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The Crystal Structure of Leifite, $Na_6[Si_{16}Al_2(BeOH)_2O_{39}].1{\cdot}5H_2O$

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The crystal structure of leifite, $Na_6[Si_{16}Al_2(BeOH)_2O_{39}].1{\cdot}5H_2O$, has been determined by X-ray methods from three-circle manual diffractometer data. Leifite crystallizes in the space group $P\bar{3}m1$ with cell constants $a=14{\cdot}352$ (2) and $c=4{\cdot}852$ (3) Å. The structure has been solved by direct methods and has been refined by full-matrix least-squares methods to an R value of 0·049. The crystal structure of leifite closely approaches the rank of a tetrahedral framework with a ratio of 20/41 between the number of the tetrahedral cations and that of the anions. The only vertex which breaks the three-dimensional linking of tetrahedra belongs to a beryllium tetrahedron and is an equipoint for diadochic (OH) and (F). The three-dimensional linkage of tetrahedra gives rise to several chains and rings.

Introduction

Leifite is essentially an aluminum, beryllium and sodium silicate, bearing water, hydroxyl groups and fluorine. It is closely associated with feldspar in the type locality of Narssârsuk, Greenland. Leifite was first described by Bøggild (1915) who reported the chemical formula quoted by Strunz (1970). Recently the whole problem of leifite has been reinvestigated by Micheelsen & Petersen (1970) who pointed out the presence of beryllium in the chemical composition. Their revised formula is given in Table 1. These authors state that the small amount of leifite available did not allow a total wet chemical analysis; the formula was built up by microchemical and instrumental techniques.

Experimental

The crystal used for data collection was an irregular hexagonal prism, 0·29 mm long, with maximum and minimum thicknesses of 0·125 × 0·083 mm; it was mounted parallel to the elongation (*c*) axis. The cell dimensions and the intensities were obtained with a GEC X-RD6 manual diffractometer, equipped with pulse-height selector and scintillator counter. Ni-filtered Cu $K\alpha$ radiation was used for the determination of the unit-cell constants and Zr-filtered Mo $K\alpha$ radiation for the determination of the intensities. To confirm the cell dimensions (Table 1), the extrapolation function $\frac{1}{2}[(\cos^2\theta/\sin\theta)+(\cos^2\theta/\theta)]$ for the $h00$ and $00l$ reflexions was used.

The intensity data were collected by the ω–2θ scanning technique with a scanning rate of 2° min^{-1} and integration range between 1·2 and 2° according to the peak width; an attenuation filter was inserted in front of the counter window when required (> 10000 counts sec^{-1}). One standard reflexion was measured twice a day; its intensity was constant within 3%; 439 unique reflexions were measured ($\theta_{\text{Mo }K\alpha}\le 25°$), of which 99 were considered to be unobservable. A standard deviation was assigned to each of the remaining 340 reflexions, on the basis of the following formula: $\sigma(I)=[I+(B_1+B_2)B_1/B_2]^{1/2}$, where B_1 and B_2 are the two backgrounds at the integration extremes, with $B_1>B_2$. The B_1/B_2 term is an empirical factor, ≥ 1, introduced to take account of the decrease in reliability of a measure when the background asymmetry increases.

The space group was determined by the symmetry and the statistics of the intensities.

No correction for absorption was made because of the low absorption coefficient of the crystal (Table 1) and the narrow diffraction range ($0<\theta\le 25°$).

The data reduction and all the calculations were carried out with a UNIVAC 1108 computer *via* terminal at the Centro di Calcoli numerici of Pavia. Refinement on F's was carried out with a locally modified *ORFLS* full-matrix least-squares program (Busing, Martin & Levy, 1962), which includes the secondary extinction correction. The atomic scattering factors used for Si(2), Si(3), O and Be were those listed by Hanson, Herman, Lea & Skillman (1964); that for Si(1) was obtained by averaging the values of (2Si + Al)/3; the scattering curves for Na^+ and $O(8)=0{\cdot}6(F^-)+0{\cdot}4(OH^-)$ were taken from *International Tables for X-ray Crystallography* (1962).

Solution and refinement of the structure

The crystal structure was solved by application of Sayre's equation, and also by taking into account the Patterson synthesis. The more consistent of the seven sign sets led to the correct solution but not in a straightforward way: several spurious peaks appeared in the first Fourier synthesis and the relative heights of the right peaks were far from the correct ratios; the beryllium atom, for instance, was represented by the most prominent peak. The very approximate starting image of the structure was improved by a trial-and-error process.

During the refinement the conventional R index dropped from the starting value of 0·60 to the final 0·049. The anisotropic thermal factors were included in the refinement after the residual was reduced to 0·065; the secondary extinction was negligible, *i.e.* no extinction factor was taken into account. No attempt was made to locate the hydrogen atoms.

