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The Crystal Structure of Bikitaite, $Li[AlSi_2O_6] \cdot H_2O$

VLADIMIR KOCMAN

Department of Geology, University of Toronto

ROBERT I. GAIT

Royal Ontario Museum

JOHN RUCKLIDGE

Department of Geology, University of Toronto,
Toronto, Canada M5S 1A1

Abstract

The crystal structure of bikitaite, $LiAlSi_2O_6 \cdot H_2O$, has been determined from three-dimensional Mo$K\alpha$ 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, β = 114.45(1)°, 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 $T(1)O_4$ and $T(3)O_4$ tetrahedra are both 1.681 Å and the mean bond length of the $T(2)O_4$ tetrahedron is 1.610 Å. These bond lengths are very similar to those in comparable tetrahedra in other tektosilicates. The lithium atom in bikitaite is tetrahedrally coordinated by three oxygen atoms and a water molecule, with the mean bond lengths of the LiO_4 tetrahedron being 1.972 Å. With the exception of the oxygen in the H_2O 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 H_2O 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 $Li_{0.95}Al_{1.10}Si_{1.95}O_6 \cdot 1.15\ H_2O$ 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 $LiAlSi_2O_6 \cdot H_2O$.

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 communication, 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.

Several electron microprobe analyses of the single crystal were carried out using the ARL-EMX instrument at operating conditions of 15kV and 0.05μA sample current. Diopside and anorthite were used as standards for Mg, Si, and Al. These data were processed by the EMPADR VII program written by Rucklidge and Gasparrini (1969). Li_2O was determined by atomic absorption. Small amounts of Na, K, and Mg were reported in bikitaite by Hurlbut (1958), but a careful check using the electron microprobe revealed no Na or K. The small amount of Mg detected, 0.01–0.02 percent, was neglected. A summary of analytical and crystal data of bikitaite is given in Table 1.

Intensity data were collected up to $\sin \theta/\lambda = 0.70$ on a Picker FACS-1 four-circle diffractometer using Zr-filtered Mo$K\alpha$ radiation. The dimensions of the crystals were 0.40 × 0.48 × 0.30 mm, and a total of 947 symmetry independent reflections were collected by the moving crystal-moving counter technique (2θ scan), using a scanning rate of 1°/min. with two stationary background counts of 40 sec. on each side of the peak. The threshold level for "unobserved" reflections was set to $3\sigma F^2$, and a total of 123 reflections were equal or less than this value. Absorption was low ($\mu_{MoK\alpha} = 7.3 cm^{-1}$) and no corrections were considered necessary. Corrections were made for Lorentz-polarization factors, and the data were put on an absolute scale by the K-curve and E-gen program. The distribution of E's clearly indicated a noncentrosymmetric space group for bikitaite, thus confirming Appleman's (1960) choice of $P2_1$:

$$\text{Av. } |E^2| = 1.019$$
$$\text{Av. } |E^2 - 1| = 0.770$$
$$\text{Av. } |E| = 0.887$$
$$|E| > 1, \% = 37.41$$
$$|E| > 2, \% = 2.42$$
$$|E| > 3, \% = 0.0$$

TABLE 1. Crystal Data and Chemical Analysis

$a = 8.613(4)$ Å	$V = 296.8$ Å^3
$b = 4.962(2)$ Å	$D_m = 2.28$ g.cm^{-3}
$c = 7.600(4)$ Å	$D_c = 2.28$ g.cm^{-3}
$\beta = 114.45(1)^\circ$	$Z = 2$

Space group $P2_1$ from structure determination

SiO_2	58.7	electron probe determination
Al_2O_3	25.1	
Li_2O	7.27	atomic absorption determination
H_2O	8.98	thermogravimetric determination
	100.05	

Formula $Li_{1.00}Al_{1.01}Si_{2.00}O_{6.01} \cdot 1.02(H_2O)$

Solution and Refinement of the Structure

A set of 181 E's > 1.4 was chosen for the direct structural determination. The origin of the cell in space group $P2_1$ was specified according to Karle and Hauptman (1966) and Hauptman and Fisher (1971) by the means of 3 reflections with high E values. Three other reflections with high E's were picked as starting phases a, b, c for the Σ_2 relationship and tangent formula refinement (Karle and Karle, 1966). All calculations were carried out by Larson and Drew's (1968) 'Tanfor' program.

The calculated E-map using starting phases listed below revealed the whole structure.

h	k	l	E	phase	symbol
$\bar{5}$	0	5	2.56	0	–
4	0	7	2.28	0	–
7	1	5	2.05	0	–
$\bar{6}$	0	2	2.90	π	a
$\bar{3}$	3	1	2.45	π	b
$\bar{5}$	2	10	2.28	$\pi/2$	c

Six cycles of XFLS (Ellison, 1962) positional least-squares refinement using 9 atoms in the asymmetric unit decreased the R-value from an initial value of 0.36 to 0.15. The difference Fourier map calculated at this stage confirmed the positions of Li and O(7) (water molecule) which originally showed up in the 'E-map', but had been left out of the refinement. The addition of these to the atom list, together with another 3 cycles of isotropic refinement wherein Al was arbitrarily assigned to the $T(3)$ site, lowered the R value to 0.076. This run, however, produced significantly different temperature factors for the tetrahedral sites $T(1)$, $T(2)$, and $T(3)$, but the calculated mean bond lengths of the tetrahedra indicated that sites $T(1)$ and $T(3)$ are occupied by 0.5 Al + 0.5 Si, while site $T(2)$ is occupied only by

Si (Jones, 1968). Therefore a new scattering curve for $T(1)$ and $T(3)$ was calculated from $[f(\mathrm{Al}) + f(\mathrm{Si})]/2$ and a further 3 cycles of isotropic refinement lowered the R value to 0.052, and also reduced the spread of the isotropic temperature factors of the T sites. A summary of this refinement is shown in Table 2.

TABLE 2. A Summary of the Isotropic Refinement of the Bikitaite Structure

Initial Refinement R=0.076				Final Refinement R=0.052		
Site	Element	B(Å^2)	Av.T-O(Å)	Element	B(Å^2)	Av.T-O(Å)
T(1)	Si	0.66	1.676	0.5Al+0.5Si	0.52	1.683
T(2)	Si	0.62	1.610	Si	0.64	1.606
T(3)	Al	0.36	1.682	0.5Al+0.5Si	0.51	1.682

Three additional cycles of full matrix least-squares refinement with anisotropic temperature factors converged to the R value of 0.037 for 824 'observed' reflections and the value of the standard deviation of an observation of unit weight was 1.003. This quantity is given by $[\Sigma w(F_o - F_c)^2/(NO - NV)]^{1/2}$ where w is the weight, F_o and F_c are the observed and calculated structure factors, NO is the number of observed structure factors and NV is the number of parameters varied in the last cycles of the refinement.

