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The Crystal Structure of Meliphanite*

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Meliphanite is a silicate of general formula $Ca(Na,Ca)BeSi_2O_6F$. It is tetragonal with space group $I\bar{4}$, $Z=8$. The cell parameters are: $a=10{\cdot}516$, $c=9{\cdot}887$, $c/a=0{\cdot}940$. The crystal structure has been solved by comparison with the structure of the closely related silicate melilite and on the basis of considerations on the electrostatic equilibrium. The final bond distances and angles are obtained from coordinates refined by the least-squares method applied to three-dimensional data (final R value 10·4 %). The crystal structure consists of infinite sheets of SiO_4 and BeO_4 tetrahedra between which Ca and (Na, Ca) are arranged; the coordination polyhedra of these cations are distorted trigonal prisms. The relationships between the crystal structures of melilite and meliphanite are described and a hypothesis is advanced in order to explain the observed differences between them.

Introduction

Meliphanite is a pegmatitic silicate which was carefully described by Brögger (1890) as tetragonal, with chemical formula: $Ca_4Na_2Be_4Si_6O_{20}F_2$. Zachariasen (1930, 1931) showed the close chemical and crystallographic relationships between meliphanite and melilite ($Ca_2MgSi_2O_7$). About this argument see also Cannillo, Giuseppetti & Tazzoli (1967).

Zachariasen measured the correct cell dimensions ($a=10{\cdot}60$, $c=9{\cdot}90$ Å) and assigned to the mineral the more general formula: $(Ca,Na)_2BeSi_2(O,OH,F)_7$. This author assumed that meliphanite could be derived from the compound $Ca_2BeSi_2O_7$ (considered as an 'ideal' meliphanite) which would have the same crystal structure as melilite with the replacement of Mg by Be. According to Zachariasen the presence of fluorine would cause some distortion in the structure of the 'ideal' compound. Thus meliphanite would have a crystal structure which is that of melilite distorted by the presence of fluorine.

The aim of this work is to determine the crystal structure of meliphanite and verify the correctness of Zachariasen's hypothesis.

Experimental

A sample of meliphanite from Brevig (Norway) was used for the determination of the crystal structure. The chemical formula, derived from two analyses carried out by us is: $Ca_{1\cdot37}Na_{0\cdot63}Be(Si_{1\cdot87}Al_{0\cdot13})O_{6\cdot25}F_{0\cdot75}$. The theoretical density, computed on the basis of that formula, is 3·024 g.cm^{-3}; the experimental density is 3·012 g.cm^{-3}.

The lattice parameters were determined by measuring the 2θ values of appropriate reflexions and extrapolating the corresponding d against $\frac{1}{2}(\cos^2\theta/\sin\theta+\cos^2\theta/\theta)$ to $2\theta=180°$. The measurements were made with a single-crystal diffractometer. The values so obtained are: $a=10{\cdot}516\pm0{\cdot}002$, $c=9{\cdot}887\pm0{\cdot}002$ Å, $c/a=0{\cdot}940$.

A specimen of meliphanite with ellipsoidal shape (axes of the ellipsoid: 0·030, 0·027, 0·023 cm) was used for recording intensities. Equi-inclination Weissenberg photographs of hkl (l from 0 to 7) reflexions were taken with Cu $K\alpha$ radiation, using the multiple film technique. Owing to the notable weakness of the levels with $l=2n+1$, the exposure time of the corresponding X-ray pictures was doubled.

The possible space groups, according to the systematic absences, are $I4$, $I\bar{4}$, $I4m$.

The intensities were measured on the integrated films with a Nonius microdensitometer. They were corrected for the Lorentz-polarization factor, absorption ($\mu=150{\cdot}84$ cm^{-1}, the transmission factors varying from 0·82 to 0·12; the correction was made assuming the shape of the crystal as spherical) and α_1–α_2 spot doubling. A secondary extinction correction was applied during the refinement.

Structure analysis

The starting points for the determination of the crystal structure of meliphanite were its chemical and crystallographic analogies with melilite. A comparison of the observed structure factors of the two minerals, and the mentioned weakness of the reflexions with $l=2n+1$, suggested that the two crystal structures would be very similar and that the differences would arise from a new distribution of the atomic species in positions maintaining nearly the same coordinates as those of melilite. On the basis of this hypothesis the space group $I\bar{4}$ ($Z=8$) was chosen because the remaining ones would involve a radical change from the crystal structure of melilite.

Starting from these considerations and taking into account the presence of fluorine, which in natural silicates is never linked to silicon, several distributions of the atoms in the chosen space group were considered,

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and the one which best fulfilled Pauling's electrostatic valency rule was submitted to refinement.

The refinement was carried out by the least-squares method (with a full-matrix program written for the Olivetti ELEA 6001 digital computer; Sgarlata, 1966) in order to minimize the unweighted differences F_o–F_c. Isotropic temperature factors for each atom were used, and in the calculation of the atomic scattering factors with Moore's (1963) constants it was assumed that calcium, sodium and fluorine were completely ionized, and silicon, beryllium and oxygen half-ionized. A few cycles of three-dimensional least-squares reduced the R value from 27% to 12%.