The shifts calculated for the parameters in the final cycle of least-squares refinement were less than one-tenth of the standard deviation. At the end of the anisotropic refinement the β_{33}-values for O(6) and O(8) were negative ($-0{\cdot}007$ and $-0{\cdot}001$ respectively); the systematic error responsible for this was not detected, but the general picture of the thermal situation obtained after the anisotropic refinement was felt to be acceptable, as the standard deviations dropped remarkably after the anisotropy was taken into account. The least-

Table 1. *Crystal data*

Starting formula	$Na_{5\cdot3}(H_3O)_{0\cdot9}Si_{16\cdot1}Al_{2\cdot6}Be_{2\cdot0}B_{0\cdot2}O_{41\cdot0}F_{0\cdot6}(OH)_{3\cdot4}$
F.W.	1353
Crystal system	Trigonal
Space group	$P\bar{3}m1$ (No. 164)
Cell constants: a	14·352 ± 0·002 Å
c	4·852 ± 0·003
Volume	865·5 Å^3
Crystal density: (obs)	2·57 g cm^{-3}
(calc)	2·59 g cm^{-3} for $Z=1$
Linear absorption coefficient for Mo $K\alpha$ radiation	8·73 cm^{-1}
Number of observed reflexions	439
Statistical distribution of intensities	Slightly hypercentric

Table 2. *Final fractional coordinates and their standard deviations* (*in parentheses*)

	Equipoint	Occupancy	x/a	y/b	z/c
Si(1) = (Si, Al)	6(h)	1·00	0	0·2163 (2)	½
Si(2)	6(g)	1·00	0	0·3441 (2)	0
Si(3)	6(i)	1·00	0·4476 (1)	0·5524	0·3055 (5)
Be	2(d)	1·00	⅓	⅔	0·3727 (45)
Na	6(i)	1·00	0·7505 (2)	0·2495	0·2038 (7)
O(1)	6(i)	1·00	0·1003 (3)	0·8997	0·3953 (13)
O(2)	12(j)	1·00	0·3070 (4)	0·2607 (4)	0·2480 (8)
O(3)	12(j)	1·00	0·3592 (4)	0·4583 (4)	0·1021 (8)
O(4)	3(f)	1·00	½	½	½
O(5)	6(i)	1·00	0·3944 (2)	0·6056	0·4836 (11)
O(6) = (H_2O)	1(a)	1·00	0	0	0
O(7) = (H_2O)	1(b)	0·56 (6)	0	0	½
O(8) = (OH, F)	2(d)	1·00	⅓	⅔	0·0409 (16)

Table 3. *Anisotropic thermal parameters and their standard deviations* (*in parentheses*)

The form of the anisotropic temperature factor ($\times 10^4$) is $\exp(-h^2\beta_{11}-k^2\beta_{22}-l^2\beta_{33}-2hk\beta_{12}-2hl\beta_{13}-2kl\beta_{23})$. The B_{eq} values are the equivalent isotropic temperature factors proposed by Hamilton (1959).

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B_{eq}
Si(1)	17 (2)	20 (2)	68 (13)	8	−10 (4)	−5	1·0
Si(2)	17 (2)	20 (2)	95 (13)	9	3 (4)	2	1·1
Si(3)	15 (2)	15	58 (11)	9 (2)	0 (2)	0	0·8
Be	23 (11)	23	113 (107)	12	0	0	1·3
Na	34 (2)	34	122 (18)	14 (3)	12 (3)	−12	1·9
O(1)	46 (5)	46	156 (34)	16 (5)	−15 (6)	15	2·6
O(2)	27 (4)	24 (4)	131 (21)	10 (3)	37 (7)	29 (7)	1·5
O(3)	24 (4)	23 (4)	100 (20)	15 (3)	−30 (7)	−35 (7)	1·2
O(4)	30 (6)	30	104 (38)	29 (7)	−8 (6)	8	1·2
O(5)	22 (4)	22	58 (27)	16 (4)	7 (4)	−7	1·0
O(6)	15 (7)	15	0 (59)	7	0	0	0·6
O(7)	61 (27)	61	910 (329)	30	0	0	5·4
O(8)	10 (4)	10	0 (37)	5	0	0	0·4

squares program automatically set the β_{33}-values for O(6) and O(8) equal to zero by giving an identical attenuation factor for all the final variations of the β_{ij}'s; this was done in order to carry out the analysis of the anisotropic thermal parameters shown in Table 4.

The final fractional atomic coordinates and the anisotropic thermal parameters, as well as their standard deviations, are listed in Tables 2 and 3. Observed and calculated structure factors are listed in Table 5.