The weighting scheme used in the refinement was of the form $w = 1/\sigma_{F_o}{}^2$, where:

$$\sigma F_o = 0.0565\ F_o - 0.9285 + 9.608/F_o.$$

The R value for all 947 reflections was 0.044. An attempt was made to establish the absolute configuration of the structure at the isotropic level (Ibers and Hamilton, 1965), but the results were rather inconclusive. The R values were 0.0480 for the configuration described in this paper (Table 3) and 0.0481 for the enantiomorph. The anomalous corrections for Si and Al ($\Delta f' = 0.1$, $i\Delta f'' = 0.1$) were taken from Templeton (1962). A final difference Fourier map showed a few spurious peaks of height of about 0.6 e/Å^3 in an overall background of about 0.3 e/Å^3. Two peaks, in suitable positions, and approximately 1 Å apart from O(7) were considered to be hydrogen atoms. They were added to the atom list, given isotropic temperature factors of O(7), and positionally refined by one cycle of least-squares. The suggested coordinates of the hydrogen atoms are as follows: H(1) 0.303, 0.334, 0.474 and H(2) = 0.455, 0.163, 0.467.

Scattering factors of neutral Si, Al, Li, and O used in the refinement were those reported by Cromer and Mann (1968). All calculations were carried out on IBM 360/65 and 370/165 systems at University

TABLE 3. Final Atomic Positional and Thermal Parameters of Bikitaite

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B(Å^2)
T(1) (0.5Al+0.5Si)	0.10364(14)	0.86463(40)	0.09564(16)	263(15)	608(49)	410(20)	14(26)	188(14)	13(30)	0.52(4)
T(2) Si	0.10577(16)	0.79994	0.50849(18)	254(16)	715(48)	358(21)	-36(23)	91(14)	-26(25)	0.64(4)
T(3) (0.5Al+0.5Si)	0.38093(14)	0.87443(40)	0.93740(16)	175(15)	661(47)	359(20)	-2(26)	86(14)	9(29)	0.51(4)
Li	0.30409(114)	0.36460(235)	0.13412(140)	669(124)	956(328)	1345(183)	-45(218)	493(128)	13(263)	1.2(2)
O(1)	0.26662(43)	0.74342(76)	0.05003(52)	339(45)	786(150)	822(67)	13(62)	217(47)	45(77)	1.08(8)
O(2)	0.07630(46)	0.69636(86)	-0.03344(56)	462(53)	957(142)	990(73)	173(75)	388(52)	109(89)	1.22(8)
O(3)	0.15760(46)	0.82766(97)	0.33043(47)	656(49)	2274(195)	455(56)	27(88)	293(45)	157(89)	1.34(8)
O(4)	0.05937(50)	0.48682(90)	0.52684(66)	465(52)	709(142)	1551(92)	-46(72)	430(60)	125(100)	1.09(8)
O(5)	0.26459(43)	0.89502(96)	0.69869(43)	485(47)	1770(162)	329(55)	-171(82)	-50(40)	-20(88)	1.22(7)
O(6)	0.55519(44)	0.68878(83)	0.97699(50)	341(48)	1027(143)	726(67)	-7(71)	306(46)	-12(82)	1.14(8)
O(7) water	0.40402(57)	0.32446(114)	0.42167(70)	883(64)	2326(254)	1777(99)	-22(106)	385(67)	211(129)	2.3(1)

The values of x,y, and z are given in fractional coordinates, the anisotropic temperature factor (x10^5) is of the form: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + \ell^2\beta_{33} + 2hk\beta_{12} + 2h\ell\beta_{13} + 2k\ell\beta_{23})]$

calculated standard deviations in parentheses.

of Toronto Computer Center. The positional and thermal parameters of the structure with their standard deviations are shown in Table 3. All important bond lengths and angles and their standard deviations as calculated by ORFFE (1964) program are given in Table 4. A comparison of the observed and calculated structure factors (10 F_o, 10 F_c) and the phase angle α are listed in Table 5.

Description of the Structure

The structure, which is of a framework type, consists of infinite zig-zag chains of SiO_4 and $(Si,Al)O_4$ tetrahedra extending along two-fold screw axes parallel to the y-axis. These chains of tetrahedra are joined together to form large and small channels parallel to the y-axis. All T sites are tetrahedrally coordinated by four oxygen atoms and the resulting tetrahedra are linked together by sharing corners with equivalent tetrahedra in the y direction and with non-equivalent tetrahedra in the other directions. Since the 2_1 axis at 1/2, y, 1/2 is not occupied by any chain, the whole network forms one large channel centered on 1/2, y, 1/2 in which the Li atoms and H_2O molecules are located. Four smaller empty channels surround the large channel, so that for every large channel there are two small channels in the unit cell. The cross section of the large channel is about 5.5 × 6.5 Å and the diameter of the small channels is approximately 4 Å. Figure 1 is a three-dimensional view of the structure as plotted by the ORTEP (1965) program and Figure 2, which is a projection of the structure along the y axis, shows the distribution of the channels in bikitaite. Part of the structure projected along z is shown in Figure 3.

TABLE 4. Important Bond Lengths and Angles in Bikitaite

$T(1)O_4$ Tetrahedron		$T(3)O_4$ Tetrahedron	
T(1)-0(1)	1.690(4) Å	T(3)-0(1)	1.680(4) Å
-0(2)	1.674(4)	-0(5)	1.674(3)
-0(2')	1.702(4)	-0(6)	1.678(4)
-0(3)	1.657(3)	-0(6')	1.692(4)
Mean	1.681 Å	Mean	1.681 Å
$T(2)O_4$ Tetrahedron		**LiO_3H_2O Tetrahedron**	
T(2)-0(3)	1.597(4) Å	Li-0(1)	1.968(12)Å
-0(4)	1.625(4)	-0(2')	1.973(10)
-0(4')	1.624(4)	-0(6')	1.946(10)
-0(5)	1.596(4)	-0(7)w	2.000(11)
Mean	1.610 Å	Mean	1.972 Å
0(7)-0(7') water-water	2.950(8) Å		
0(7)-0(3')	3.137(6)		
0(7)-0(3)	3.163(6)		
Angles at T(1)		**Angles at T(3)**	
0(1)-T(1)-0(2)	110.4(2)°	0(5)-T(3)-0(6)	108.5(2)°
0(2)-T(1)-0(3)	110.8(2)	0(5)-T(3)-0(1)	111.2(2)
0(3)-T(1)-0(1)	107.3(2)	0(1)-T(3)-0(6)	111.4(2)
0(1)-T(1)-0(2')	108.6(2)	0(5)-T(3)-0(6')	108.3(2)
0(2)-T(1)-0(2')	109.4(2)	0(1)-T(3)-0(6')	109.2(2)
0(3)-T(1)-0(2')	110.7(2)	0(6)-T(3)-0(6')	108.2(2)
Mean	109.5°	Mean	109.5°
Angles at T(2)		**Angles at Li**	
0(3)-T(2)-0(4)	108.7(2)°	0(6')-Li-0(2')	109.9(4)°
0(4)-T(2)-0(5)	110.8(2)	0(2')-Li-0(7)w	106.9(4)
0(5)-T(2)-0(3)	107.9(2)	0(7)w-Li-0(6')	111.5(4)
0(3)-T(2)-0(4')	110.1(2)	0(6')-Li-0(1)	109.6(4)
0(4)-T(2)-0(4')	109.3(2)	0(2')-Li-0(1)	106.0(4)
0(5)-T(2)-0(4')	110.2(2)	0(7)w-Li-0(1)	112.9(4)
Mean	109.5°	Mean	109.5°
T(1)-0(1)-T(3)	132.7(3)°	T(1)-0(2)-T(1)	129.3(3)°
T(1)-0(3)-T(2)	150.4(3)	T(2)-0(4)-T(2)	139.6(3)
T(2)-0(5)-T(3)	150.2(3)	T(3)-0(6)-T(3)	134.4(3)

* Calculated standard deviations, in parentheses, are given in terms of the last decimal place cited.

