

## Roweite from Franklin, New Jersey: A Restudy

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### Abstract

The type specimen was restudied. Roweite  $\text{Ca}_2\text{Mn}_2(\text{OH})_4[\text{B}_4\text{O}_7(\text{OH})_2]$  is orthorhombic, with space group *Pbam*;  $a = 9.057(1)$ ,  $b = 13.357(2)$ ,  $c = 8.289(1)$  Å;  $V = 1002.8(1)$  Å<sup>3</sup>;  $Z = 4$ . Crystals are subidiomorphic {100} laths that are elongated along [010] to maximum lengths of 5 mm; forms {001}, {100}, {201}, {021}, and {401} are present. The original unit cell was reoriented with the transformation to the new setting given by the matrix 010/002/100. The strongest lines of the X-ray pattern (in Å) are: 3.974, 100 (201); 2.600, 72 (042), 2.184, 49 (401); 2.264, 32 (400); 1.708, 32 (442).

Roweite is amber to brownish; thin plates are transparent and colorless.  $H = 4\frac{1}{2}$ . Cleavages are {100} fair, {001} and {021} poor. The specific gravity (meas) = 2.935(5); density (calc) = 2.93, g cm<sup>-3</sup>.

The mineral is biaxial negative,  $\alpha = 1.646(1)$ ,  $\beta = 1.658(1)$ ,  $\gamma = 1.660(1)$ ;  $2V_\alpha = 28(2)^\circ$  (Na); dispersion  $r < v$ , strong;  $X = c$ ,  $Y = b$ ,  $Z = a$ ; moderately pleochroic with *Z* (yellowish brown)  $> Y$  (pale amber)  $> X$  (very pale brown to colorless). Nonfluorescent.

The original chemical analysis has been recast, on the basis of a new X-ray structural analysis by Moore and Araki (1974), as  $\text{Ca}_2(\text{Mn}_{0.8}\text{Mg}_{0.1}\text{Zn}_{0.1})_2(\text{OH})_4[\text{B}_4\text{O}_7(\text{OH})_2]$ .

### Introduction

Roweite, found at an unspecified location in the zinc mines of Franklin, New Jersey, was described by Berman and Gonyer (1937). Only a single specimen from the type locality (Harvard University Collection No. 96262) is known to exist, although other specimens may exist in some of the numerous private mineral collections from the Franklin district. The work reported here was performed on a few cleavage fragments of the type specimen. We have selected a new unit cell in the conventional setting and have redetermined X-ray, optical, and physical data for roweite.

### Occurrence

In the original description the mineral was said to occur in a narrow veinlet (approximately 6 mm thick) of almost pure roweite intimately associated with a silky, white, fibrous material which was believed to be thomsonite. We found roweite in very close association, and in places intergrown, with clinochrysolite [ $\alpha = 1.548(2)$ ,  $\gamma = 1.554(2)$ ], but

with no associated thomsonite. The wall-forming minerals of the roweite veinlet are franklinite, zincite, and willemite; inclusions of these minerals are sparse in some roweite crystals. The most abundant included material, however, is clinochrysolite with which roweite may occur as parallel or, less commonly, as complex intergrowths. Roweite replaces anhedral masses of calcite which are in optical continuity throughout a roweite crystal and which show effects of solution. Much of the roweite, however, is essentially free from inclusions of any kind. This is confirmed by the slight amount of insoluble residue found in the analysis of purified roweite by Gonyer (Berman and Gonyer, 1937).

### Crystallography

#### X-ray Data

Unit-cell dimensions were determined using precession photographs (Zr-filtered Mo radiation) with  $a$ ,  $b$ , and  $c$  as precession axes for zero and first levels; the  $b$ -axis for second level; and cone-axis photo-

graphs for the *a* and *b* axes. The resulting data (Table 1) were then refined on the basis of the indexed powder pattern. Systematic extinctions indicate that the space group is *Pbam* or *Pba2*. The X-ray structure determination by Moore and Araki (1974) shows *Pbam* to be correct. A piezoelectric test of the mineral gave a negative response. We have reoriented the unit cell from Berman and Gonyer (1937) to a conventional setting. This was necessary because our unit-spacing along the fiber length was double the value reported by Berman and Gonyer. This is in agreement with the cell chosen by Malinko, Stolyarova, and Shashkin (1972) for magnesian roweite, except they chose *c* > *a*. Transformation from Berman and Gonyer's setting to our new one is accomplished by the matrix 010/002/100. Our X-ray powder diffraction data for roweite (Table 2) are not in good agreement with those reported by Malinko *et al* (1972) for magnesian roweite from the Soviet Union. As noted above, Malinko *et al* chose *c* > *a*, but the indices and space group are given for a cell with *c* < *a*.