Table 4. *Analysis of the anisotropic thermal parameters*

Root mean square thermal vibrations (Å) along the ellipsoid axes and angles (≤90°) between the crystallographic axes and the principal axes (U_i) of the vibration ellipsoids.

	R.m.s.	U_ia	U_ib	U_ic
Si(1)	0·08	68	90	25
	0·12	39	90	65
	0·13	60	0	90
Si(2)	0·10	72	90	21
	0·12	36	90	69
	0·13	60	0	90
Si(3)	0·08	88	88	2
	0·10	30	30	88
	0·11	60	60	90
Be	0·12	90	90	0
	0·13	—	—	90
	0·13	—	—	90
Na	0·11	73	73	19
	0·16	60	60	90
	0·19	35	35	71
O(1)	0·13	76	76	16
	0·18	60	60	90
	0·22	34	34	74
O(2)	0·07	68	73	41
	0·15	55	17	74
	0·17	43	86	53
O(3)	0·06	82	65	36
	0·12	23	38	84
	0·17	68	64	54
O(4)	0·01	35	35	70
	0·12	73	73	20
	0·18	60	60	90
O(5)	0·06	56	56	41
	0·11	49	49	49
	0·14	60	60	90
O(6)	0·00	90	90	0
	0·11	—	—	90
	0·11	—	—	90
O(7)	0·33	90	90	0
	0·22	—	—	90
	0·22	—	—	90
O(8)	0·00	90	90	0
	0·09	—	—	90
	0·09	—	—	90

Description of the structure

Interatomic distances and angles and their standaıd deviations are listed in Table 6; Fig. 1 shows the atomic labelling; the sign (′) refers to equivalent atoms of which the *z* coordinate is quoted.

Table 5. *Observed and calculated structure factors* (×10)

An asterisk denotes an unobserved reflexion.