The symbol w indicates oxygen of water molecule.

Each lithium atom is tetrahedrally coordinated by three oxygen atoms and a water molecule in such a way that only oxygens from Al-rich $T(1)$ and $T(3)$ tetrahedra participate in this bonding. This configuration maintains the charge balance of the structure. The Li–O bond lengths vary from 1.946 to 2.000 Å with an average length of 1.972 Å, which is in agreement with the average value of 1.974 Å found for this bond in $LiOH \cdot H_2O$ (Agron, Busing and Levy, 1972) and with the value of 1.98 Å given for tetrahedrally coordinated lithium compounds (Ondik and Smith, 1962). The water molecules in the structure are held in the large channel mainly by the longest coordination bonds in the LiO_4 tetrahedra (2.000 Å), but weak hydrogen bonding also is expected between the water molecules themselves. The O(7)–O(7′) distance (water–water) is 2.95 Å, the hydrogen atom H(2′) being 0.91 Å from O(7′) and forming an O(7)...H(2′)–O(7′) angle of 173°. No contacts closer than 3.14 Å [O(3)–O(7)] exist between the water oxygen and the rest of the silicate structure. Such a situation is not unknown (Baur, 1964, 1972; Hamilton and Ibers, 1968) and the hydrogen bonding of H(1) can be explained by extremely weak or bifurcated hydrogen bonds. Valence sum calculations carried out on the structure (Donnay, personal communication, 1972) and assuming no hydrogen bond for H(1) indicated that