*Morphology*

Crystals of roweite are subidiomorphic, lath-shaped, being elongated along [010] and tabular on {100}. The crystals have a maximum length of 5 mm. The length:width ratio varies from 10:1 to 3:1 for most crystals, but some acicular crystals have a ratio of up to 100:1. The crystals are arranged parallel to the axis of elongation (*b*) and to the wall of the veinlet. Faces in the zone [010] are striated parallel to *b* and give poor goniometric measurements; however, forms {001}, {100}, {201}, and {401} were identified. The form {021} was also identified. Neither we nor the previous workers could find terminated crystals, but a few small growth hillocks found on {100} surfaces show {010} and {021} as terminating forms.

**Physical and Optical Properties**

Cleavages are {100} fair, {001} and {021} poor. The mineral is brittle and, if broken, forms tabular fragments with a rough prismatic shape. The ends of the cleavage tablets shows a poor but fairly consistent direction of breaking in the zone [100] forming an angle of approximately 47–49° with the *b* axis (calculated angle 51° 10'). This we interpret as the poor {021} cleavage called {101} by Berman and Gonyer (1937) for their setting. This cleavage is accentuated by etching with dilute acid, and values

of 51° were measured for the etched trace of {021} on {100} surfaces. The fracture is conchoidal. Hardness 4½. Roweite is nonfluorescent in UV light.

The optical properties of roweite are summarized in Table 3; the optical orientation is shown in Figure 1. Indices of refraction were determined in sodium light using a spindle stage, and immersion liquids checked by means of an Abbe refractometer at the temperature of determination (25°C). The optical orientation data shown in Figure 1 were measured with a 4-axis universal stage using a small single crystal immersed in a liquid of *n* = 1.656 within a Waldmann hollow glass sphere.

Basal {001} sections of roweite show anomalous interference colors due to strong dispersion *r* < *v*. Such grains fail to extinguish in any position, probably because of the strong dispersion and combined effects of internal and external conical refraction.

In order to characterize the dispersion more fully, the mineral was examined conoscopically and by means of the universal stage in light of various wavelengths obtained by means of a calibrated graded interference filter. Normal to (001) the acute bisectrix figure in 45° position shows extreme dispersion

TABLE 1. Unit Cell Data for Roweite

	kowitze		Magnesian roweite Solongo, U.S.S.R. Malinko et al. (1972)
	Franklin, New Jersey This study	Berman and Gonyer (1937)	
<i>a</i> (Å)	9.05 <sub>7</sub> (1)	8.29(1)*	8.27(2)
<i>b</i>	13.35 <sub>7</sub> (2)	9.03(1)	13.25(2)
<i>c</i>	8.28 <sub>9</sub> (1)	6.63(2)	9.01(2)
Vol. (Å <sup>3</sup> )	1002.8(1)	496.3**	987.29
a:b:c	0.6781:1:0.6206	0.918:1:0.735	0.6242:1:0.6800
<i>Z</i>	4 <sup>c</sup> ***	4†	
Space group	<u>Pbam</u>		<u>Pba2 or Pbam</u>
Specific gravity (meas)	2.935(5)	2.92(2)	2.73(1)
Density (g cm <sup>-3</sup> ) (calc)	2.93 <sub>3</sub> ††	2.84†††	2.74

\* Calculated from original values given in kX (Berman and Gonyer, 1937; Palacne, Berman, and Frondel, 1951, p.377).

\*\* Calculated from Berman and Gonyer's (1937) values.

\*\*\* For the structural formula Ca<sub>2</sub>Mn<sub>2</sub>(OH)<sub>4</sub>[B<sub>4</sub>O<sub>7</sub>(OH)<sub>2</sub>] (Moore and Araki, 1973)

† For the original empirical formula, H<sub>2</sub> Mn Ca (B<sub>3</sub>O)<sub>2</sub>, and cell volume.

†† Calculated using the cell data (this study) and the calculated chemical composition derived from the structural formula with Mn, Mg, and Zn oxides in the proportion of the original chemical analysis.

††† Calculated from the data of Berman and Gonyer (1937).

