212	5.604	6.333	6.005	5.427	5.596	6.216
Cr <sup>3+</sup>	—	0.006	0.004	—	—	—	—	—	—
Fe <sup>3+</sup>	0.372	0.040	0.085	0.314	—	—	0.310	—	—
Mg <sup>2+</sup>	3.694	2.779	2.337	3.901	3.061	3.986	3.373	4.172	2.091
Ti <sup>4+</sup>	0.015	0.018	0.048	—	—	—	—	—	0.043
Fe <sup>2+</sup>	—	0.893	0.956	0.508	0.733	0.533	0.979	0.265	1.315
Mn <sup>2+</sup>	0.005	—	—	—	—	—	—	—	0.009
Ca <sup>2+</sup>	—	0.008	0.024	—	—	—	—	0.068	—
Na <sup>+</sup>	0.007	0.019	0.032	—	—	0.272	0.399	0.328	0.175
K <sup>+</sup>	0.003	—	—	—	—	0.098	—	0.013	—
OH <sup>-</sup>	0.248	0.811	0.888	0.169	—	—	—	0.083	0.575
O <sup>2-</sup>	21.752	21.189	21.112	21.831	22.000	22.000	22.000	21.917	21.425

1. Mautia Hill, Tanganyika (table I).
2. Green variety, Lac Ste-Marie, Quebec (Girault, 1952).
3. Yellow variety, Lac Ste-Marie, Quebec (Girault, 1952).
4. Biaxial variety, Ceylon (analysis I of Hey *et al.*, 1941).
5. Pseudoniaxial variety, Ceylon (anal. II, Hey *et al.*, 1941).
6. Pseudoniaxial variety, Ceylon (anal. III, Hey *et al.*, 1941).
7. Waldheim, Saxony (anal. IV, Hey *et al.*, 1941).
8. Itrongay, Madagascar (Lacroix, 1922, corrected as anal. V of Hey *et al.*, 1941).
9. Port Shepstone, Natal (de Villiers, 1940, corrected as anal. VI of Hey *et al.*, 1941).

the three possible space groups is four. The conclusion of Hey *et al.* (1941) that the unit-cell contains only 86 anions can no longer be accepted. The distinction between 86 and 88 anions requires considerable precision in the determination of density and unit-cell dimensions and the use of highly accurate complete chemical analyses; unit-cell dimensions were determined by Hey *et al.* merely by measurement of uncalibrated photographs and their analyses had to be made on samples of less than 0.1 g. Vogt (1947) has already expressed a preference, although not on compelling evidence, for an anion content of 88, which he found to give relatively 'simple formulae'.

The contents of the asymmetric unit, one-quarter of the unit-cell, calculated to 22 anions from all available kornerupine analyses, with

the exception of five early incomplete analyses rejected by Hey *et al.* (1941), are shown in table III, where cations are listed in order of increasing radius. The range of variation of kornerupine compositions is shown in terms of the system  $(\text{Mg,Fe})\text{O}-(\text{Al,Fe})_2\text{O}_3-\text{SiO}_2$  in fig. 1. The