TABLE 5. Observed and Calculated Structure Factors for Bikitaite**

L	FO	FC	ALPHA
H= -12, K= 0			
4	77	74	4
5	92	91	2
H= -11, K= 0			
1	93	86	1
2	91	87	3
3	14*	3	575
4	39*	41	502
5	175	174	503
6	131	134	502
7	214	211	503
8	64	61	501
H= -11, K= 1			
1	54	51	607
2	129	130	571
3	105	105	120
4	74	72	504
5	94	93	131
6	62	61	263
7	63	56	159
H= -11, K= 2			
2	98	96	562
3	43*	45	98
4	58	60	390
5	158	157	175
6	98	98	306
H= -10, K= 0			
1	48	45	4
2	147	151	6
3	83	84	500
4	25*	15	23
5	98	102	503
6	91	94	499
7	135	138	503
8	39*	33	3
9	105	105	503
H= -10, K= 1			
1	98	98	130
2	75	77	108
3	98	99	111
4	37*	35	176
5	40*	40	684
6	82	80	623
7	142	142	631
8	140	132	626
H= -10, K= 2			
1	167	169	879
2	207	210	710
3	149	150	973
4	55	98	720
5	133	132	7
6	32*	26	355
7	119	117	78
8	69	68	628
H= -10, K= 3			
1	60	58	864
2	62	79	822
3	81	75	832
4	44*	43	949
5	26*	27	445
6	75	77	342
7	110	109	326
H= -9, K= 0			
1	107	108	504
2	21*	18	502
3	243	248	502
4	46	45	503
5	125	128	504
6	59	49	2
7	12*	9	996
8	177	176	3
9	91	88	3
H= -9, K= 1			
1	69	70	279
2	142	146	163
3	81	78	263
4	147	151	174
5	61	60	298
6	30*	37	239
7	139	139	570
8	63	61	118
9	104	105	592
H= -9, K= 2			
1	130	129	140
2	95	96	437
3	246	248	168
4	135	136	412
5	144	146	146
6	79	74	543
7	41*	34	955
8	155	152	677
9	103	99	808
H= -9, K= 3			
1	110	114	911
2	161	167	841
3	158	158	890
4	153	154	862
5	130	127	913
6	42*	30	729
7	64	60	176
8	44*	40	646
H= -9, K= 4			
1	58	58	822
2	76	74	139
3	150	153	877
4	129	130	109
5	107	108	848
6	54	49	151
H= -8, K= 0			
1	42*	22	2
2	102	94	499
3	99	84	504
4	160	165	502
5	224	229	502
6	118	117	502
7	82	79	502
8	68	64	499
9	36*	27	499
10	49	44	2
H= -8, K= 1			
1	113	114	531
2	158	160	101
3	225	231	602
4	75	71	763
5	203	208	643
6	77	76	753
7	149	152	667
8	152	152	37
9	42*	26	988
10	198	196	70
H= -8, K= 2			
1	106	107	863
2	48	29	603
3	93	89	9
4	69	67	318
5	142	139	165
6	42*	33	220
7	42*	32	24
8	18*	9	127
9	42*	41	881
H= -8, K= 3			
1	77	71	15
2	117	113	711
3	127	127	264
4	175	176	447
5	164	167	324
6	185	187	390
7	137	137	325
8	74	72	527
H= -8, K= 4			
1	36*	26	354
2	69	65	178
3	71	66	988
4	133	131	96
5	127	123	11
6	89	82	100
7	49	44	142
H= -8, K= 5			
1	59	58	642
2	93	91	290
3	67	65	878
4	165	159	167
5	91	86	943
H= -7, K= 0			
1	38*	20	510
2	177	173	501
3	6*	5	995
4	28*	30	1
5	68	66	6
6	110	112	3
7	256	260	2
8	55	58	5
9	117	116	3
10	20*	14	511
H= -7, K= 1			
1	143	145	78
2	297	307	76
3	69	62	655
4	200	206	42
5	249	259	630
6	76	75	5
7	143	145	626
8	39*	36	918
9	108	103	587
10	88	82	91
H= -7, K= 2			
1	69	69	162
2	125	128	763
3	33*	30	122
4	55	54	843
5	60	58	794
6	117	119	789
7	214	213	722
8	83	81	871
9	97	94	644
H= -7, K= 3			
1	128	126	892
2	108	104	700
3	106	103	145
4	127	127	529
5	174	180	294
6	107	107	441
7	93	92	281
8	88	86	487
9	62	58	187
H= -7, K= 4			
1	84	85	945
2	56	55	953
3	33*	34	961
4	81	81	565
5	64	63	511
6	146	144	512
7	162	161	465
8	125	121	570
H= -7, K= 5			
1	176	177	662
2	34*	30	398
3	169	169	766
4	105	106	181
5	108	108	871
6	107	104	140
H= -6, K= 0			
1	203	198	501
2	577	591	501
3	235	240	501
4	376	387	501
5	29*	1	148
6	41*	44	503
7	88	85	5
8	34*	26	0
9	126	124	3
10	88	64	502
H= -6, K= 1			
1	164	160	617
2	143	143	598
3	211	207	651
4	63	58	174
5	150	155	615
6	100	101	119
7	111	113	121
8	163	155	118
9	79	79	113
10	158	156	99
H= -6, K= 2			
1	92	91	101
2	337	346	143
3	88	83	261
4	229	234	108
5	96	98	736
6	87	89	899
7	123	129	681
8	102	103	888
9	128	129	642
10	74	68	102
H= -6, K= 3			
1	51	53	301
2	180	182	385
3	81	82	319
4	49	49	331
5	71	69	186
6	36*	31	869
7	142	140	912
8	106	106	884
9	97	93	904
H= -6, K= 4			
1	155	155	93
2	128	127	917
3	218	219	124
4	61	57	872
5	103	103	258
6	63	64	445
7	94	96	316
8	88	85	583
H= -6, K= 5			
1	52	54	884
2	163	165	142
3	45	45	896
4	73	75	151
5	74	72	738
6	39*	38	435
H= -6, K= 6			
1	170	170	749
2	112	109	658
3	196	197	778
H= -5, K= 0			
1	64	43	492
2	91	78	998
3	404	406	1
4	27*	12	6
5	484	491	1
6	105	109	999
7	129	121	2
8	80	75	506
9	42*	41	996
10	177	171	504
H= -5, K= 1			
1	125	117	730
2	55	39	731
3	326	332	679
4	143	145	665
5	197	204	676
6	71	69	735
7	69	71	893
8	44*	43	108
9	133	132	61
10	23*	10	34
H= -5, K= 2			
1	37*	28	390
2	133	127	887
3	295	294	647
4	88	84	51
5	343	352	630
6	51	38	22
8	157	155	229
9	137	136	411
10	211	208	221
H= -5, K= 3			
1	84	76	184
2	193	200	282
3	220	231	364
4	237	251	323
5	170	175	336
6	124	129	355
7	70	60	504
8	44*	44	97
9	84	79	724
H= -5, K= 4			
1	74	77	115
2	148	154	611
3	118	122	356
4	155	157	654
5	136	142	365
6	132	132	687
7	76	74	98
8	123	124	850
H= -5, K= 5			
1	107	111	707
2	42*	47	79
3	50	54	51
4	95	96	104
5	62	61	965
6	44*	40	176
7	20*	15	456
H= -5, K= 6			
1	71	73	728
2	114	116	291
3	27*	23	86
4	155	155	259
H= -4, K= 0			
1	41*	44	503
2	4*	3	624
3	237	229	2
4	176	172	1
5	232	238	3
6	142	140	1
7	131	134	3
8	5*	6	509