TABLE 2. X-ray Powder Diffraction for Roweite

Roweite Franklin, New Jersey This Study				Magnesian roweite Solongo, U.S.S.R. Malinko et al. (1972)			
<i>h k l</i>	<i>d</i> (calc)* (Å)	<i>d</i> (obs)** (Å)	I/I	<i>d</i> (obs)† (Å)	I/I†	<i>d</i> (calc)† (Å)	<i>h k l</i> †
001	8.29	8.29	26	--	--	--	--
110	7.50	7.49	6	--	--	--	--
020	6.68	--	--	--	--	--	--
111	5.56	--	--	--	--	--	--
120	5.38	5.37	13	--	--	--	--
021	5.20	--	--	--	--	--	--
200	4.528	4.530	10	--	--	--	--
121	4.510	4.512	17	--	--	--	--
210	4.289	4.287	9	--	--	--	--
002	4.144	4.145	13	--	--	--	--
130	3.996	--	--	--	--	--	--
201	3.974	3.974	100	3.90	6	3.95	201
211	3.809	3.805	7	--	--	--	--
220	3.748	--	--	3.69	2	3.72	220
112	3.627	3.626	16	--	--	--	--
131	3.599	--	--	--	--	--	--
022	3.522	--	--	--	--	--	--
221	3.415	--	--	--	--	--	--
040	3.339	--	--	--	--	--	--
122	3.282	3.283	22	--	--	--	--
230	3.175	--	--	3.17	5	3.16	230
140	3.133	--	--	--	--	--	--
041	3.097	3.097	16	--	--	--	--
202	3.057	3.059	27	--	--	--	--
212	2.980	2.978	8	2.98	7	2.98	212
231	2.965	--	--	--	--	--	--
310	2.945	2.944	11	--	--	--	--
141	2.931	--	--	--	--	--	--
132	2.876	--	--	--	--	--	--
222	2.780	--	--	--	--	--	--
311	2.775	--	--	--	--	--	--
003	2.763	2.762	9	--	--	--	--
320	2.751	2.751	23	--	--	--	--
240	2.688	2.684	7	2.68	4	2.67	240
321	2.61	--	--	--	--	--	--
042	2.600	2.600	72	--	--	--	--
113	2.592	--	--	--	--	--	--
150	2.562	--	--	--	--	--	--
241	2.556	2.556	13	--	--	--	--
023	2.553	--	--	2.56	10	2.55	023
232	2.520	2.523	1	--	--	--	--
330	2.499	2.495	3	--	--	--	--
123	2.457	--	--	--	--	--	--
151	2.448	2.448	8	--	--	--	--
312	2.400	2.399	11	--	--	--	--
331	2.392	--	--	--	--	--	--
203	2.359	--	--	--	--	--	--
213	2.323	2.322	7	--	--	--	--
250	2.301	--	--	--	--	--	--
322	2.292	2.291	19	--	--	--	--
133	2.272	--	--	--	--	--	--
400	2.264	2.264	32	2.25	5	2.25	004
242	2.255	--	--	--	--	--	--
340	2.239	--	--	--	--	--	--
410	2.232	--	--	--	--	--	--
060	2.226	--	--	2.21	3	2.21	060
223	2.224	--	--	--	--	--	--
251	2.217	--	--	--	--	--	--
401	2.184	2.184	49	--	--	--	--
152	2.179	--	--	--	--	--	--

\*All calculated spacings listed for  $d \geq 2.000$  Å; *hkl*'s between 2.000 and 1.272 Å are given only for observed lines. Indices and *d*(calc) from least-square analysis of X-ray powder data using the digital computer program of Appleman and Evans (1973). Unit cell: *a*(Å) 9.057, *b* 13.357, *c* 8.289.

\*\*Harvard Museum No. 96262. X-ray diffractometer conditions are: Chart X-339; Cu/Ni radiation,  $\lambda$  Cu  $K\alpha_1$  = 1.50451 Å; Al used as internal standard; scanned at 1/4° per minute from 9-80° 2 $\theta$ .

†Data from Table 1 (p. 467) of Malinko et al. (1972) for magnesian roweite, calculated formula  $\text{Ca}_{0.98}\text{Mg}_{0.39}\text{Hf}_{0.52}\text{Fe}_{0.03}^{2+}\text{O}_{3.94}\text{B}_{2.02}[\text{O}_{3.7}(\text{OH})_{2.3}]\text{S}_6$ . Powder camera PKU, diameter 114 mm. Unit cell: *a*(Å) 8.27, *b* 13.25, *c* 9.01.