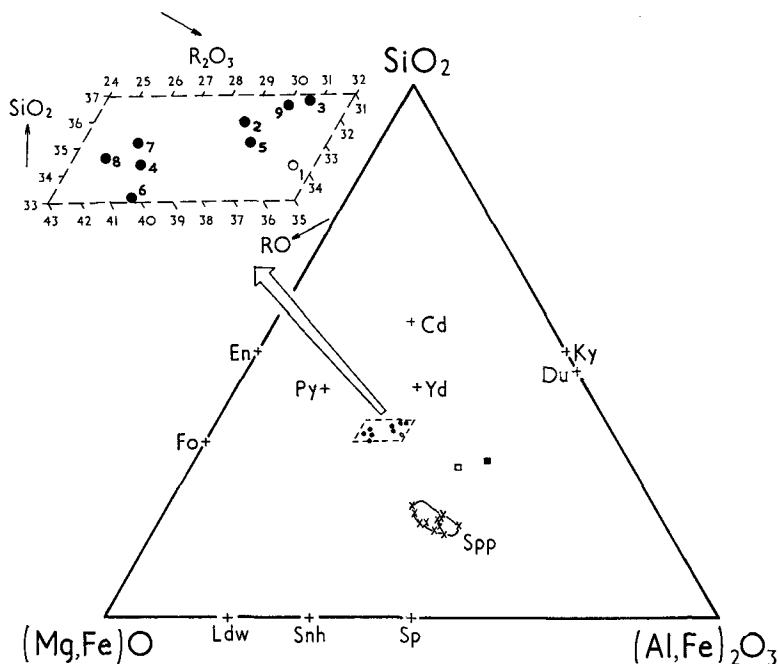


FIG. 1. Projection of kornerupine and grandierite compositions on the triangle  $(\text{Mg,Fe})\text{O}-(\text{Al,Fe})_2\text{O}_3-\text{SiO}_2$ . Circles: kornerupine,  $\circ$  Mautia (table II),  $\bullet$  2 Quebec (green), 3 Quebec (yellow), 4 Ceylon (normal), 5 Ceylon (uniaxial), 6 Ceylon (uniaxial), 7 Saxony, 8 Madagascar, 9 Natal (2-9 numbered as columns of table III). Squares: grandierite,  $\square$  Madagascar (new analysis, column 1 of table V),  $\blacksquare$  Madagascar (column 2 of table V). En, enstatite. Fo, forsterite. Ldw, ludwigite. Snh, sinhalite. Sp, spinel. Du, dumortierite. Ky, kyanite. Cd, cordierite. Yd, yoderite. Py, pyrope. Spp, sapphirine (compositions shown by crosses, after McKie, 1963b).

new analysis of kornerupine from Mautia Hill (column 1) has the highest Al and by far the lowest B content and is exceptional in having its small iron content completely oxidized; attention has previously been drawn (McKie, 1963b) to the high oxidation ratios and low iron contents of a number of minerals from Mautia Hill. In projection on the triangle  $(\text{Mg,Fe})\text{O}-(\text{Al,Fe})_2\text{O}_3-\text{SiO}_2$  the new material lies (fig. 1) particularly

close, in relation to other analysed kornerupines, to the intersection of the pyrope–corundum and cordierite–spinel joins. The total number of cations in the asymmetric unit varies between 14.2 and 15.2, increasing with decreasing OH content and exceeding 15.0 only in analyses 6, 7, and 8, where the alkali content is high; it is therefore suggested that the asymmetric unit contains sixteen cation sites, two of which are only partially filled. The boron content is always less than one and therefore boron presumably lies on fourfold sites, where it substitutes for silicon. Since  $\sum (B + Si + P)$  lies between four and five, there must be at least five fourfold sites occupied by B, Si, P, and Al, probably in a disordered manner, although it must be borne in mind that boron may be concentrated on a single special position, occupied by (B, Si). The number of Al atoms not certainly in fourfold positions lies between five and six; the sum of the excess of such Al atoms over five and all the remaining cations lies between 4.2 and 5.2. It is therefore suggested that the excess Al and all cations larger than  $Al^{3+}$  lie on four completely filled sixfold sites and on two partially filled eightfold, or relatively loosely coordinated sixfold sites. The contents of the asymmetric unit may then be represented as:  $R_{<2}^{[8,6]}R_4^{[6]}Al_5^{[6,4]}(Al, Si)_4^{[4]}(Si, B)_1^{[4]}(O, OH)_{22}$ , where  $R^{[8]}$  represents the larger cations and must in some cases include ions no larger than  $Mg^{2+}$ , and  $R^{[6]}$  contains principally  $Mg^{2+}$ , invariably includes some  $Al^{3+}$ , and may include ions as large as  $Fe^{2+}$ .