9	6*	6	20
10	70	67	503
H= -4, K= 1			
1	156	147	728
2	130	127	412
3	260	247	32
4	101	93	506
5	298	300	77
6	227	235	131
7	154	157	74
8	59	33	212
9	94	98	70
10	159	157	593
H= -4, K= 2			
1	244	239	405
2	94	92	252
3	209	205	622
4	116	105	830
5	237	250	636
6	148	144	852
7	134	138	686
8	61	56	974
9	34*	29	625
10	81	80	61
H= -4, K= 3			
1	113	117	571
2	176	177	176
3	179	178	694
4	122	121	189
5	194	198	764
6	154	158	897
7	116	118	734
8	56	50	958
9	78	77	668
H= -4, K= 4			
1	229	231	69
2	91	81	901
3	75	63	322
4	102	100	597
5	138	142	360
6	132	131	589
7	84	85	437
8	45	38	622
H= -4, K= 5			
1	47	48	150
2	93	94	874
3	19*	18	307
4	88	87	802
5	65	65	578
6	129	127	658
7	39*	35	491
H= -4, K= 6			
1	149	146	734
2	37*	28	278
3	35*	26	448
4	119	117	238
5	49	46	165
H= -3, K= 0			
1	313	298	1
2	28*	3	467
3	27*	17	486
4	120	101	0
5	35*	36	503
6	184	191	502
7	97	101	504
8	72	68	506
9	157	160	502
10	37*	30	997
H= -3, K= 1			
1	522	501	742
2	255	260	743
3	313	300	927
4	119	122	674
5	336	354	28
6	59	61	165
7	248	259	83
8	40*	31	465
9	123	121	89
10	84	80	521
H= -3, K= 2			
1	277	262	671
2	101	92	26
3	102	99	502
4	100	97	972
5	111	116	408
6	220	229	207
7	128	130	287
8	126	128	247
9	167	168	250
10	37*	28	351
H= -3, K= 3			
1	487	501	404
2	429	440	335
3	224	232	462
4	221	235	245
5	183	195	658
6	139	143	41
7	139	139	785
8	90	85	29
9	81	74	756
H= -3, K= 4			
1	127	128	408
2	36*	35	653
3	75	77	410
4	66	66	678
5	39*	35	263
6	132	132	918
7	58	58	917
8	103	102	946
H= -3, K= 5			
1	215	225	74
2	131	137	8
3	89	92	96
4	121	125	781
5	96	99	402
6	174	176	681
7	82	78	513
H= -3, K= 6			
1	30*	27	256
2	65	65	134
3	40*	37	92
4	61	58	96
5	62	52	923
H= -2, K= 0			
1	213	203	1
2	663	734	1
3	24*	4	360
4	600	612	1
5	82	73	1
6	106	100	1
7	104	100	503
8	34*	4	974
9	135	131	503
10	23*	11	999
H= -2, K= 1			
1	419	401	73
2	179	169	440
3	89	103	181
4	179	176	316
5	131	126	178
6	251	261	548
7	79	53	454
8	194	197	566
9	143	137	596
10	170	166	577
H= -2, K= 2			
1	146	144	687
2	356	319	748
3	43*	46	680
4	342	317	701
5	54	53	776
6	48	39	414
7	111	110	284
8	75	64	313
9	117	114	220
H= -2, K= 3			
1	241	246	748
2	146	146	29
3	192	197	782
4	232	245	945
5	179	186	764
6	78	72	108
7	58	52	656
8	53	56	244
9	112	104	433
H= -2, K= 4			
1	239	249	538
2	199	203	506
3	244	256	552
4	154	156	443
5	171	176	601
6	59	57	973
7	61	56	883
8	105	100	978
H= -2, K= 5			
1	46	48	372
2	99	100	662
3	85	87	405
4	134	139	630
5	120	121	337
6	34*	9	567
7	118	114	213
H= -2, K= 6			
1	145	151	214
2	154	152	140
3	138	192	233
4	128	125	111
5	134	130	293
H= -1, K= 0			
1	172	168	501
2	232	230	1
3	77	38	511
4	121	116	0
5	321	327	502
6	158	162	0
7	164	167	502
8	109	110	3
9	37*	40	0
10	182	183	3
H= -1, K= 1			
1	173	162	29
2	89	84	293
3	168	180	82
4	149	151	127
5	381	385	110
6	31*	18	166
7	130	128	82
8	23*	18	992
9	36*	33	641
H= -1, K= 2			
1	172	160	439
2	62	22	763
3	111	110	402
4	171	177	415
5	267	283	225
6	119	108	513
7	144	146	214
8	83	79	583
9	72	70	867
H= -1, K= 3			
1	86	82	716
2	183	186	22
3	130	132	808
4	183	192	910
5	212	219	844
6	83	82	975
7	57	51	733
8	20*	15	88
9	68	66	326
H= -1, K= 4			
1	55	62	452
2	107	115	32
3	59	62	703
4	227	239	62
5	174	177	846
6	136	139	56
7	97	95	825
8	56	54	127
H= -1, K= 5			
1	75	74	359
2	143	149	654
3	115	117	504
4	184	187	624
5	128	126	567
6	115	112	687
7	35*	30	412
H= -1, K= 6			
1	68	71	227
2	59	57	805
3	73	73	339
4	131	134	786
5	91	91	468
H= 0, K= 0			
1	221	213	1
2	685	813	1
3	152	131	998
4	177	175	0
5	349	361	502
6	59	14	987
7	202	201	503
8	64	52	500
9	83	83	503
H= 0, K= 1			
1	54	52	623
2	80	83	92
3	107	104	413
4	73	65	900
5	182	187	543
6	64	61	614
7	139	140	567
8	122	117	605
9	65	63	459
H= 0, K= 2			
0	767	785	655
1	185	161	427
2	335	304	557
3	119	113	386
4	162	158	377
5	319	344	234
6	128	122	361
7	172	175	181
8	79	75	335
9	63	60	117
H= 0, K= 3			
1	69	68	537
2	97	98	733
3	22*	29	156
4	174	183	628
5	103	104	313
6	70	68	561
7	86	86	373
8	68	69	454
H= 0, K= 4			
0	213	208	429
1	300	317	626
2	72	47	144
3	176	182	684
4	156	160	989
5	167	176	868
6	150	146	41
7	94	97	821
H= 0, K= 5			
1	48	50	255
2	20*	16	221
3	41*	39	59
4	111	112	230
5	106	105	80
6	100	96	114
H= 0, K= 6			
0	176	170	140
1	276	287	273
2	88	79	52
3	136	137	299
4	56	93	773
H= 1, K= 0			
0	255	244	1
1	366	364	501
2	48	5	475
3	420	413	501
4	47	26	4
5	181	177	501
6	79	78	4
7	33*	25	494
8	132	133	3
9	31*	24	9
H= 1, K= 1			
0	555	547	100
1	421	427	146
2	161	174	95
3	416	420	154
4	189	196	92
5	195	208	541
6	54	39	864
7	198	197	562
8	109	109	660
9	133	135	581
H= 1, K= 2			
0	108	91	739
1	156	141	92
2	44*	34	848
3	195	186	134
4	114	120	844
5	135	134	4
6	126	130	728
7	118	125	901
8	157	161	745
H= 1, K= 3			
0	333	321	783
1	250	254	872
2	260	261	789
3	278	290	898
4	198	209	776
5	138	141	197
6	94	93	605
7	150	152	229
8	102	102	454
H= 1, K= 4			
0	135	132	135
1	122	126	644