TABLE 2, continued

Roweite Franklin, New Jersey This Study				Magnesian Roweite Solongo, U.S.S.R. Malinko et al. (1972)			
<i>h k l</i>	<i>d</i> (calc)* (Å)	<i>d</i> (obs)** (Å)	I/I	<i>d</i> (obs)† (Å)	I/I†	<i>d</i> (calc)† (Å)	<i>h k l</i> †
341	2.162	--	--	--	--	--	--
160	2.162	--	--	--	--	--	--
411	2.156	2.156	17	2.14	4	2.15	411
061	2.150	2.150	11	--	--	--	--
420	2.144	--	--	--	--	--	--
332	2.140	--	--	--	--	--	--
043	2.129	2.128	37	2.11	7	2.12	043
161	2.092	--	--	--	--	--	--
233	2.084	--	--	--	--	--	--
421	2.076	--	--	--	--	--	--
143	2.072	--	--	--	--	--	--
004	2.072	2.071	15	--	--	--	--
430	2.018	--	--	--	--	--	--
313	2.015	--	--	--	--	--	--
252	2.012	2.014	7	--	--	--	--
350	2.001	--	--	--	--	--	--
124	1.934	1.932	16	--	--	--	--
243	1.926	1.926	18	1.920	2	1.920	243
162	1.917	1.916	15	1.892	7	1.894	422
441	1.828	1.827	7	--	--	--	--
224	1.814	1.813	6	--	--	--	--
510	1.795	1.795	6	1.793	3	1.793	352
520	1.748	1.749	7	--	--	--	--
442	1.708	1.708	32	1.689	9	1.689	423
080	1.670	1.670	11	--	--	--	--
324	1.655	1.655	8	--	--	--	--
244	1.641	1.641	29	--	--	--	--
--	--	--	--	1.625	8	1.625	433
--	--	--	--	1.620	5	1.621	181
443	1.551	1.551	13	--	--	--	--
254	1.540	1.540	6	1.539	5	1.539	173
404	1.529	1.528	7	--	--	--	--
600	1.509	1.510	5	1.513	2	1.512	064
601	1.485	1.485	6	--	--	--	--
045	1.485	1.485	6	--	--	--	--
282	1.465	1.465	8	--	--	--	--
145	1.465	1.465	8	--	--	--	--
453	1.465	1.465	8	--	--	--	--
602	1.418	1.418	8	--	--	--	--
183	1.412	1.411	6	--	--	--	--
245	1.411	1.411	6	--	--	--	--
382	1.378	1.377	5	--	--	--	--
463	1.376	1.376	5	--	--	--	--
641	1.357	1.357	5	--	--	--	--
514	1.357	1.357	5	--	--	--	--
480	1.344	1.344	5	1.347	3	1.349	164
405	1.338	1.337	10	1.331	5	1.331	345
1·10 <sup>0</sup>	1.321	1.321	7	1.314	3	1.314	613
206	1.300	1.300	7	1.295	3	1.295	1·10 <sup>-2</sup>
084	1.300	1.300	7	1.295	3	1.295	1·10 <sup>-2</sup>
046	1.276	1.275	5	--	--	--	--
355	1.276	1.275	5	--	--	--	--
265	1.276	1.275	5	--	--	--	--
--	--	--	--	1.118	4	1.118	3·11·0
--	--	--	--	1.110	3	1.110	237
--	--	--	--	1.098	3	1.098	625
--	--	--	--	1.046	3	1.045	067
--	--	--	--	1.033	10	1.033	376
--	--	--	--	1.019	6	1.019	128
--	--	--	--	1.005	3	1.005	1·13·1

of the optic axes such that  $2V_\alpha$  has a maximum observed value of 42° for violet light (430 nm) and decreases through 28° for sodium light (589 nm) to about 16° for red light (678 nm), as shown in Figure 2. It is therefore likely that roweite becomes sensibly uniaxial in the uppermost part of the visible spectrum at about 760 nm.