k	l	$10F_o$	$10F_c$
0 k l			
0	1	216	-196
0	2	659	550
0	3	183	-158
0	4	1175	1110
0	5	325	-363
1	0	211	-223
1	1	302	-338
1	2	105	92
1	3	356	322
1	4	537	470
1	5	* 59	108
2	0	293	282
2	1	130	-145
2	2	181	155
2	3	605	576
2	4	187	-195
2	5	416	-408
3	0	626	630
3	1	2113	2090
3	2	295	313
3	3	410	397
3	4	694	644
3	5	405	391
4	0	776	761
4	1	338	-385
4	2	92	82
4	3	212	-202
4	4	574	563
5	0	* 34	13
5	1	1459	-1371
5	2	445	432
5	3	491	-482
5	4	728	694
6	0	* 38	106
6	1	* 39	-29
6	2	1505	1421
6	3	729	724
6	4	* 56	118
7	0	476	-465
7	1	165	156
7	2	499	-495
7	3	172	-196
7	4	* 58	-108
8	0	551	509
8	1	422	-411
8	2	480	492
8	3	314	-318
8	4	* 60	-1
9	0	1276	1233
9	1	406	-424
9	2	469	497
9	3	599	601
10	0	* 51	111
10	1	476	-494
10	2	466	489
10	3	466	-445
11	0	466	456
11	1	561	539
11	2	* 57	84
12	0	170	183
12	1	651	612
12	2	141	171
13	0	* 60	34
13	1	351	-359
1 k l			
0	1	500	-610
0	2	434	403
0	3	493	-488
0	4	317	-306
0	5	* 59	57
1	0	236	-293
1	1	323	-369
1	2	142	90
1	3	170	-187
1	4	183	-193
1	5	* 60	33
2	0	550	-575
2	1	250	215
2	2	499	-468
2	3	214	203
2	4	449	-433
2	5	269	302
3	0	385	366
3	1	441	-489
3	2	550	-559
3	3	177	167
3	4	188	192
3	5	310	-298
4	0	219	190
4	1	371	299
4	2	288	289
4	3	324	-333
4	4	450	-436
5	0	251	267
5	1	60	-72
5	2	* 43	-63
5	3	216	230
5	4	201	217
6	0	258	238
6	1	482	466
6	2	163	-174
6	3	433	-416
6	4	91	124
7	0	389	-418
7	1	* 44	38
7	2	272	-292
7	3	205	222
7	4	* 59	-31
8	0	97	-109
8	1	291	273
8	2	474	474
8	3	117	-117
8	4	178	200
9	0	* 49	-24
9	1	466	-465
9	2	* 53	31
9	3	247	-243
10	0	* 52	-69
10	1	* 53	99
10	2	137	-117
10	3	120	-129
11	0	231	-243
11	1	313	-305
11	2	* 59	52
12	0	* 58	-73
12	1	* 59	-80
2 k l			
0	1	387	345
0	2	170	142
0	3	149	139
0	4	73	-84
0	5	* 60	-120
1	1	1119	1083
1	2	119	-146
1	3	71	-82
1	4	83	88
1	5	170	198
2	0	653	-688
2	1	205	-247
2	2	* 38	-58
2	3	155	137
2	4	195	-195
2	5	* 61	-49
3	0	181	-191
3	1	1016	956
3	2	* 40	-42
3	3	250	-248
3	4	* 54	64
4	0	119	-146
4	1	305	-333
4	2	656	658
4	3	168	-182
4	4	141	-144
5	0	139	-152
5	1	* 40	17
5	2	641	-642
5	3	123	-112
5	4	179	-177
6	0	204	-210
6	1	195	179
6	2	259	250
6	3	202	187
6	4	234	-224
7	0	* 45	-48
7	1	130	124
7	2	411	-416
7	3	* 54	105
7	4	* 60	-115
8	0	* 48	31
8	1	134	-141
8	2	173	-155
8	3	113	-117
9	0	641	659
9	1	176	161
9	2	254	-226
9	3	243	245
10	0	315	-319
10	1	87	107
10	2	147	-144
11	0	* 57	-29
11	1	* 58	115
11	2	339	-293
12	0	* 60	-11
12	1	323	318
3 k l			
0	1	74	-79
0	2	837	827
0	3	521	485
0	4	322	354
0	5	400	445
1	1	72	-88
1	2	197	180
1	3	79	63
1	4	192	194
1	5	319	-310
2	1	193	-192
2	2	361	353
2	3	155	153
2	4	392	-419
3	0	1049	1060
3	1	487	493
3	2	269	-246
3	3	1203	1175
3	4	221	235
4	0	* 38	-28
4	1	105	87
4	2	319	-299
4	3	71	91
4	4	* 56	-20
5	0	159	175
5	1	251	-237
5	2	127	121
5	3	430	424
5	4	* 58	14
6	0	335	356
6	1	886	867
6	2	362	359
6	3	93	93
6	4	445	441
7	0	335	-340
7	1	187	180
7	2	361	-372
7	3	* 56	102
8	0	363	-350
8	1	603	610
8	2	126	-121
8	3	218	233
9	0	* 53	-25
9	1	115	104
9	2	694	640
9	3	281	284
10	0	* 56	12
10	1	* 57	44
10	2	* 59	19
11	0	* 59	-37
11	1	* 60	57
4 k l			
0	1	629	-627
0	2	654	-643
0	3	1230	-1202
0	4	679	691
1	1	312	-368
1	2	278	268
1	3	120	-108
1	4	* 67	86
2	1	652	-599
2	2	140	135
2	3	101	-108
2	4	151	166
3	1	225	199
3	2	121	117
3	3	* 50	-25
3	4	565	-555
4	0	897	868
4	1	316	-323
4	2	113	102
4	3	595	-628
4	4	* 58	26
5	0	225	-227
5	1	766	-751
5	2	595	602
5	3	316	341
5	4	157	184
6	0	183	169
6	1	383	-365
6	2	114	-137
6	3	* 56	-36
7	0	342	-335
7	1	185	178
7	2	125	157
7	3	91	119
8	0	282	261
8	1	100	-99
8	2	274	-285
8	3	* 60	57
9	0	* 55	-82
9	1	475	-455
9	2	* 59	5
10	0	175	165
10	1	177	-175
5 k l			
0	1	45	-33
0	2	1738	1693
0	3	404	-421
0	4	260	260
1	1	101	84
1	2	337	-326
1	3	104	89
1	4	* 56	-91
2	1	* 40	18
2	2	324	-356
2	3	213	231
2	4	113	-90
3	1	202	-196
3	2	123	-126
3	3	397	370
3	4	315	299
4	1	84	71
4	2	297	305
4	3	751	-737
4	4	146	156
5	0	816	812
5	1	438	-417
5	2	* 51	69
5	3	440	-416
6	0	* 49	13
6	1	514	495
6	2	431	-438
6	3	108	-107
7	0	309	-302
7	1	* 53	41
7	2	* 56	51
7	3	* 60	64
8	0	140	142
8	1	* 56	-16
8	2	165	179
9	0	424	404
9	1	149	-162
9	2	387	374
10	0	315	355
6 k l			
0	1	1204	1182
0	2	405	432
0	3	132	-124
0	4	588	572
1	1	* 41	-36
1	2	224	-224
1	3	* 51	36
1	4	229	-216
2	1	540	553
2	2	* 47	-48
2	3	* 52	72
2	4	* 58	44
3	1	348	357
3	2	1067	1081
3	3	132	140
3	4	* 60	5
4	1	* 48	-34
4	2	* 51	97
4	3	79	-72
5	1	* 50	21
5	2	225	231
5	3	115	147
6	0	678	698
6	1	* 53	80
6	2	166	187
6	3	610	595
7	0	377	-372
7	1	117	135
7	2	153	-139
8	0	474	489
8	1	197	-204
8	2	* 60	-10
9	0	229	244
9	1	458	441
7 k l			
0	1	210	-195
0	2	464	-470
0	3	770	767
0	4	* 58	-2
1	1	* 44	46
1	2	281	-300
1	3	112	125
1	4	326	-340
2	1	* 46	-57
2	2	439	-428
2	3	210	236
2	4	* 60	34
3	1	156	153
3	2	272	-280
3	3	137	-120
4	1	481	-483
4	2	297	-271
4	3	* 58	-26
5	1	526	537
5	2	* 56	62
5	3	* 60	0
6	1	141	-134
6	2	108	-98
7	0	81	-62
7	1	* 58	89
7	2	* 60	-54
8	0	220	-233
8	1	* 61	-51
8 k l			
0	1	587	612
0	2	247	248
0	3	423	-407
0	4	477	491
1	1	515	-510
1	2	319	289
1	3	141	-146
1	4	61	-39
2	1	77	-78
2	2	* 52	30
2	3	* 57	80
3	1	308	324
3	2	235	226
3	3	198	237
4	1	* 53	-14
4	2	* 56	-122
4	3	* 60	-12
5	1	375	-368
5	2	* 58	62
6	1	148	-167
6	2	* 60	37
7	1	297	297
9 k l			
0	1	479	479
0	2	705	727
0	3	186	208
1	1	123	-93
1	2	* 53	19
1	3	299	-291
2	1	* 52	64
2	2	300	-310
2	3	72	103
3	1	824	824
3	2	247	249
3	3	172	200
4	1	217	-197
4	2	262	279
5	1	101	105
5	2	* 61	0
6	1	* 75	99
10 k l			
0	1	816	-819
0	2	597	612
0	3	364	-387
1	1	219	-209
1	2	270	-206
1	3	* 60	40
2	1	117	-100
2	2	100	-80
3	1	184	-195
3	2	151	-169
4	1	367	-363
11 k l			
0	1	* 55	65
0	2	* 57	-1
1	1	377	378
1	2	124	123
2	1	148	180
2	2	317	-280
3	1	355	359
12 k l			
0	1	* 58	114
0	2	281	279
1	1	* 59	-19
2	1	129	-113
13 k l			
0	1	* 61	-140