*Paragenesis and stability.* Since Vogt (1947) discussed the paragenesis of kornerupine in sapphirine–cordierite-bearing assemblages at Fiskenaeset in Greenland, in the granulites of Waldheim, Saxony, in sapphirine-bearing sakénites at Itrongay, Madagascar, and in quartz–tourmaline–biotite–garnet–grandidierite rocks at Port Shepstone, Natal, the mineral has been described from biotite–tourmaline–orthoclase gneisses near Lac Ste-Marie, Quebec (Girault, 1952), and from spinel–corundum–sapphirine–sillimanite–biotite schists at Rannu in Uttar Pradesh (Murthy, 1954). Vogt (1947) considered it to be formed in rocks of suitable boron content metamorphosed in what he termed the sillimanite–gedrite–gneiss facies, perhaps better regarded as a possible subdivision of the granulite facies, while Girault (1952) supposed it, from its constant association with tourmaline, to be invariably a product of boron metasomatism of rocks of appropriately aluminous composition. The new occurrence at Mautia Hill adds little to knowledge of the metamorphic status of kornerupine; only a single nodule has been found and that contains inclusions of blue prismatic corundum and of talc and is sheathed in an optically positive, magnesian chlorite. The nodule

certainly came from close to the junction between dolomite marble and quartz-yoderite-kyanite-talc schist, where högbomite-enstatite-hornblende-chlorite-dolomite assemblages (McKie, 1963*a*) and enstatite-hornblende-sapphirine assemblages (McKie, 1963*b*) are also variously developed. The kornerupine-bearing assemblage may well also be a product of reaction between dolomite marble and the adjacent highly magnesian yoderite-bearing schist. There is as yet no certain evidence for boron metasomatism at Mautia Hill; tourmaline has not been recorded and the boron content of the sapphirine is below the limit of spectrographic sensitivity.

No synthetic study has yet been made of the system  $\text{MgO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$ , in which the composition of kornerupine essentially lies. Preliminary hydrothermal decomposition runs have shown that Mautia kornerupine becomes unstable below  $900^\circ\text{C}$  at  $p_{\text{H}_2\text{O}}$  500 bars and at  $p_{\text{H}_2\text{O}}$  2000 bars, while no change was observed in one week at  $500^\circ\text{C}$ ,  $p_{\text{H}_2\text{O}}$  2000 bars.

#### *Grandidierite*

In the course of establishing the identity of yoderite from Mautia Hill some years ago a museum specimen labelled grandidierite was examined. It too was found to have the axial spacing characteristic of  $\text{AlO}_6$  chains and more recently a fuller examination of the mineral was undertaken. The material studied was a grandidierite-biotite rock from Sakatelo, Madagascar, numbered 195716 in the University of Cambridge Mineralogical Museum. Nothing is presently known of the field association of the specimen and this communication will be concerned only with the mineralogy of grandidierite.

*Unit-cell dimensions and space group.* Inspection of oscillation photographs taken about the shortest axis confirmed the assignment of grandidierite by Lacroix (1922) to the orthorhombic system. Measurement of zero, first, and second layer  $a$ -axis, zero layer  $b$ -axis, and zero layer  $c$ -axis Weissenberg photographs taken on  $\text{CuK}\alpha$  radiation served to determine the unit-cell dimensions approximately as  $a$  10.94,  $b$  10.35,  $c$  5.75 Å. With these approximate dimensions most of the peaks on a diffractometer trace could be indexed down to  $d$  2.2 Å. A diffractometer trace of grandidierite with an internal quartz standard, taken with  $\text{CuK}\alpha$  radiation at 2.6 cm per degree of  $2\theta$ , was then run three times over the range  $15^\circ < 2\theta < 35^\circ$  and, by measurement with a vernier rule reading to 0.01 cm, accurate  $2\theta$  values were obtained for the 200, 211, 310, 221, 031, and 400 reflections relative to the precisely known  $2\theta$