Table 1. *Atomic coordinates and isotropic thermal parameters*

	x/a	y/b	z/c	B
Ca	0·2549	0·0903	0·2556	1·34 Å^2
(Na, Ca)	0·2419	0·0851	0·7506	1·53
Si(1)	0·0000	0·0000	0·0000	0·94
Si(2)	0·0000	0·0000	0·5000	0·61
Si(3)	0·5000	0·0000	0·0045	0·75
Si(4)	0·2528	0·8885	0·9699	0·72
Be	0·2468	0·8915	0·4736	0·09
O(1)	0·2518	0·2563	0·0879	1·36
O(2)	0·1279	0·9657	0·4048	1·32
O(3)	0·1273	0·9547	0·9003	1·18
O(4)	0·3731	0·9604	0·4097	1·10
O(5)	0·3743	0·9598	0·9092	1·34
O(6)	0·2525	0·8927	0·1458	1·41
F	0·2478	0·8895	0·6340	1·38

A plot of $\ln(I_c/I_o)$ against I_c for the most intense reflexions showed some secondary extinction effect. A linear relationship between $\ln(I_c/I_o)$ and I_c was assumed and a least-squares secondary extinction coefficient was derived. This was applied to all the F_o's by means of the formula: $F_{o\text{corr}} = F_{o\text{ext}} \, . \exp(0{\cdot}5\varepsilon I_c)$, where $\varepsilon = 5{\cdot}55 \, . \, 10^{-6}$. After this correction R was 10·4% for the 395 observed reflexions and 12·7% for all 505 reflexions. This rather high value of the discrepancy index is due to the fact that one half of the total number of reflexions, belonging to the group with $l = 2n+1$, is very weak; this weakness considerably increases the errors in measuring intensities.

The anisotropic least-squares refinement did not give any acceptable result, probably because the ratio between the number of parameters and the experimental data was too high: 108 atomic and thermal parameters against 395 observed reflexions.

The coordinates and isotropic temperature factors are given in Table 1. The standard deviations in atomic coordinates which are not fixed by symmetry (Booth, 1946) are: $\sigma_{\text{Ca}} = 0{\cdot}0002$, $\sigma_{\text{Na,Ca}} = 0{\cdot}0003$, $\sigma_{\text{Si}} = 0{\cdot}0003$, $\sigma_{\text{Be}} = 0{\cdot}0070$, $\sigma_{\text{O,F}} = 0{\cdot}0006$. The interatomic distances and angles are listed in Table 2. The standard deviations in bond distances and angles (Ahmed & Cruick-

Table 2. *Interatomic distances and angles*

The distances and angles preceded by an asterisk occur twice, those preceded by a dagger occur four times.

	Bond length	Mean
Si(1)–O(3)	†1·729 Å	1·729 Å
Si(2)–O(2)	†1·680	1·680
Si(3)–O(4)	*1·631	
Si(3)–O(5)	*1·681	1·656
Si(4)–O(1)	1·582	
Si(4)–O(3)	1·643	
Si(4)–O(5)	1·598	
Si(4)–O(6)	1·739	1·640
Be–O(1)	1·590	
Be–O(2)	1·623	
Be–O(4)	1·639	
Be–F	1·586	1·610
Ca–O(6)	2·335	
Ca–O(2)	2·382	
Ca–O(4)	2·394	
Ca–O(6′)	2·404	
Ca–O(1)	2·407	
Ca–F	2·498	
Ca–O(3)	2·717	
Ca–O(4′)	2·736	
(Na, Ca)–O(1)	2·318	
(Na, Ca)–O(3)	2·350	
(Na, Ca)–F	2·358	
(Na, Ca)–O(5)	2·476	
(Na, Ca)–O(6)	2·480	
(Na, Ca)–F′	2·607	
(Na, Ca)–O(2)	2·707	
(Na, Ca)–O(5′)	2·815	

	Angle	Mean
O(3)–Si(1)–O(3′)	†110·5°	
O(3)–Si(1)–O(3″)	*109·0	110·0°
O(2)–Si(2)–O(2′)	†111·9	
O(2)–Si(2)–O(2″)	*108·3	110·7
O(4)–Si(3)–O(5)	*107·2	
O(4)–Si(3)–O(5′)	*105·5	
O(4)–Si(3)–O(4′)	118·0	
O(5)–Si(3)–O(5′)	111·2	109·1
O(1)–Si(4)–O(3)	105·2	
O(1)–Si(4)–O(5)	106·4	
O(1)–Si(4)–O(6)	112·6	
O(3)–Si(4)–O(5)	106·6	
O(3)–Si(4)–O(6)	114·0	
O(5)–Si(4)–O(6)	111·4	109·4
O(1)–Be–O(2)	105·6	
O(1)–Be–O(4)	106·1	
O(1)–Be–F	111·7	
O(2)–Be–O(4)	104·5	
O(2)–Be–F	115·5	
O(4)–Be–F	112·7	109·4

shank, 1953; Darlow, 1960) are: 0·006 Å for all distances except the Be–O distances, for which they are 0·070 Å; 0·3° for O–Si–O angles and 4·0° for O–Be–O angles. The observed and calculated structure factors are compared in Table 3.