There are four unique tetrahedrally coordinated cations in the structure: Be, Si(1), Si(2) and Si(3), all lying on mirrors or diads. Beryllium was readily identified on the basis of its electron density in the F_o Fourier map and of its multiplicity compared with the formula contents (it lies on a triad); the other tetrahedral cations were identified on the basis of their average distance from the surrounding oxygen atoms: 1·655 Å for Si(1), 1·605 Å for Si(2) and 1·617 Å for Si(3). Therefore the equipoints Si(2) and Si(3) were considered as filled with 'pure silicon', and the whole aluminum present in the structure was recognized to occupy the equipoint Si(1). The refinement and the balance of the electrostatic valences were assessed with the hypothesis of $\frac{2}{3}$ (Si) and $\frac{1}{3}$ (Al) in the latter position.

The crystal structure of leifite closely approaches, without reaching, the rank of a tetrahedral framework; in fact the ratio between the number of tetrahedral cations and that of the anions is 20/41. Only one vertex breaks the three-dimensional linkage of tetrahedra: O(8), *i.e.* an equipoint for diadochic (OH) and (F) that belongs to a beryllium tetrahedron. This feature is common to other silicates containing beryllium and fluorine or hydroxyl groups, for instance leucophanite, meliphanite and aminoffite (Coda, 1969); beryllium appears to compete with silicon in its ability to clasp these anions. The equipoint O(8) was filled with 0·6 (F) and 0·4 (OH) per unit cell. This ratio agrees well with the chemical analysis.

The three-dimensional linkage of tetrahedra gives rise to several chains and rings, which may be seen in Fig. 2. Pyroxene-like chains (*i.e.* with repeat units of two tetrahedra), all equivalent by symmetry and interconnected, run along the *c* axis; they are composed of Si(1) and Si(2), and the unit translation along **c**, 4·85 Å, is related to the existence of these chains. Moreover, two equivalent and interlinked chains, with repeat units of three tetrahedra, are composed of the sequence Si(3)–Si(2)–Si(3), and also run along **c**.