values of the  $10\bar{1}0$  and  $10\bar{1}1$  quartz reflections ( $20.876^\circ$  and  $26.664^\circ$  respectively). Similarly a diffractometer trace with an internal NaCl standard, run three times over the range  $27^\circ < 2\theta$  ( $\text{CuK}\alpha$ )  $< 47^\circ$ , yielded  $2\theta$  for the 221, 031, 400, 022, and 222 reflections relative to  $2\theta_{200}$  31.732 and  $2\theta_{220}$  45.492 for NaCl. The mean and its standard deviation were calculated for each  $2\theta$  value. Unit-cell dimensions were

TABLE IV. X-ray powder data for grandidierite

$d$ (Å)	$I$	$hkl$	$d$ (Å)	$I$	$hkl$	$d$ (Å)	$I$	$hkl$
*5.482	vs	200	2.92	vw	230	2.337	vw	240
5.17	vvs	020	2.878	w	002	*2.287	mw	222
5.04	vvs	011	2.855	vw	131	2.210	mw	312
4.84	w	210	*2.744	vs	400	2.166	s	{ 132
4.59	vw	111	2.66B	vw	{ 410			{ 241
3.97	vw	201			{ 321	2.149	m	510
3.75	vw	220	2.602	m	231	2.072	vw	322
*3.708	ms	211	2.584	ms	040	2.050	vw	232
*3.449	w	310	2.551	mw	202	2.031	mw	150
3.29	vw	130	*2.515	w	022	2.012B	vw	{ 511
*3.150	w	221	2.48B	vw	{ 212			{ 431
2.99	vw	320			{ 401	1.946	mw	051
*2.956	m	031	2.41B	vw	411			

$d$ -spacings  $> 1.90$  Å only are listed.

Sequence of intensities: vvs, vs, s, ms, m, mw, w, vw.

B = broad peak.

\* indicates reflections used for refinement of unit-cell dimensions.

computed from the mean  $2\theta$  values for the eight observed reflections, simply weighted according to standard deviation, by the method described by Kelsey (1964) for which an EDSAC II programme is available. Accurate unit-cell dimensions for grandidierite are  $a$  10.978,  $b$  10.335,  $c$  5.760 Å (all to better than  $\pm 0.002$  Å).

Inspection of the five Weissenberg photographs yielded the diffraction symbol  $mmmPna$ , which is consistent with two possible space groups,  $Pna2_1$  and  $Pnam$  (conventionally  $Pnma$ ); no point group evidence is available to distinguish between the two.

*X-ray powder pattern.* The powder pattern, recorded on a diffractometer trace taken with  $\text{CuK}\alpha$  radiation at 2.6 cm per degree of  $2\theta$  over the range  $6^\circ < 2\theta < 47^\circ$ , is shown in table IV. Indexing was achieved by comparison with a list of sorted  $d$ -spacings, calculated for me by Dr. C. H. Kelsey from the accurate unit-cell dimensions given above, account being taken of relative intensities known from the five Weissenberg photographs. The three strongest lines are 5.17 (1), 5.04 (2), and 5.482 Å (3). A powder photograph taken with  $\text{FeK}\alpha$  radiation in a

Philips 11.46 cm camera displays a large number of weak lines at  $d$ -spacings below 1.9 Å; these cannot be indexed and have not been included in table IV.

*Optics.* The refractive indices of Sakatelo grandidierite are  $\alpha$  1.590,  $\beta$  1.618, and  $\gamma$  1.623, with  $-2V$   $30^\circ$ , pleochroism  $\alpha, \beta$  colourless,  $\gamma$  blue, and dispersion of  $2V$   $v > r$ . The material from Andrahomana was reported by Lacroix (1902) to have the rather higher refractive indices