Description and discussion of the structure

The silicon and beryllium atoms have a tetrahedral coordination. Fluorine is never linked to silicon but only to beryllium, calcium and sodium. The Si–O and Be–O distances are in good agreement with those found in other silicates. The Si(1)–O(3) distances (1·73 Å) are rather long for an SiO_4 tetrahedron; it is possible that the amount of aluminum found in the analyses is concentrated in the site of Si(1).

In the chemical formula about two-thirds calcium and one-third sodium are present. The best agreement with the observed data was obtained by putting pure calcium in one position ('Ca' in Tables 1 and 2) and $\frac{2}{3}Na+\frac{1}{3}Ca$ in the other ('Na, Ca' in the Tables).

Calcium is surrounded by five oxygen atoms and one fluorine atom (actually, as one can see in the chemical formula, only $\frac{3}{4}F$ is present in one formula unit)

Table 3. *Structure factors of meliphanite* (× 10)

Reflexions marked by an asterisk were unobservably weak; in these cases F_o is derived from $\frac{1}{2}I_o$ min.

h	k	F_o	F_c	A	B
h k 0					
1	1	n.d.	10	10-	0
3	1	464	351	351-	0
5	1	228*	17	17+	0
7	1	449	294	294-	0
9	1	551	511	511-	0
11	1	553	485	485-	0
13	1	178	122	122+	0
0	2	n.d.	310	310-	0
2	2	197*	74	74-	0
4	2	1374	1511	1511+	0
6	2	1391	1518	1518+	0
8	2	814	784	784+	0
10	2	475	380	380-	0
12	2	148*	90	90+	0
1	3	459	337	337+	0
3	3	220*	28	28-	0
5	3	1203	1318	1318-	0
7	3	773	634	634-	0
9	3	519	404	404+	0
11	3	431	418	418+	0
13	3	184	169	169-	0
0	4	1123	1183	1183+	0
2	4	1354	1444	1444+	0
4	4	1856	2082	2082-	0
6	4	242*	300	300+	0
8	4	619	506	506+	0
10	4	1355	1563	1563+	0
12	4	205	173	173+	0
1	5	228*	0	0	0
3	5	1287	1344	1344+	0
5	5	242*	30	30+	0
7	5	520	517	517+	0
9	5	300	262	262-	0
11	5	152*	18	18-	0
0	6	1936	2155	2155-	0
2	6	1499	1566	1566+	0
4	6	242*	314	314+	0
6	6	1836	2213	2213+	0
8	6	597	537	537-	0
10	6	398	385	385+	0
12	6	296	335	335-	0
1	7	485	315	315+	0
3	7	838	630	630+	0
5	7	615	586	586-	0
7	7	228*	32	32+	0
9	7	504	476	476+	0
11	7	492	588	588+	0
0	8	1889	2292	2292+	0
2	8	791	706	706+	0
4	8	494	422	422+	0
6	8	590	513	513-	0
8	8	677	602	602+	0
10	8	359	345	345+	0
1	9	549	468	468+	0
3	9	512	365	365-	0
5	9	217*	243	243+	0
7	9	455	455	455-	0
0	10	225*	152	152-	0
2	10	431	337	337-	0
4	10	1424	1589	1589+	0
6	10	394	398	398+	0
8	10	342	354	354+	0
1	11	570	512	512+	0
3	11	483	468	468-	0
5	11	152*	59	59-	0
7	11	496	550	550-	0
0	12	710	748	748+	0
2	12	148*	64	64+	0
4	12	252	163	163+	0
6	12	352	301	301-	0
h k 1					
0	1	n.d.	222	153+	162+
2	1	491	573	485-	306-
4	1	200	189	79+	172-
6	1	315	187	66-	176+
8	1	203	269	260+	69+
10	1	241	225	223-	34+
12	1	149	118	47+	109-
1	2	321	228	133+	186-
3	2	337	342	141-	312+
5	2	410	534	401+	353-
7	2	282	328	284-	166+
9	2	252	215	49+	210-
11	2	264	310	107-	291+
13	2	169	231	210+	97-
0	3	120	137	79-	113-
2	3	376	396	333+	216+
4	3	137*	67	24+	63+
6	3	211	166	135-	97+
8	3	221	224	95-	203-
10	3	128*	205	158+	131+
12	3	82*	98	96+	21-
1	4	290	303	187+	239-
3	4	137*	178	149-	98-
5	4	144*	58	34-	48+
7	4	147*	124	12+	124+
9	4	137*	223	214+	66+
11	4	175	123	57-	109-
0	5	359	348	326-	123+
2	5	221	19	19+	4-
4	5	374	351	168-	309-
6	5	340	384	334+	191+
8	5	142*	92	92-	11-
10	5	245	155	14+	155+
12	5	167	244	168-	178-
1	6	451	446	277-	350+
3	6	292	322	297+	126-
5	6	210	230	66+	221+
7	6	335	342	40-	340-
9	6	249	261	207-	159+
0	7	160*	200	85+	182-
2	7	227	182	139+	119+
4	7	207	180	73+	165+
6	7	254	182	182-	5-
8	7	125*	130	122-	45-
10	7	130	132	71+	112-
1	8	147*	125	124-	20+
3	8	308	305	13+	305-
5	8	238	271	255-	94+
7	8	125*	168	167+	23-
9	8	173	196	80-	179+
0	9	225	239	13+	239+
2	9	349	324	306-	108-
4	9	137*	158	121+	103-
6	9	121*	157	30+	155-
8	9	211	212	88+	193+
1	10	135*	126	2-	126+
3	10	128*	167	8+	167+
5	10	181	209	184+	100-
7	10	175	158	146-	61-
0	11	117*	74	64+	38-
2	11	113*	59	38+	46-
4	11	264	261	36+	259+
6	11	128	142	124-	70-
1	12	193	233	66+	224-
3	12	137	183	181-	31+
5	12	113	155	42+	150-
0	13	174	226	166-	154+
2	13	62*	34	32-	12-
h k 2					