The rings of tetrahedra are listed at the end of the paper, for classification purposes. But, first, attention is drawn to the six-membered ring composed of Si(1) tetrahedra only, interlinked by O(1), surrounding the triad passing across the cell origin. The Fourier density map displays a maximum corresponding to an oxygen atom, O(6), on the origin; it can be interpreted as a water molecule, statistically distributed to fit the symmetry of the equipoint $\bar{3}m$. The water molecule O(6) is surrounded by six O(1) atoms and the O(1)–O(6) distance, 3·14 Å, may correspond to a weak hydrogen bond. Another maximum O(7), weaker than the previous one, was found in the same 'hollow', with coordinates (0, 0, $\frac{1}{2}$); the refinement of the weight of O(7), which was thought to be another water molecule, led to an occupancy factor of 0·56, and O(7) was interpreted as $\frac{1}{2}(H_2O)$, statistically distributed. The O(6)–O(7) and O(1)–O(7) distances, with the corresponding angles (Table 6), are consistent with a statistical system of hydrogen bonding.

As regards the silicon–oxygen distances (Cruickshank, 1961), a brief discussion is significant only for the 'pure' silicon atoms Si(2) and Si(3). The Si–O distance corresponding to the biggest Si–O–Si angle is the shortest for both silicons, as expected:

Si(2)–O(2)	1·59 Å	Si(2)–O(2)–Si(1)	139°
Si(2)–O(3)	1·62	Si(2)–O(3)–Si(3)	132
Si(3)–O(4)	1·61	Si(3)–O(4)–Si(3′)	180
Si(3)–O(3)	1·64	Si(3)–O(3)–Si(2)	132

The Si(3)–O(5) distance is naturally excluded from these considerations because the bridge refers to a beryllium atom.

The sodium ion, located on a mirror plane, has a coordination number of 5+2 (Fig. 1 and Table 6). The balance of the electrostatic valences is shown in Table 7; as one might expect, the longest Si–O distances cor-

Table 6. *Interatomic distances* (Å), *angles* (°) *and their standard deviations* (*in parentheses*)

An asterisk denotes atoms equivalent to those labelled by one cell translation along the *c* axis.

Si(1)–O(1)	(2×)	1·645 (3)
Si(1)–O(2)	(2×)	1·664 (5)
mean		1·655
O(1)–O(1′)		2·692 (8)
O(1)–O(2)	(2×)	2·738 (6)
O(1)–O(2′)*	(2×)	2·668 (7)
O(2)–O(2′)*		2·703 (8)
mean		2·701
Si(2)–O(2)	(2×)	1·589 (5)
Si(2)–O(3)	(2×)	1·621 (5)
mean		1·605
O(2)–O(2′)		2·667 (8)
O(2)–O(3)	(2×)	2·642 (7)
O(2)–O(3′)	(2×)	2·555 (6)
O(3)–O(3′)		2·657 (9)
mean		2·620
Si(3)–O(3)	(2×)	1·641 (4)
Si(3)–O(4)		1·609 (3)
Si(3)–O(5)		1·579 (6)
mean		1·617
O(3)–O(3″)		2·619 (9)
O(3)–O(4)	(2×)	2·638 (4)
O(3)–O(5)	(2×)	2·661 (7)
O(4)–O(5)		2·627 (6)
mean		2·641
Be—O(5)	(3×)	1·610 (9)
Be—O(8)		1·610 (3)
O(5)–O(5′)	(3×)	2·629 (12)
O(5)–O(8)	(3×)	2·630 (9)
Na—O(8)		2·398 (6)
Na—O(5)*	(2×)	2·405 (5)
Na—O(3)	(2×)	2·437 (5)
Na—O(2′)	(2×)	2·848 (6)
O(6)–O(7)		2·426 (3)
O(6)–O(1)		3·145 (7)
O(7)–O(1)		2·544 (8)

O(2)–Si(1)–O(2′)*		108·7 (0·4)
O(2)–Si(1)–O(1)	(2×)	111·7 (0·3)
O(2)–Si(1)–O(1′)	(2×)	107·5 (0·3)
O(1)–Si(1)–O(1′)		109·8 (0·6)
mean		109·5
O(2)–Si(2)–O(2′)		114·1 (0·4)
O(3)–Si(2)–O(3′)		110·1 (0·4)
O(2)–Si(2)–O(3′)	(2×)	110·8 (0·4)
O(2)–Si(2)–O(3)	(2×)	105·5 (0·2)
mean		109·5
O(3)–Si(3)–O(4)	(2×)	108·5 (0·3)
O(3)–Si(3)–O(3″)		105·9 (0·3)
O(3)–Si(3)–O(5)	(2×)	111·4 (0·4)
O(4)–Si(3)–O(5)		110·9 (0·4)
mean		109·5
O(5)–Be–O(5′)	(3×)	109·4 (0·4)
O(5)–Be–O(8)	(3×)	109·5 (0·4)
Si(1)–O(2)–Si(2)		138·5 (0·3)
Si(1)–O(1)–Si(1′)		141·3 (0·4)
Si(2)–O(3)–Si(3)		132·4 (0·4)
Si(3)–O(4)–Si(3′)*		180·0
Si(3)–O(5)–Be		127·3 (0·5)
O(1)–O(6)–O(7)		127·6 (0·5)
O(1)–O(7)–O(6)		101·5 (0·6)