TABLE 3. Optical Properties of Roweite

	Franklin, New Jersey		Magnesian roweite
	This study	Berman and Gonyer (1937)	U.S.S.R. Malinko et al. (1972)
$\alpha$	1.646(1)	1.648(3)	1.631
$\beta$	1.658(1)	1.660(3)	1.640
$\gamma$	1.660(1)	1.663(3)	1.641
$2V_a$	$28(2)^\circ$	$15^\circ$	$20^\circ$
Birefringence	Weak(0.014)	Weak(0.015)	Weak (0.010)
Dispersion	$\underline{r} < \underline{v}$ , strong	$\underline{r} < \underline{v}$ , strong	$\underline{r} < \underline{v}$ , strong
X	$\underline{c}$	$\underline{a}$	
Y	$\underline{b}$	$\underline{c}$	
Z	$\underline{a}$	$\underline{b}$	
Absorption	$Z < Y < X$		$Z < Y < X$
Pleochroism	Z(yellowish brown) Y(pale amber) X(very pale brown to colorless)		Z (Strong yellow) Y X (colorless)

The optic axial plane for visible light of all wavelengths remains parallel to (010). This and the absence of inclined dispersion for the indicated  $Y = b$  orientation supports the conclusion that roweite has symmetry no lower than that afforded by the orthorhombic system.

### Chemical Composition

#### Analysis

The only chemical analysis of roweite gave the values indicated in column 1, Table 4 (reproduced from Berman and Gonyer's paper). These authors suggested the formula  $H_2(Mn, Mg, Zn)Ca(BO_3)_2 \cdot (OH)_2$  (Palache, Berman, and Frondel, 1951).

Using the atomic proportions resulting from that

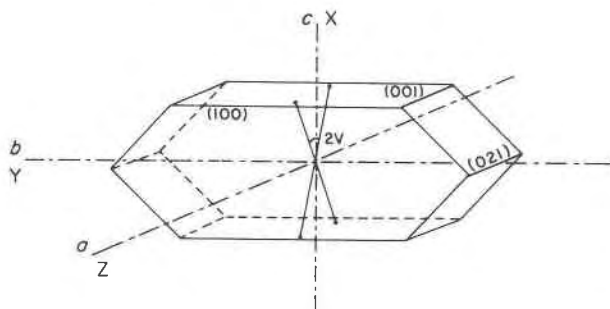


FIG. 1. Drawing of an idealized cleavage fragment of roweite showing its optical orientation.

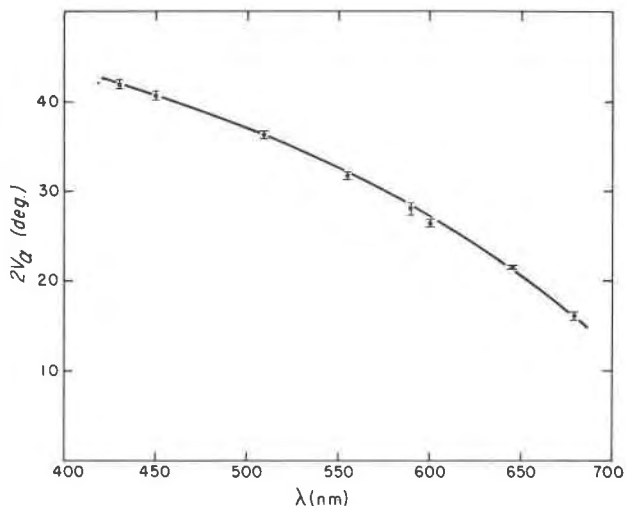


FIG. 2. Variation of roweite  $2V$  with respect to wavelength of visible light.

analysis, the calculated density is  $2.81 \text{ g cm}^{-3}$ . Recently, Moore and Araki (1974) solved the structure and found that the structural formula is  $Ca_2Mn^{2+}_2(OH)_4[B_4O_7(OH)_2]$ . Using this formula and Mn, Mg, and Zn oxides in proportion to the original analysis, the chemical composition given in column 2 of Table 4 was calculated. These values agree well with those of column 1, except for water which seems to be low in the analysis performed by Gonyer.

The oxide formula of the values of column 2 is  $2 \text{ CaO} \cdot 2(\text{Mn}_{0.835}\text{Mg}_{0.080}\text{Zn}_{0.080})\text{O} \cdot 2 \text{ B}_2\text{O}_3 \cdot 3 \text{ H}_2\text{O}$ . The molecular weight is 443.79 and the calculated density  $2.939 \text{ g cm}^{-3}$ . This density agrees very well with the measured specific gravity.