1	1	n.d.	307	79-	297-
3	1	2254	2063	2063-	25-
5	1	574	509	190+	473-
7	1	408	318	59+	313-
9	1	871	806	737+	328-
11	1	447	391	391-	10+
0	2	1387	1290	1197+	482-
2	2	1704	1735	1735+	9-
4	2	557	497	275-	415+
6	2	413	467	450+	125-
8	2	377	247	54+	242-
10	2	639	688	684+	78+
12	2	539	517	495+	152+
1	3	2214	2106	2106+	57-
3	3	1646	1601	27+	1601-
5	3	943	947	855+	408+
7	3	1526	1613	1591-	266-
9	3	233*	180	173+	50-
11	3	505	450	333-	304-
0	4	1629	1717	395+	1671-
2	4	600	538	330-	426-
4	4	723	822	822+	15+
6	4	784	833	823+	129+
8	4	889	1014	1004+	152-
10	4	201*	294	223+	192+
12	4	230	265	16+	265+
1	5	623	535	199-	497-
3	5	886	953	843-	445+
5	5	319	370	46+	368+
7	5	745	693	467+	513+
9	5	552	600	562+	211-
0	6	1239	1453	1451+	79+
2	6	442	439	420+	131+
4	6	778	737	731+	95-
6	6	246*	158	158-	14-
8	6	322	306	306+	8-
10	6	332	284	284+	22+
1	7	355	262	15-	262-
3	7	1385	1571	1549+	265-
5	7	669	707	505-	496+
7	7	416	362	9-	362+
9	7	641	578	578-	16+
11	7	431	488	474+	117-
0	8	889	910	756+	507+
2	8	247*	221	6-	221+
4	8	903	1008	998+	142+
6	8	379	395	395+	7+
8	8	717	769	769+	14-
10	8	185	200	81-	183-
1	9	867	872	793-	365-
3	9	237*	207	200-	54-
5	9	610	577	551-	172-
7	9	604	597	597+	4+
9	9	306	323	13+	323-
0	10	361	378	275+	260+
2	10	683	707	705+	58-
4	10	397	329	265+	196-
6	10	302	231	229+	34-
8	10	167	182	55-	174+
1	11	471	452	452+	10+
3	11	415	453	315+	326-
5	11	146*	84	70+	48+
7	11	444	489	475-	118-
0	12	297	278	274-	48-
2	12	432	462	438+	148-
4	12	253	256	39+	254-
1	13	104*	63	60+	20+
h k 3					
0	1	n.d.	386	206+	327-
2	1	488	478	441-	186+
4	1	323	313	217+	226-
6	1	343	293	13+	293+
8	1	279	257	202+	159-
10	1	246	241	240-	31+
12	1	147	55	22+	51-
1	2	390	428	53-	425-
3	2	243	57	37-	44+
5	2	412	479	417+	236+
7	2	148*	170	170-	0
9	2	230	140	62-	126-
11	2	161	157	106-	117-
0	3	387	388	136-	364+
2	3	319	372	335+	162-
4	3	246	262	97-	244+
6	3	283	359	58-	355-
8	3	397	390	150-	361+
10	3	124*	162	143+	78-
12	3	191	253	0	253+
1	4	384	373	243+	283+
3	4	220	176	176-	9-
5	4	353	332	167-	287-
7	4	149*	75	21-	73+
9	4	134*	171	152+	79+
11	4	133	119	50-	108+
0	5	296	320	237-	216+
2	5	317	387	31+	386-
4	5	507	442	249-	366+
6	5	239	333	333+	20-
8	5	302	271	126-	240+
10	5	274	321	0	321-
12	5	148	181	150-	103+
1	6	433	415	363-	202-
3	6	255	250	237+	80-
5	6	149*	114	17+	113+
7	6	227	152	79+	130+
9	6	293	274	208-	179-
0	7	307	266	54+	261+
2	7	148*	176	100+	146+
4	7	207	141	0	141-
6	7	208	214	152-	152-
8	7	120*	20	14-	15+
10	7	120	142	86+	114+
1	8	199	222	77+	209+
3	8	148*	78	56-	55+
5	8	338	362	200-	302-
7	8	120*	93	88+	33-
9	8	134	64	59+	27-
0	9	311	356	136+	330-
2	9	323	345	282-	199+
4	9	196	224	135+	179-
6	9	324	416	18-	416+
8	9	247	268	131+	234-
1	10	229	226	11+	226-
3	10	124*	52	29-	44-
5	10	197	178	174+	41+
7	10	155	117	97-	67+
0	11	112*	110	48+	100+
2	11	139	202	79+	186+
4	11	196	198	3-	198-
6	11	98	145	127-	71-
1	12	212	254	143+	210+
3	12	145	135	125-	52+
5	12	85	83	43-	72-
0	13	117	134	105-	84-
2	13	38*	59	5+	59-
h k 4					
1	1	1325	1190	62-	1189-
3	1	1612	1540	1524+	225-
5	1	681	638	241+	591-
7	1	542	559	142+	541+
9	1	686	627	522-	349-
11	1	210*	61	55+	28-
0	2	973	904	26+	904-
2	2	360	243	234-	68+
4	2	2083	2026	1922+	643+
6	2	774	721	703+	163+
8	2	692	778	644+	438-
10	2	249*	164	160-	40-
12	2	356	393	353+	173+
1	3	1584	1489	1485-	118-
3	3	265*	140	24+	138+
5	3	542	517	420-	302-
7	3	1057	1038	1018+	205-
9	3	399	373	68+	367-
11	3	272	346	307+	161+
0	4	962	929	928+	60-
2	4	1950	1896	1800+	596-
4	4	290*	43	42+	11-
6	4	584	567	434+	366-
8	4	288*	405	218-	342+
10	4	798	781	771+	127+
12	4	255	287	197+	209+
1	5	644	579	221-	536-
3	5	493	535	472+	252-
5	5	358	394	19+	394+
7	5	638	634	133-	620+
9	5	701	715	714-	46-
11	5	221	210	120-	173-
0	6	621	562	543-	147-
2	6	736	688	682+	94-
4	6	561	570	434+	371+
6	6	1118	1218	1216+	76-
8	6	257*	155	102+	118-
10	6	177*	343	288+	187-
1	7	537	548	178-	519+
3	7	1064	1094	1069-	237-
5	7	595	622	73+	618+
7	7	260*	331	31+	330-
9	7	371	347	272+	216+
0	8	696	705	610+	354+
2	8	738	722	589+	418+
4	8	288	424	235-	353-
6	8	257*	171	149+	85+