respond to O(3), with the largest negative charge excess (2·2). O(1), with a remarkable charge deficiency (1·84), is involved in the hydrogen-bonding system with the water molecules O(6) and O(7). O(2) and O(5) are slightly deficient also, but the former obtains some residual charge from Na^+ [Na–O(2) distance = 2·85 Å] while the latter has the shortest distance from silicon.

The chemical formula most consistent with the structure investigation is the following:

$$\mathrm{Na_6[Si_{12}(Si_4Al_2)\,(BeX)_2O_{39}]\;.\;1{\cdot}5H_2O}\;.$$

$\mathrm{X=(OH,F)}$ in general, and in this case $\mathrm{X=(F_{0\cdot6}OH_{0\cdot4})}$. A shorter version of the formula is given in the title of this paper. This formula is consistent with Micheelsen & Petersen's analysis.

From a classificatory point of view, according to recent suggestions (Zoltai, 1960; Coda, 1969), leifite can be considered as a silicate belonging to the type of three-dimensional non-terminated structures of tetrahedra, with a Zoltai sharing coefficient $c=1{\cdot}975$ ($c=2$ in frameworks), or with a modified sharing coefficient $C=3{\cdot}9$ ($C=4$ in frameworks).

The n-membered loops of tetrahedra (Fig. 2), listed in order of decreasing frequencies f (which are given in parentheses), are as follows: $n=5$, Si(1)–Si(2)–Si(3)–Si(3)–Si(2), ($f=6$); $n=6$, Si(1)–Si(1)–Si(2)–Si(1)–Si(1)–Si(2), ($f=6$); $n=7$, Si(1)–Si(1)–Si(2)–Si(3)–Be–Si(3)–Si(2), ($f=6$); $n=4$, Si(2)–Si(3)–Si(2)–Si(3), ($f=3$); $n=6$, Si(1) × 6, ($f=1$). No silicate of this type was previously known; therefore this mineral establishes the structural family of leifite.

We wish to thank Dr Ole V. Petersen, Mineralogical Museum, Copenhagen, who made this investigation possible by providing a fine sample of leifite.

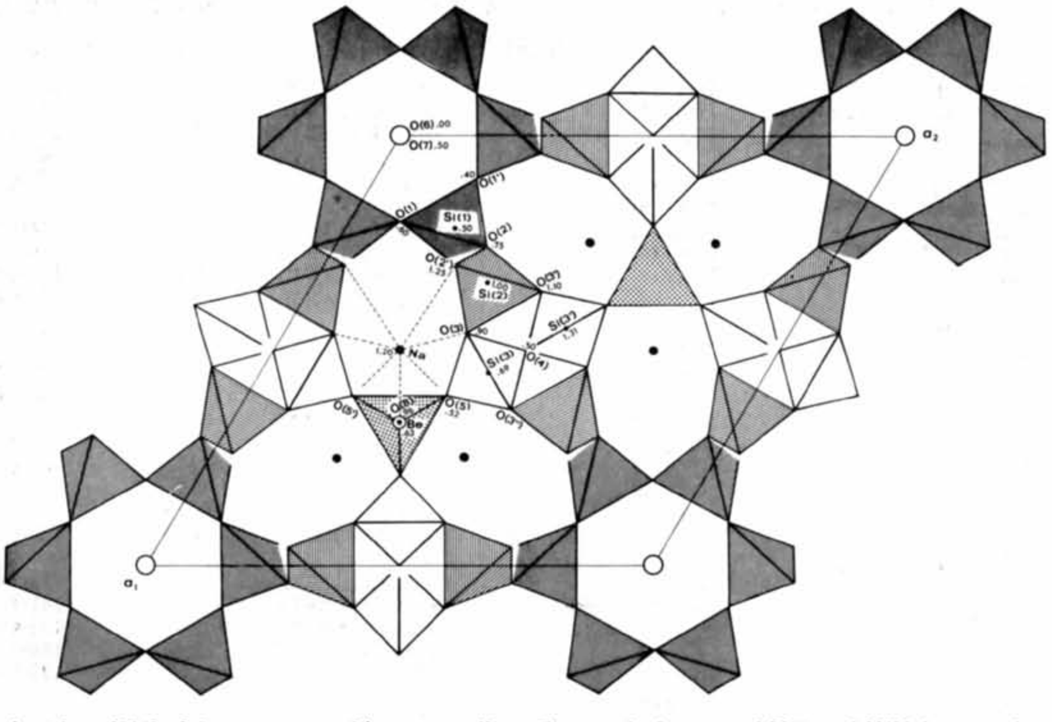

Fig. 1. Projection along [001] of the structure and its surroundings. The tetrahedra around Si(1) and Si(3′) have not been completed in order to avoid in the projection the false images of two tetrahedra Si(1), Si(2) sharing an edge and of a three-membered ring Si(3), Si(2), Si(3′). The atom O(2) completing the Si(1) tetrahedron is one c-translation below, while the atom O(4) completing the Si(3′)-tetrahedron is one c-translation above.