2	141	146	133
3	51	45	714
4	54	44	243
5	83	82	592
6	108	109	317
7	102	105	557
H= 1, K= 5			
0	75	68	559
1	160	158	622
2	109	109	575
3	171	167	619
4	53	53	492
5	41*	38	880
6	88	88	205
H= 1, K= 6			
0	100	95	860
1	86	84	365
2	120	119	813
3	41*	31	474
4	67	63	735
H= 2, K= 0			
0	118	109	2
1	244	232	501
2	40*	5	914
3	289	283	502
4	293	306	502
5	17*	2	747
6	82	81	502
7	15*	8	11
8	107	111	1
H= 2, K= 1			
0	367	359	32
1	363	349	477
2	80	75	947
3	304	302	521
4	75	50	597
5	232	242	525
6	67	23	786
7	101	105	466
8	120	116	113
H= 2, K= 2			
0	121	108	236
1	225	210	250
2	150	151	231
3	308	308	271
4	302	315	236
5	86	86	337
6	97	101	273
7	33*	39	375
8	90	86	697
H= 2, K= 3			
0	325	322	695
1	271	269	115
2	225	224	697
3	155	154	171
4	86	83	697
5	152	154	163
6	103	99	653
7	119	112	73
H= 2, K= 4			
0	42*	24	866
1	91	88	773
2	125	121	928
3	176	177	974
4	200	200	944
5	86	83	998
6	69	65	945
7	30*	31	33
H= 2, K= 5			
0	164	163	331
1	93	94	735
2	143	142	312
3	17*	14	183
4	89	84	213
5	45*	35	924
H= 2, K= 6			
0	94	89	994
1	25*	4	799
2	88	85	795
3	110	106	759
H= 3, K= 0			
0	16*	12	504
1	61	46	497
2	76	75	998
3	68	18	12
4	65	70	501
5	127	130	3
6	26*	24	498
7	94	95	4
8	86	84	502
H= 3, K= 1			
0	150	152	268
1	345	319	395
2	109	95	195
3	320	332	540
4	200	201	634
5	220	224	566
6	82	78	728
7	172	177	599
8	75	74	29
H= 3, K= 2			
0	135	128	957
1	83	77	530
2	113	110	795
3	72	67	786
4	50	41	889
5	137	145	699
6	99	99	875
7	113	113	697
H= 3, K= 3			
0	420	424	803
1	258	262	985
2	239	243	769
3	160	162	237
4	156	155	484
5	168	168	269
6	128	130	504
7	140	140	305
H= 3, K= 4			
0	77	75	693
1	78	78	164
2	33*	20	571
3	39*	33	60
4	29*	17	429
5	92	94	252
6	87	82	557
H= 3, K= 5			
0	157	160	458
1	86	86	608
2	89	87	305
3	89	88	91
4	174	170	153
5	106	105	37
H= 3, K= 6			
0	69	66	341
1	50	47	626
2	64	57	427
3	86	81	547
H= 4, K= 0			
0	417	413	502
1	31*	10	967
2	509	513	501
3	63	51	1
4	72	71	503
5	160	161	3
6	47	8	17
7	227	231	3
H= 4, K= 1			
0	148	143	964
1	73	72	546
2	155	149	987
3	70	71	142
4	61	61	848
5	97	101	84
6	82	91	82
7	67	61	95
H= 4, K= 2			
0	384	383	193
1	219	214	406
2	391	399	209
3	70	64	468
4	68	66	13
5	132	129	678
6	102	94	874
7	193	189	722
H= 4, K= 3			
0	126	122	699
1	135	133	272
2	94	91	655
3	87	76	187
4	54	47	477
5	27*	12	854
6	50	46	891
H= 4, K= 4			
0	263	260	883
1	277	277	70
2	215	215	907
3	125	125	87
4	94	91	607
5	99	93	304
H= 4, K= 5			
0	31*	30	520
1	36*	35	978
2	23*	10	803
3	65	61	856
4	43*	31	861
H= 4, K= 6			
0	111	105	570
1	205	201	751
2	89	82	616
H= 5, K= 0			
0	252	250	501
1	107	89	3
2	275	284	501
3	49	36	8
4	118	119	502
5	56	53	5
6	176	188	501
7	41*	21	2
H= 5, K= 1			
0	194	191	574
1	125	120	541
2	298	309	614
3	218	218	582
4	138	145	590
5	68	63	608
6	54	64	526
H= 5, K= 2			
0	152	151	89
1	121	121	772
2	170	164	66
3	91	89	742
4	113	105	950
5	85	84	750
6	105	98	134
H= 5, K= 3			
0	30*	18	536
1	126	123	412
2	164	165	412
3	168	166	345
4	61	56	343
5	60	58	463
H= 5, K= 4			
0	71	73	678
1	86	82	232
2	85	84	611
3	127	124	238
4	104	102	524
5	92	88	254
H= 5, K= 5			
0	79	76	5
1	184	183	143
2	150	147	120
3	171	167	106
H= 5, K= 6			
0	44*	42	383
1	88	85	763
H= 6, K= 0			
0	379	403	501
1	54	40	4
2	33*	31	497
3	222	226	3
4	84	77	5
5	177	182	3
6	85	80	2
H= 6, K= 1			
0	131	130	600
1	217	224	95
2	176	174	592
3	75	72	6
4	38*	31	547
5	110	110	54
6	76	59	614
H= 6, K= 2			
0	187	188	137
1	104	102	797
2	131	134	858
3	209	209	738
4	125	121	752
5	142	146	752
H= 6, K= 3			
0	111	108	103
1	73	75	788
2	150	147	174
3	52	46	535
4	92	91	102
5	44*	43	718
H= 6, K= 4			
0	33*	28	974
1	95	93	237
2	145	144	531
3	128	125	384
4	132	127	485
H= 6, K= 5			
0	128	125	704
1	55	52	373
2	112	109	740
H= 7, K= 0			
0	39*	14	515
1	53	53	502
2	33*	30	501
3	85	88	999
4	51	54	500
5	15*	16	509
H= 7, K= 1			
0	352	368	596
1	116	110	633
2	161	170	563
3	110	103	65
4	47	30	301
5	189	195	97
H= 7, K= 2			
0	63	67	454
1	90	87	235
2	64	65	416
3	46	38	693
4	63	65	350
H= 7, K= 3			
0	173	175	306
1	138	136	439
2	114	112	192
3	90	91	676
4	69	62	990
H= 7, K= 4			
0	29*	26	136
1	98	95	995
2	27*	26	101
3	29*	23	98
H= 7, K= 5			
0	91	83	73
1	168	165	165
H= 8, K= 0			
0	147	153	4
1	91	84	4
2	168	170	4
3	37*	35	5
4	69	71	4
H= 8, K= 1			
0	86	86	646
1	104	99	931
2	73	69	672
3	140	143	22
4	63	41	725
H= 8, K= 2			
0	206	214	711
1	169	174	851
2	207	209	690
3	113	115	880
H= 8, K= 3			
0	120	117	256
1	123	121	482
2	114	114	280
3	72	69	596
H= 8, K= 4			
0	133	136	396
1	116	115	538
H= 9, K= 0			
0	22*	4	442
1	35*	1	805
2	96	95	3
3	67	63	503
H= 9, K= 1			
0	65	65	65
1	100	99	78
2	110	104	117
3	137	141	106
H= 9, K= 2			
0	75	75	466
1	84	81	2
2	92	93	610
H= 9, K= 3			
0	37*	18	150
1	56	53	852
H= 9, K= 4			
0	56	55	245
H= 10, K= 0			
0	112	110	5
1	38*	39	502
H= 10, K= 1			
0	63	62	627
1	67	70	599
H= 10, K= 2			
0	152	150	691
1	78	73	983
H= 11, K= 0			
0	137	137	3