8	8	392	312	312+	18+
10	8	503	637	629+	104+
1	9	585	652	500+	419-
3	9	419	366	30-	365-
5	9	692	698	698+	4-
7	9	253	292	234-	175+
9	9	98*	159	46-	153-
0	10	571	550	517+	189-
2	10	249*	177	118-	132+
4	10	781	814	811+	76-
6	10	285	354	310+	172+
8	10	501	645	636+	113-
1	11	210*	29	3+	29-
3	11	288	377	330-	184+
5	11	217	182	83+	163-
0	12	961	1054	1031+	223+
2	12	368	389	331+	206-
4	12	238	290	168+	237-
h k 5					
0	1	n.d.	112	108+	30+
2	1	330	408	382-	146-
4	1	202	236	15+	236-
6	1	322	382	111+	366+
8	1	141*	203	185+	85+
10	1	125*	162	125-	104+
12	1	182	215	60-	207-
1	2	333	358	158+	322-
3	2	429	405	125-	386+
5	2	359	418	306+	286-
7	2	283	271	215-	166+
9	2	304	318	16-	318-
11	2	261	271	92-	255+
0	3	110*	115	95-	65+
2	3	447	468	327+	336+
4	3	186	101	5+	101+
6	3	143*	103	103-	10+
8	3	353	275	167-	219-
10	3	181	185	11-	185+
1	4	268	258	204+	158-
3	4	279	299	288-	81-
5	4	213	184	13-	184-
7	4	249	171	66-	158+
9	4	118*	150	150+	7+
11	4	175	149	143-	45-
0	5	164	174	42-	169+
2	5	280	241	168-	174-
4	5	267	245	220-	110-
6	5	214	228	190+	127+
8	5	126*	114	30+	111+
10	5	88*	40	10-	39+
1	6	342	334	217-	255+
3	6	143*	230	216+	81-
5	6	248	268	122-	239+
7	6	386	411	88+	402-
9	6	133	193	174-	84+
0	7	144*	120	69+	99-
2	7	283	240	124+	206+
4	7	216	180	44+	175+
6	7	223	150	113-	100-
8	7	103*	19	12-	15-
10	7	106	62	47+	41-
1	8	141*	66	22-	63+
3	8	414	418	1-	418-
5	8	189	192	157-	112+
7	8	139	178	165+	68-
9	8	233	272	52+	268+
0	9	183	151	140+	57+
2	9	281	250	234-	89-
4	9	118*	76	22+	73-
6	9	97*	29	9-	28+
8	9	214	195	132+	144+
1	10	114*	49	41+	28+
3	10	183	235	45+	231+
5	10	88*	49	18+	46-
7	10	147	135	69-	117-
0	11	93*	33	31-	13+
2	11	216	192	178+	73+
4	11	205	201	22-	200+
1	12	228	291	125+	263-
3	12	109	153	153-	6-
h k 6					
1	1	571	528	38+	527-
3	1	1336	1235	1233-	84-
5	1	656	617	617+	5+
7	1	776	748	417+	621+
9	1	745	715	712+	72-
0	2	796	816	533+	618-
2	2	760	789	787+	63+
4	2	823	821	773+	278+
6	2	461	422	49+	420+
8	2	324	233	89-	216-
10	2	454	466	434+	170-
1	3	1282	1261	1259+	78+
3	3	967	929	19-	929+
5	3	1228	1288	1178+	523-
7	3	771	741	741-	11+
9	3	171*	181	138+	118-
11	3	474	543	294-	457+
0	4	1360	1424	295+	1394+
2	4	803	842	817+	204-
4	4	887	833	833+	3-
6	4	1071	1068	825+	679-
8	4	687	640	290+	571+
10	4	127*	152	128+	83-
1	5	638	668	667-	37+
3	5	1243	1305	1220-	465-
5	5	210	136	8+	136+
7	5	376	328	326+	40+
9	5	224	144	128+	66+
0	6	1116	1217	1199+	211-
2	6	453	401	135+	378-
4	6	1077	1034	833+	614+
6	6	314	282	273-	74-
8	6	396	424	424+	11-
10	6	414	393	161+	359-
1	7	692	694	371-	587+
3	7	708	750	750+	30-
5	7	372	311	311-	8-
7	7	562	594	18-	594-
9	7	744	814	772-	259+
0	8	202*	170	170+	2-
2	8	278	271	60-	265+
4	8	580	639	306+	561-
6	8	409	447	447+	1-
8	8	563	660	660+	4+
1	9	706	740	722-	166-
3	9	171*	146	101-	106-
5	9	145*	166	85-	143+
7	9	762	793	761+	225+
0	10	809	907	637+	646-
2	10	468	508	452+	232+
4	10	127*	157	122+	99+
6	10	395	387	67+	382+
1	11	276	285	278+	67-
3	11	532	576	308+	487+
h k 7					
0	1	179	184	108+	149-
2	1	216	170	33-	167+
4	1	79	100	97+	28-
6	1	264	236	71-	226+
8	1	81*	59	11+	58-
10	1	177	99	97-	21+
1	2	229	284	132-	252-
3	2	77*	89	68+	58+
5	2	199	155	20-	154+
7	2	85*	106	86+	62-
9	2	142	148	98-	111-
11	2	157	167	10-	167-
0	3	256	232	2+	232+
2	3	77*	53	38-	37+
4	3	129	165	108-	125+
6	3	191	227	24-	226-
8	3	117	164	25+	163+
10	3	49*	6	6+	0
1	4	164	164	33+	161+
3	4	133	62	44-	44-
5	4	323	290	96-	274-
7	4	120	74	63-	40-
9	4	60*	52	47+	23-
0	5	159	148	93-	116+
2	5	207	267	95+	250-
4	5	351	370	35-	369+
6	5	120	131	78+	106-
8	5	177	216	93-	195+
10	5	207	265	19+	265-
1	6	277	232	40-	229-
3	6	143	17	17+	5+
5	6	82*	59	36+	47+
7	6	68*	43	18+	40+
9	6	194	167	0	167-
0	7	129	127	10-	127+
2	7	85*	138	42+	132+
4	7	112	145	121-	80-
6	7	68*	69	27+	64-
8	7	77	30	9+	29+
1	8	81*	146	118+	86+
3	8	76*	55	54-	14+
5	8	167	124	15-	124-
7	8	46*	62	57-	26-
0	9	221	288	9+	288-
2	9	142	120	27-	117+
4	9	60*	87	86+	15+
6	9	269	345	44-	343+
1	10	229	290	20-	290-
3	10	50*	21	9+	20+
5	10	134	67	0	67+
0	11	81	97	52+	82+
2	11	117	163	43-	158+