TABLE V. Chemical composition of grandidierite

	1	2		1a	2a		1b
SiO <sub>2</sub>	20.39	20.46	B <sup>3+</sup>	0.974	0.253	Be	—
TiO <sub>2</sub>	0.13	n.d.	Si <sup>4+</sup>	0.995	1.067	Ga	18
Al <sub>2</sub> O <sub>3</sub>	52.12	51.75	Al <sup>3+</sup>	2.998	3.180	Cr	25
Fe <sub>2</sub> O <sub>3</sub>	0.80	7.29	Fe <sup>3+</sup>	0.029	0.286	V	28
FeO	2.87	4.11	Mg <sup>2+</sup>	0.876	0.615	Sn	220
MnO	0.04	n.d.	Ti <sup>4+</sup>	0.005	—	Li	—
MgO	12.04	7.91	Fe <sup>2+</sup>	0.117	0.179	Ni	—
CaO	nil	0.86	Mn <sup>2+</sup>	0.002	—	Co	18
Na <sub>2</sub> O	0.04	2.94	Ca <sup>2+</sup>	—	0.048	Sc	—
K <sub>2</sub> O	0.09	0.38	Na <sup>+</sup>	0.004	0.297	Zr	220
H <sub>2</sub> O <sup>+</sup>	n.d.	1.64	K <sup>+</sup>	0.006	0.025	Cu	20
H <sub>2</sub> O <sup>-</sup>	nil	n.d.				Y	—
B <sub>2</sub> O <sub>3</sub>	11.57	2.81	OH <sup>-</sup>	—	0.570	Sr	—
	100.09	100.15	O <sup>2-</sup>	9.000	8.430	Ba	—
						Rb	—

1. Grandidierite, Sakatelo, Madagascar. Min. Mus. Cambridge 195716. Analyst: J. H. Scoon.
2. Grandidierite, Andrahomana, Fort Dauphin, Madagascar (Lacroix, 1922, p. 393).
- 1a, 2a. Contents of a quarter of the unit-cell, calculated to  $\sum(\text{O,OH}) = 9$ , for analyses 1 and 2 respectively.
- 1b. Trace elements in p.p.m. determined spectrographically on the material of analysis 1. Analyst: R. Allen.

$\alpha$  1.6018,  $\beta$  1.6360,  $\gamma$  1.6385, similar  $2V$   $-30^\circ 16'$ , and stronger pleochroism  $\alpha$  deep green-blue,  $\beta$  colourless,  $\gamma$  deep green, with absorption  $\gamma > \alpha > \beta$ . The indicatrix is oriented with  $\alpha \parallel a$ ,  $\beta \parallel c$ ,  $\gamma \parallel b$ .

*Unit-cell contents.* The chemical composition of grandidierite, determined for me by Mr. J. H. Scoon, is set down in column 1 of table V. B<sub>2</sub>O<sub>3</sub> and FeO were determined by the same methods as were used in kornerupine. The new analysis exhibits conspicuously higher boron, higher magnesium and correspondingly lower iron, and markedly lower calcium, sodium, and water than the analysis (column 2) of Lacroix (1922). A trace element analysis, for which I have to thank Dr. S. R. Nockolds, is shown in column 1b of table V.

The specific gravity, estimated as  $2.97_6$  in precisely the same manner as for kornerupine, taken together with the unit-cell dimensions and composition leads to an oxygen content of  $35.9_3$  atoms in the unit-cell, sufficiently close for the true oxygen content to be 36 atoms. Of the two possible space groups,  $Pna2_1$  has general positions of multiplicity 4 and no special positions, while  $Pnam$  has 8-fold general positions and special positions of multiplicity 4; in either case the asymmetric unit is one-quarter of the unit-cell and the two analyses are shown recalculated in atomic units to  $\sum (\text{O,OH}) = 9$  in columns 1a and 2a of table V. The two analyses are similar to the extent that the new specimen has 6.006 and Lacroix's specimen 5.950 cations in the asymmetric unit and both can be represented with some precision as  $(\text{K} \dots \text{Mg})^{[6]}(\text{Mg,Fe}^{\text{III}}, \text{Al})_3^{[6,4]}(\text{Al,Si,B})_2^{[4]}(\text{O,OH})_9$ ; the proportions of individual cations, however, differ considerably and column 2a must be considered in the light of the age of Lacroix's separation and analysis. The contents of the unit-cell of the new material (column 1a) approximate fairly closely to the simple formula  $4(\text{Mg,Fe})\text{Al}_3\text{SiBO}_9$ . The relationship of both analysed grandidierites to the hypersthene-pyrope-corundum join is shown in fig. 1.