TABLE 4. Chemical Analysis of Roweite

	1.	2.
MnO	28.30	26.70
MgO	1.66	1.54
ZnO	3.13	2.93
CaO	25.40	25.27
$B_2O_3$	32.40	31.38
$H_2O$	8.51	12.18
Insol.	0.84	
Sum or total	100.24	100.00

1. F. A. Gonyer, analyst. Franklin zinc mines, New Jersey, U.S.A. (Berman and Gonyer, 1937)
2. Calculated composition using the structural formula  $Ca_2Mn_2(OH)_4[B_4O_7(OH)_2]$  and Mn, Mg, and Zn oxides in proportion of the analysis of column 1.

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## The Crystal Structure of Bikitaite, $\text{Li}[\text{AlSi}_2\text{O}_6]\cdot\text{H}_2\text{O}$

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### Abstract

The crystal structure of bikitaite,  $\text{LiAlSi}_2\text{O}_6\cdot\text{H}_2\text{O}$ , has been determined from three-dimensional  $\text{MoK}\alpha$  counter data by direct methods and refined by full matrix least-squares calculations using anisotropic temperature factors to an unweighted  $R$ -value of 0.037 for 824 observed reflections on a crystal from Bikita, Rhodesia. The cell parameters are:  $a = 8.613(4)$ ,  $b = 4.962(2)$ ,  $c = 7.600(4)$  Å,  $\beta = 114.45(1)^\circ$ , space group  $P2_1$ ,  $Z = 2$ .

There are three basic tetrahedral sites in the asymmetric unit of bikitaite, designated  $T(1)$ ,  $T(2)$ , and  $T(3)$ . Refinement of the structure indicated (0.5 Al + 0.5 Si) in  $T(1)$  and  $T(3)$  and Si only in the  $T(2)$  site. The mean bond lengths of the  $T(1)\text{O}_4$  and  $T(3)\text{O}_4$  tetrahedra are both 1.681 Å and the mean bond length of the  $T(2)\text{O}_4$  tetrahedron is 1.610 Å. These bond lengths are very similar to those in comparable tetrahedra in other tectosilicates. The lithium atom in bikitaite is tetrahedrally coordinated by three oxygen atoms and a water molecule, with the mean bond lengths of the  $\text{LiO}_4$  tetrahedron being 1.972 Å. With the exception of the oxygen in the  $\text{H}_2\text{O}$  molecule, all oxygens in the structure are bridging, forming zig-zag chains of tetrahedra parallel to [010]. These chains are joined together to form a three-dimensional network with one large channel containing Li and  $\text{H}_2\text{O}$  and with several smaller, empty channels.

### Introduction

Bikitaite, a lithium-aluminosilicate from the lithium-rich pegmatites in Bikita, Southern Rhodesia, was described by Hurlbut (1957). Preliminary analytical, optical, and X-ray investigations (Hurlbut, 1957, 1958) have shown that the chemical formula of bikitaite is close to  $\text{Li}_{0.95}\text{Al}_{1.10}\text{Si}_{1.95}\text{O}_6\cdot 1.15\text{H}_2\text{O}$  and that the mineral crystallizes in the monoclinic system with two possible space groups  $P2_1$  or  $P2_1/m$ . Leavens, Hurlbut, and Nelson (1968) reported bikitaite in the lithium-rich pegmatites at King's Mountain, North Carolina. Chemical analyses of samples from this locality have the nearly ideal composition of  $\text{LiAlSi}_2\text{O}_6\cdot\text{H}_2\text{O}$ .

The first X-ray crystal structure studies of bikitaite were carried out by Appleman (1960) who reported the basic outline of the bikitaite structure in the space group  $P2_1$ . Accurate determination of the structure was prevented by the poor quality of crystals available at that time (Appleman, personal communica-

tion, 1972) and consequently structural details of Appleman's refinement were never published. The thermal and chemical properties of bikitaite were studied by Phinney and Stewart (1961), who described dehydration and ion exchange properties of the mineral. Bikitaite has been synthesized at pressures between 1 to 2.5 kbar and at temperatures ranging from 300–350°C by Drysdale (1971).

### Experimental

Excellent crystals of bikitaite (specimen #M27924 kindly provided for this study by the Royal Ontario Museum) were selected from the specimen. Crystals were examined under polarized light and by X-ray diffraction, and a crystal with well developed faces, elongated along the  $b$  axis, was chosen for the study. The crystal was cut in two; one part was saved for electron microprobe analysis, and the other part was used for determination of cell dimensions and data collection.