with distances ranging from 2·33 to 2·50 Å and by two more oxygen atoms at distances of 2·72 and 2·74 Å. These two oxygen atoms are not thought to participate in the coordination of calcium; the remaining oxygen atoms surround calcium at the corners of a distorted trigonal prism. (Na, Ca) has four oxygen and two fluorine atoms at an average distance of 2·44 Å and two oxygen atoms at distances of 2·72 and 2·82 Å. Also the coordination polyhedron of (Na, Ca), considering only the shortest distances, is a distorted trigonal prism (Fig. 1).

The crystal structure of meliphanite is closely related to that of melilite (Smith, 1953) and leucophanite (Cannillo *et al.*, 1967). In melilite (Fig. 2) Si_2O_7 groups are present. They are held together by isolated MgO_4 tetrahedra to form twisted sheets of tetrahedra. Between these sheets the calcium atoms are located. In meliphanite the positions occupied in melilite by magnesium are not accupied by beryllium but by a silicon atom, and beryllium occurs in a position that in melilite is occupied by a silicon atom. Thus no Si_2O_7 group is present in meliphanite, but SiO_4 tetrahedra form intersecting zigzag chains that build up 16-membered rings, the centres of which are occupied by isolated SiO_4 groups that are connected with the rings through BeO_4 tetrahedra. As in melilite, the whole system of tetrahedra forms twisted sheets parallel to (001) which are held together by Ca and (Na, Ca) arranged between them. From this more convenient point of view (Zoltai, 1960) meliphanite can be classified as a single-sheet silicate like melilite and leucophanite.