*Structural speculations.* The shortest axis of grandidierite,  $c$  5.760 Å, is similar to the length of two octahedral groups in  $\text{AlO}_6$  chains characteristic of the aluminium silicates and the epidote group, especially sillimanite whose  $c$ -axis is 5.75 Å. The dimensional similarity is closer in that sillimanite has  $[110] \simeq [1\bar{1}0] \simeq 10.63$  Å, with  $[110] \wedge [1\bar{1}0] = 91^\circ 08'$ ; grandidierite has  $a$  10.978 Å,  $b$  10.335 Å, but no lattice point at the centre of the (001) face of the unit-cell. The presence of four  $\text{AlO}_6$  chains running parallel to the  $c$ -axis, with  $x,y$  co-ordinates  $0\ 0, \frac{1}{2}\ 0, 0\ \frac{1}{2}, \frac{1}{2}\ \frac{1}{2}$ , is inferred and accounts for eight Al cations in octahedral co-ordination. The grandidierite unit-cell contains four oxygen atoms less than the corresponding double unit-cell of sillimanite and consequently has a volume per anion of  $18.15$  Å<sup>3</sup>, larger than the  $16.2$  Å<sup>3</sup> of sillimanite; looser packing is an expected consequence of the presence of the larger, less strongly bonding  $\text{Mg}^{2+}$  cation. Taking the unit-cell contents of grandidierite as  $\text{Mg}_4\text{Al}_{12}\text{Si}_4\text{B}_4\text{O}_{36}$ ,  $\text{Al}_8$  and  $\text{O}_{32}$  are accounted for by the chains, leaving sixteen cations, as in sillimanite, but only four, instead of eight, anions outside the chains. If Si and B only are in fourfold co-ordination and correspond to  $\text{Si}^{[4]}$  and  $\text{Al}^{[4]}$  in sillimanite, the remaining cations  $\text{Mg}_4$  and  $\text{Al}_4$  must be in sixfold co-ordination and must form direct links between chains, or, by increasing the co-ordination of non-chain oxygens from two to three, links between chain

oxygens and non-chain oxygens; such positions should readily tolerate extreme variation in cation radius, enabling the  $\text{Na}^+$  recorded by Lacroix to be accommodated.

*Paragenesis.* The occurrence of grandidierite in a Madagascar granite was first noticed briefly by Lacroix (1902). The next record (Hlawatsch, 1918) is of ?grandidierite in a quartz-biotite-muscovite-garnet rock from Gömör in Hungary. A full chemical and optical account of the Madagascar occurrence, grandidierite with poecilitic enclosures of quartz, microcline, almandine, pleonaste, andalusite, and biotite in pegmatite and aplite at Andrahomana, west-south-west of Fort Dauphin, was given by Lacroix (1922). De Villiers (1940) suspected that enclosures in kornerupine from Port Shepstone, Natal, might be iron-rich grandidierite. The newly described material occurs as a major constituent in a grandidierite-biotite assemblage.

None of the occurrences so far described has yielded clear evidence of the physical and chemical conditions requisite for the stable crystallization of grandidierite, nor has any synthetic work been done in the system  $\text{MgO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$ . What evidence there is suggests that grandidierite need not necessarily be a product of boron metasomatism, but may, if the structural evidence cited above is valid, have crystallized instead of an  $\text{Al}_2\text{SiO}_5$  phase from a boron enriched contaminated magma.

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