** 10 F_o and 10 F_c. Unobserved reflections marked by*, phase angle alpha in millicycles.

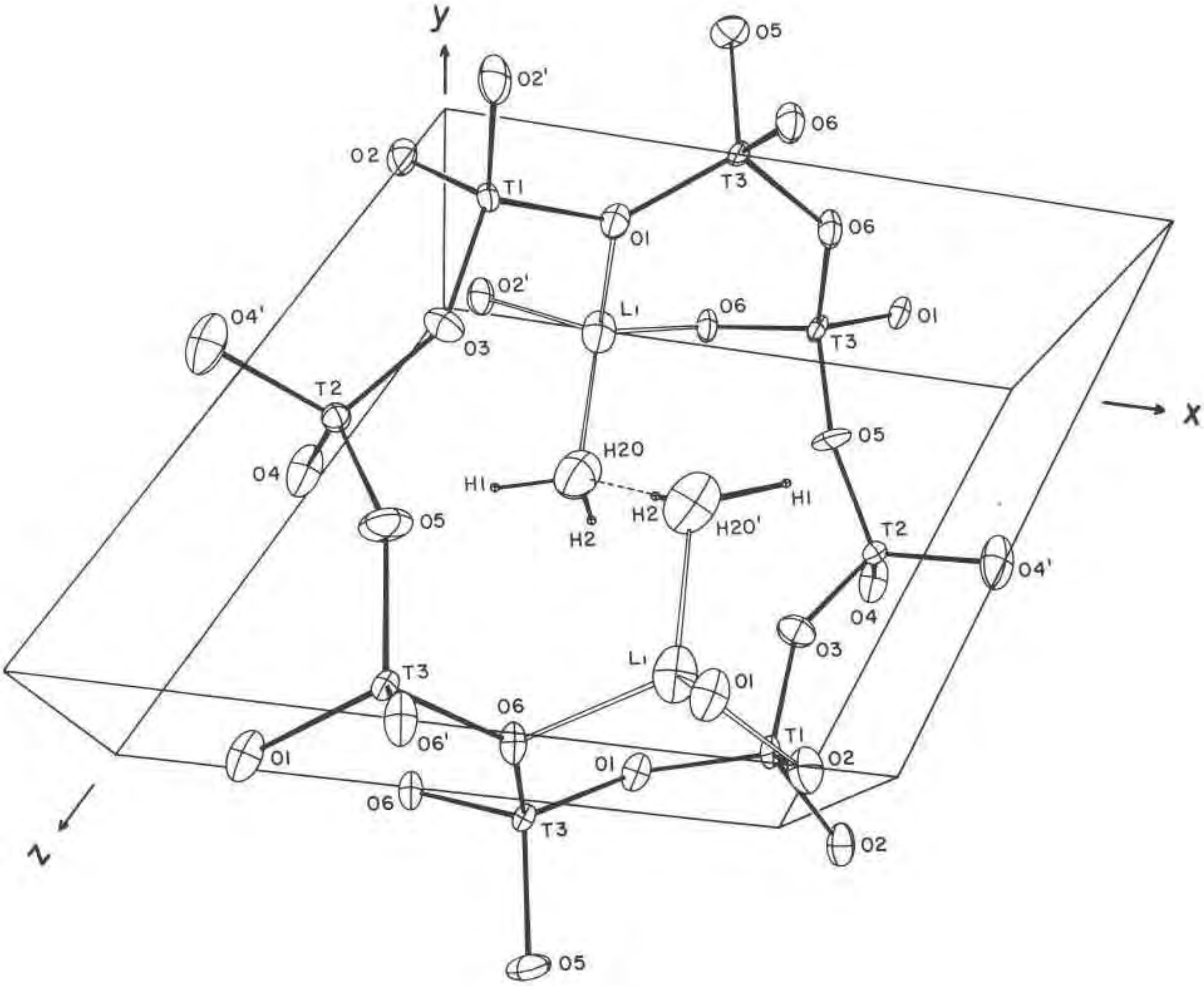

FIG. 1. A three-dimensional view of the bikitaite structure. Plotted with the ORTEP program, ellipsoids are drawn at 60 percent probability.

all valence sums fall within the expected limits except O(7) which has a residual charge of ≈ 0.24 v.u., a value which suggests that O(7) must participate in weak hydrogen bonding with either O(3) or O(4) or both. Clarification of the hydrogen bonding in bikitaite must await the results of a neutron diffraction study of the mineral. A thermogravimetric analysis of the mineral failed to reproduce the three-stage dehydration curve described by Phinney and Stewart (1961), who suggested that the water molecules were located at two different sites in the crystal structure. Figure 4 shows the DTA and TGA data which indicate a one-stage dehydration which is consistent with the crystal structure here described.

The Si/Al contents of the tetrahedra as predicted from bond lengths according to the linear model of Jones (1968) are $Si_{1.0}$ for $T(2)$, and $Si_{0.5}Al_{0.5}$ for both $T(1)$ and $T(3)$. This curious combination of perfect order and perfect disorder is completely consistent with the chemical formula, and leads to some interesting observations. The oxygens of the $T(2)$ tetrahedron are all in 2-fold coordination, forming bridges to $T(1)$ or $T(3)$ tetrahedra. On the other hand, in the $T(1)$ and $T(3)$ tetrahedra three of the oxygens are in planar 3-fold coordination, having a link to Li as well as to the adjacent $Al_{0.5}Si_{0.5}$. The Li^+ thus provides the necessary charge balance, as mentioned above, and in this way the structure forces both $T(1)$ and $T(3)$ cations to have an equal

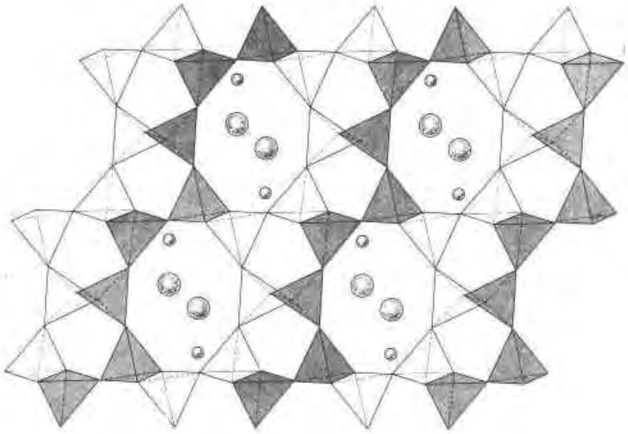

FIG. 2. The bikitaite structure projected along the y axis. The shaded tetrahedra, at $b \geq 1/2$ share corners with the unshaded tetrahedra at $b \leq 1/2$. The apparent tetrahedral edge-sharing is an illusion of the projection (see Fig. 3). H_2O is shown as large circles, Li as small circles occupying the large channels in the structure. The z-axis is parallel to the shaded tetrahedral "chains", the x-axis is horizontal.

charge which must be less than 4+ and can only be attained by complete disorder of the remaining Si and Al.

It is perhaps instructive to tabulate the mean bond lengths of the bridging oxygens between the various types of tetrahedra, and to compare with similar types in low albite (Ribbe *et al*, 1969) and maximum microcline (Brown and Bailey, 1964).

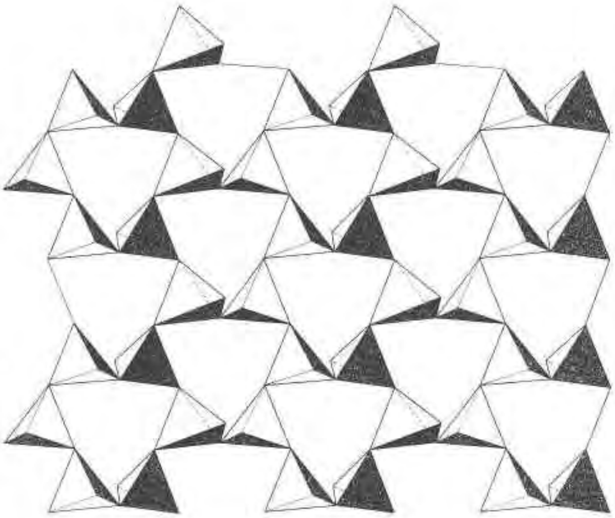

FIG. 3. Part of the bikitaite structure projected on the z-axis from $c = +1/3$ to $c = -1/3$. Only the tetrahedra are shown. The y-axis is vertical and the x-axis is horizontal.