As one can see, the suggestion of Zachariasen that the presence of fluorine in meliphanite would produce a distorted 'melilite' structure can be accepted but needs further consideration.

The lower tetragonal symmetry of meliphanite is not due only to the presence of fluorine but also to the fact that the calcium–sodium substitution is partially ordered (*cf.* also leucophanite). The presence of notable amounts of sodium in these pegmatitic minerals is due to the necessity of balancing the diminution of the negative charges as a consequence of the introduction of fluorine. Furthermore Zachariasen, without a complete structural analysis, could not explain how fluorine modifies the 'ideal' meliphanite structure. About this argument these observations can be made: synthetic Be-akermanite ($Ca_2BeSi_2O_7$, Goria, 1953) and gugiaite ($Ca_2BeSi_2O_7$, Peng, Tsao & Chou, 1962) have crystal structures identical with that of Mg-melilite, beryllium taking the place of magnesium; in meliphanite if beryllium were to remain in the position occupied in Be-akermanite, fluorine would be connected with silicon while, in natural silicates, fluorine is never linked to silicon; the only way for fluorine to avoid a bond with silicon in a structure which is basically that of Be-akermanite, is for the silicon to occupy the site of beryllium in Be-akermanite and beryllium the place of one of the two silicon atoms.

The three silicates melilite, meliphanite and leucophanite are characterized by the presence of increasing amounts of fluorine and sodium and by a corresponding diminution of symmetry according to the following scheme:

	Atoms F per formula unit	Atoms Na per formula unit	Space group
Melilite	0	0	$P\bar{4}2_1m$
Meliphanite	$\frac{3}{4}$	$\frac{2}{3}$	$I\bar{4}$
Leucophanite	1	1	$P1$

In order to explain completely the structural modifications due to fluorine, it would be of some interest

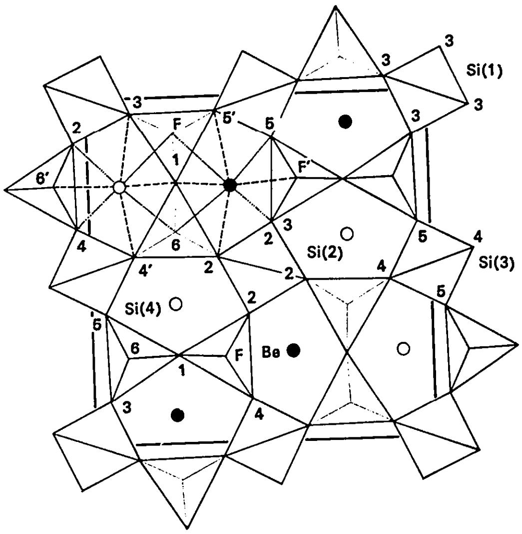

Fig. 1. Schematic view of the crystal structure of meliphanite and key to the identification of the atoms and their coordination. One-half of the content of the unit cell is projected along [001]. Open circles represent Ca; filled circles (Na, Ca). The numbers without other specification refer to oxygen atoms.

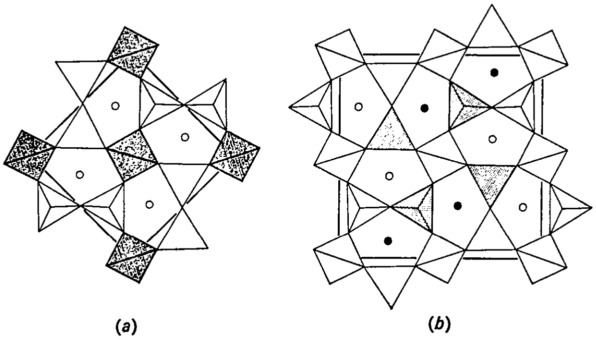

Fig. 2. (*a*) Schematic view of the crystal structure of melilite; the whole content of the unit cell is projected along [001]. Hatched tetrahedra represent MgO_4 groups; open circles represent Ca atoms. (*b*) Schematic view of the crystal structure of meliphanite; one-half of the content of the unit cell is projected along [001]; dotted tetrahedra are BeO_4 groups; open circles represent Ca, filled circles (Na, Ca). The tetrahedra lie at about $z=0$, Ca and (Na, Ca) at about $z=0{\cdot}250$.

to perform an experimental study of the melilite system with the introduction of increasing amounts of fluorine.