Table 7. *Balance of electrostatic valences*

Cation	Ionic strength	O(1)	O(2)	O(3)	O(4)	O(5)	O(8) = $0{\cdot}6(F^{-})+0{\cdot}4(\mathrm{OH}^{-})$
Si(1)	0·92	× 2	× 1				
Si(2)	1		× 1	× 1			
Si(3)	1			× 1	× 2	× 1	
Be	0·5					× 1	× 1
Na	0·2			× 1		× 2	× 3
		1·84	1·92	2·2	2	1·9	1·1

ADDENDUM

The referee raised some doubt about the validity of the structure proposed by us because of the angle Si(3)–O(4)–Si(3′) = ω of 180°: the correct space group could also have been $P321$ or $P3m1$, allowing O(4) to shift and the ω-angle to approach 140°. Although the intensity statistics had a slightly hypercentric distribution and the O(4) atom did not show any splitting in the Fourier map, we tried to refine the structure in the space groups $P321$ and $P3m1$ ($\omega = 140°$) to obtain additional evidence for the centrosymmetric model. At the end of the refinements the standard deviations had increased tenfold on average, and the ω angle again became nearly 180°. The form of the O(4) thermal ellipsoid is exactly that expected with an angle $\omega = 180°$, and confirms that the general picture of the thermal situation has physical meaning. Moreover, we used the '*DLS*' program written by Meier & Villiger (1969) to find the framework with the best bond lengths and angles in space groups $P321$ and $P3m1$, starting from $\omega = 170°$, and after several least-squares cycles the symmetry again became $P\bar{3}m1$, with ω nearly equal to 180°. Si–O–Si angles of 180° have been detected in at least four well refined structures, such as thortveitite and coesite (Baur, 1971).

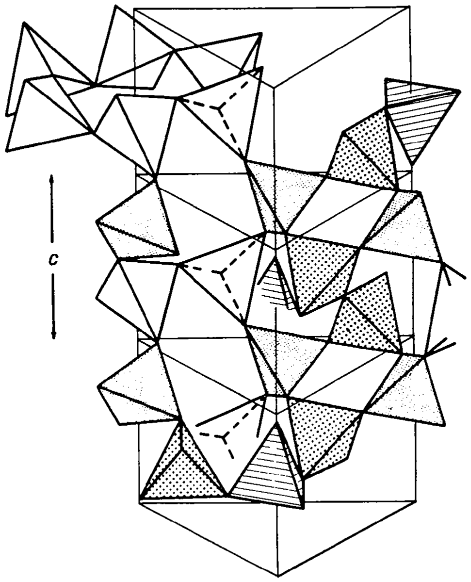

Fig. 2. Picture of the chains running along [001]. Unstippled tetrahedra refer to Si(1), thickly stippled to Si(2), thinly stippled to Si(3) and ruled tetrahedra to Be.

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Crystal Structure of Zinc *o*-Ethoxybenzoate Monohydrate

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Zinc *o*-ethoxybenzoate monohydrate, $ZnC_{18}H_{18}O_6.H_2O$, is monoclinic with $a = 9{\cdot}535\,(8)$, $b = 11{\cdot}610\,(10)$, $c = 8{\cdot}384\,(9)$ Å, $\beta = 92{\cdot}9\,(1)°$, $Z = 2$. The space group is determined as Pc after solving the structure from 1761 observed X-ray intensities collected on a diffractometer with Cu $K\alpha$ radiation and balanced filters. The final R is 7·1 % for the observed reflections. Zn is tetrahedrally coordinated by four oxygen atoms at 1·988 (2), 2·076 (9), 2·037 (7) and 2·054 (9) Å.

Introduction

Zinc *o*-ethoxybenzoate monohydrate ($ZnC_{18}H_{18}O_6.H_2O$) is the reaction product formed in ethoxybenzoic acid (EBA) dental cement (Brauer, 1965, 1967, 1972). The same compound can be synthesized from 12·3 g of ethoxybenzoic acid dissolved in 20 ml of methanol and 8·8 g of zinc oxide by heating for 6 h in a steam