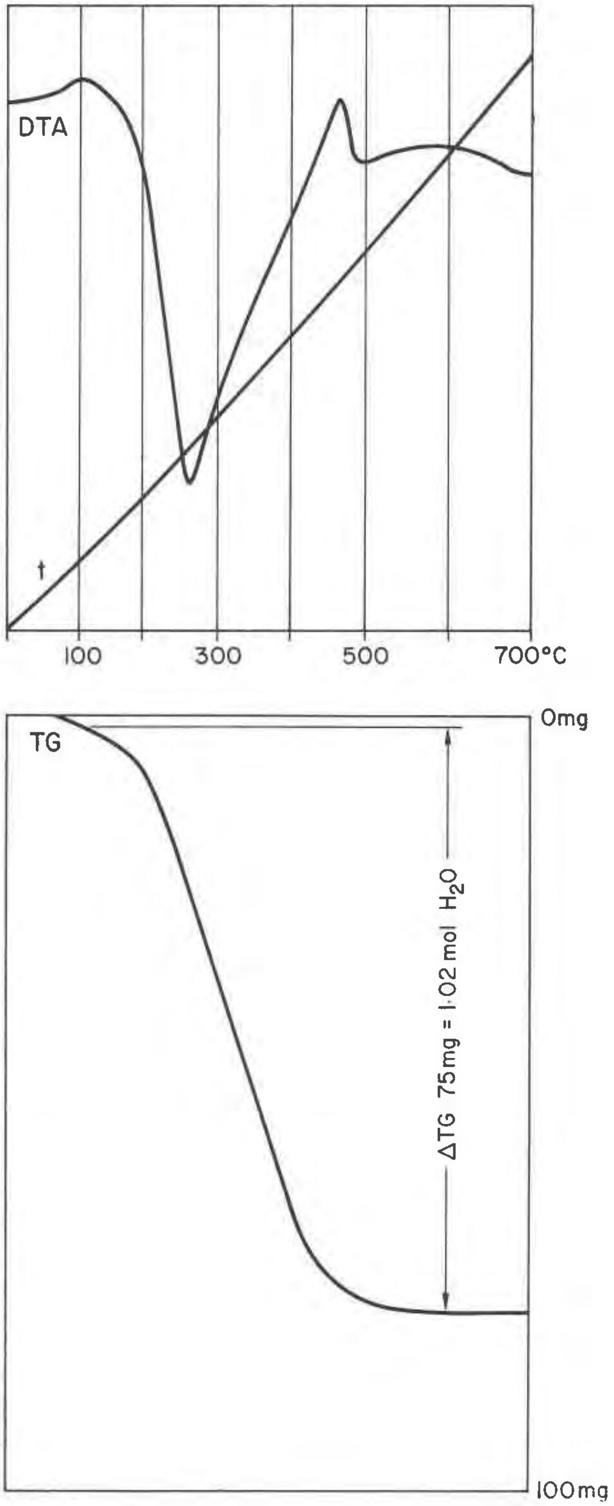

FIG. 4. Differential thermal analysis and dehydration curve of bikitaite. Initial sample weight = 0.8344 g, heating rate 5°C/min. Both DTA and TG curves taken simultaneously on the "Derivatograph" (Orion, Budapest).

	Bikitaite	Low Albite	Max. Microcline
Si-O(→Al)	—	1.596Å	1.588Å
Si-O(→$Al_{0.5}Si_{0.5}$)	1.597Å	—	—
Si-O(→Si)	1.625Å	1.621Å	1.624Å
$Al_{0.5}Si_{0.5}$-O(→Si)	1.666Å	—	—
$Al_{0.5}Si_{0.5}$-O(→$Al_{0.5}Si_{0.5}$)	1.686Å	—	—

The asymmetrical positioning of oxygen with respect to Si and $Al_{0.5}Si_{0.5}$ is to be expected, but a further asymmetry exists in the $Al_{0.5}Si_{0.5}$–O–$Al_{0.5}Si_{0.5}$ linkage which is less easily explained. In this case the mean length of one arm of the arrangement is 1.678Å, the other 1.696Å. The influence of the Li on the O position is negligible. This is so because in the cases of the coordination triangle of both O(1) and O(2), the *T*-cation which is further from O is closer to Li; only in the case of O(6) is one *T*-cation closer to both Li and O together. Perhaps some asymmetry in the sp^2 hybridization of oxygen is responsible, but beyond this the authors feel unable to comment.

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References

Agron, P. A., W. R. Busing, and H. A. Levy (1972) A neutron diffraction study of LiOH·H_2O. A.C.A. Winter Meeting, University of New Mexico, Albuquerque, N.M., p. 52.

Appleman, D. E. (1960) The crystal structure of bikitaite $LiAlSi_2O_6H_2O$ (abstr.). *Acta Crystallogr.* **13,** 1002.

Baur, W. (1964) On the crystal chemistry of salt hydrates, a neutron diffraction study of magnesium sulfate tetrahydrate. *Acta Crystallogr.* **17,** 863–869.

——— (1972) Prediction of hydrogen bonds and hydrogen atom positions in crystalline solids. *Acta Crystallogr.* **B28,** 1456–1465.

Brown, B. E., and S. W. Bailey (1964) The structure of maximum microcline. *Acta Crystallogr.* **17,** 1391–1400.

Cromer, D. T., and J. B. Mann (1968) X-ray scattering factors computed from numerical Hartree-Fock wave functions. *Acta Crystallogr.* **A24,** 321–324.

Drysdale, D. J. (1971) A synthesis of bikitaite. *Amer. Mineral.* **56,** 1718–1723.

Ellison, R. D. (1962) Xfls—an extensively modified version of Orfls. *U.S. Nat. Tech. Inform. Serv.* Ornl-tm-**305.**

Hamilton, W. C., and J. A. Ibers (1968) *Hydrogen Bonding in Solids.* Benjamin, N.Y.

Hauptman, H., and J. Fisher (1971) Phase determination by least-squares analysis of structure invariants. *Acta Crystallogr.* **B27,** 1550–1561.

Hurlbut, C. S., Jr. (1957) Bikitaite $LiAlSi_2O_6·H_2O$, a new mineral from Southern Rhodesia. *Amer. Mineral.* **42,** 792–797.

——— (1958) Additional data on bikitaite. *Amer. Mineral.* **43,** 768–770.

Ibers, J., and C. Hamilton (1964) Dispersion corrections and crystal structure refinements. *Acta Crystallogr.* **17,** 781–782.

Jones, J. B. (1968) Al–O and Si–O tetrahedral distances in aluminosilicate framework structures. *Acta Crystallogr.* **B24,** 355–358.

Karle, I. L., and J. Karle (1966) An application of the symbolic addition procedure to space group $P2_1$ and the structure of the alkaloid panamine $C_{20}H_{33}N_3$. *Acta Crystallogr.* **21,** 860–868.

Karle, J., and H. Hauptman (1966) Structure invariants and semi-invariants for non-centrosymmetric space groups. *Acta Crystallogr.* **21,** 849–859.

Larson, A. C., and M. Drew (1968) Tanfor, a program for investigating phase relationships and tangent formula refinement in non-centrosymmetric crystals. Lawrence Radiation Laboratory, University of California, Berkeley, California, 94720. (Second version extensively modified by S. Motherwell.)

Leavens, P. B., C. S. Hurlbut, Jr., and J. A. Nelson 1956) Eucryptite and bikitaite from King's Mountain, North Carolina. *Amer. Mineral.* **53,** 1202–1207.

Ondik, H., and D. Smith (1962) Interatomic distances in inorganic compounds. *International Tables for X-ray Crystallography,* Vol. III, Kynoch Press, pp. 213–215.

Orffe (1962) A Fortran crystallographic function and error program. *Oak Ridge Nat. Lab. Rep.* **TM-306.**

Ortep (1965) A Fortran thermal-ellipsoid plot program for crystal structure illustrations. *Oak Ridge Nat. Lab. Rep.* **3794.**

Phinney, W. C., and D. B. Stewart (1961) Some physical properties of bikitaite and its dehydration and decomposition products. *U.S. Geol. Surv. Prof. Pap.* **424,** 353–357.

Ribbe, P. H., H. D. Megaw, and W. H. Taylor (1969) The albite structures. *Acta Crystallogr.* **B25,** 1503–1518.

Rucklidge, J. C., and E. L. Gasparrini (1969) *A computer program for processing electron microprobe analytical data.* Department of Geology, University of Toronto.

Templeton, D. H. (1962) Dispersion corrections for atomic scattering factors. *International Tables for X-ray Crystallography,* Vol. III, Kynoch Press, pp. 213–215.

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