References

AHMED, F. R. & CRUICKSHANK, D. W. J. (1953). *Acta Cryst.* **6**, 385.
BOOTH, A. D. (1946). *Proc. Roy. Soc.* A, **188**, 77.
BRÖGGER, W. C. (1890). *Z. Kristallogr.* **16**, 279.
CANNILLO, E., GIUSEPPETTI, G. & TAZZOLI, V. (1967). *Acta Cryst.* **23**, 255.
DARLOW, S. F. (1960). *Acta Cryst.* **13**, 683.
GORIA, C. (1953). *Atti Accad. Torino, Classe sci. fis. mat. nat.* **88**, 153.
MOORE, F. H. (1963). *Acta Cryst.* **16**, 1169.
PENG, C.-S., TSAO, Y.-L. & CHOU, T.-Y. (1962). *Scientia Sinica*, **11**, 977.
SGARLATA, F. (1965). *Period. Min.* **34**, 401.
SMITH, J. V. (1953). *Amer. Min.* **38**, 643.
ZACHARIASEN, W. H. (1930). *Z. Kristallogr.* **74**, 226.
ZACHARIASEN, W. H. (1931). *Norsk geol. Tidsskr.* **12**, 577.
ZOLTAI, T. (1960). *Amer. Min.* **45**, 960.

Acta Cryst. (1967). **23**, 264

The Crystal Structure of Pb_3UO_6

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The structure of Pb_3UO_6 has been determined from single-crystal data, by analysis of the three-dimensional Patterson distribution, Fourier and $\Delta\varrho$ syntheses and subsequent block-diagonal least-squares refinement to a final R value of 0·068. The unit cell is orthorhombic, space group *Pnam*, with $a = 13{\cdot}71$, $b = 12{\cdot}36$, $c = 8{\cdot}21$ Å and $Z = 8$. The uranium atoms are octahedrally coordinated to six oxygen atoms and the slightly distorted octahedra, by sharing apices, form infinite staggered chains in the z direction, the lead atoms and the remaining oxygen atoms being distributed in a rather irregular array between the chains.

Introduction

In the course of a systematic study of mixed oxides of uranium(VI) and lead(II), four discrete compounds, Pb_3UO_6, $Pb_{11}U_5O_{26}$, $PbUO_4$ and $Pb_5U_{19}O_{62}$ were prepared by solid-state reactions of oxide mixtures and characterized by chemical and X-ray powder phase analysis. Of these, only the monouranate $PbUO_4$ has been described in the literature (Frondel & Barnes, 1958; Kovba, Polunina, Simanov & Ippolitova, 1961) and the conclusion of Frondel & Barnes that it is isostructural with $BaUO_4$, the structure of which has been determined by Samson & Sillén (1947), was confirmed by means of X-ray powder data. The new uranate Pb_3UO_6 could have been expected to be similar in structure to the known uranates Ba_3UO_6, Sr_3UO_6 and Ca_3UO_6, all of which have the same distorted cryolite type structure (Rüdorff & Pfitzer, 1954; Sleight & Ward, 1962; Rietveld, 1966) but a preliminary X-ray investigation of the polycrystalline material indicated a completely different type of structure, previously not encountered in any uranate. Therefore, when single-crystal fragments were isolated from preparations of this phase, a complete structure determination was undertaken, the results of which are described here. A general survey of the system Pb–U–O and X-ray work on the other lead uranates will be published separately.

Experimental

Single-phase material Pb_3UO_6 was prepared in polycrystalline form by heating pelleted stoichiometric mixtures of $PbUO_4$ (or U_3O_8) and PbO at 600–650 °C. Heating at higher temperatures, to achieve sintering and possibly an increase in the crystallite size, resulted in decomposition of Pb_3UO_6 to $Pb_{11}U_5O_{26}$ and PbO. Only by heating Pb_3UO_6 in an excess of PbO (Pb:U ~20:1) at 800 °C could sintered dark red Pb_3UO_6 be obtained, in a matrix of pale yellow PbO. The latter could not be leached out selectively, since any solvent for PbO also dissolves the uranate. The two phases had therefore to be separated by hand-picking the crushed mass under the microscope, and after careful examination for phase purity fragments suitable for single-crystal work were selected. The crystal fragments were usually lath-shaped, with no morphological faces, the longest dimension being mainly along the c axis and the shortest along the b axis.

Unit-cell dimensions were determined from oscillation and Weissenberg photographs and also from Guinier powder patterns of the polycrystalline material, calibrated internally with potassium chloride. The unit cell is orthorhombic;

$$a = 13{\cdot}71 \pm 0{\cdot}01,\quad b = 12{\cdot}36 \pm 0{\cdot}01,\quad c = 8{\cdot}21 \pm 0{\cdot}005 \text{ Å},$$
$$U = 1391 \text{ Å}^3,\ \text{F.W. } 955{\cdot}6.$$