

Table 6. Coordination of U atoms

Compound	Atom(1)-atom(2)	Distance	Number of equivalent distances
CaUO ₄	U-O(1)	1.963 (2) Å	2
	U-O(2)	2.298 (1)	6
SrUO ₄	U-O(1)	1.886 (4)	2
	U-O(2)	2.208 (2)	2
	U-O(3)	2.186 (2)	2
BaUO ₄	U-O(1)	1.887 (5)	2
	U-O(2)	2.214 (3)	2
	U-O(3)	2.187 (2)	2
Ca ₂ UO ₅	U(1)-O(2)	2.022 (7)	2
	U(1)-O(4)	2.027 (7)	2
	U(1)-O(5)	2.247 (9)	2
	U(2)-O(1)	2.128 (8)	2
	U(2)-O(3)	1.953 (8)	2
Sr ₂ UO ₅	U(2)-O(5)	2.206 (9)	2
	U(1)-O(2)	2.005 (7)	2
	U(1)-O(4)	2.012 (8)	2
	U(1)-O(5)	2.217 (9)	2
	U(2)-O(1)	2.118 (7)	2
Ca ₃ UO ₆	U(2)-O(3)	1.968 (8)	2
	U(2)-O(5)	2.189 (8)	2
	U-O(1)	2.102 (30)	1
	U-O(2)	2.034 (27)	1
	U-O(3)	2.023 (32)	1
Sr ₃ UO ₆	U-O(4)	2.112 (28)	1
	U-O(5)	2.026 (28)	1
	U-O(6)	2.181 (33)	1
	U-O(1)	2.104 (34)	1
	U-O(2)	1.975 (39)	1
	U-O(3)	2.157 (46)	1
	U-O(4)	2.091 (37)	1
	U-O(5)	2.077 (38)	1
	U-O(6)	2.047 (42)	1

A list of U-O distances appears in Table 6. The U atoms in all compounds are 6-coordinated except in CaUO₄. In this compound the U-atom coordination is eight. The alkaline-earth metals are in most cases 7-coordinated, except in CaUO₄, where the Ca atom is 5-coordinated, and in Sr₃UO₆ and Ca₃UO₆, where two of the three alkaline-earth-metal atoms are 6-coordinated.

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Crystal Structure of Y₂SiBe₂O₇

BY S. F. BARTRAM

General Electric Company, Nuclear Systems Programs, Cincinnati, Ohio 45215, U.S.A.

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Dyttrium silicon beryllate, Y₂SiBe₂O₇, is tetragonal with $a = 7.283 \pm 0.002$, $c = 4.755 \pm 0.001$ Å, $Z = 2$. Refinement of its crystal structure in space group $P\bar{4}2_1m$ by full-matrix least-squares calculations gave $R = 0.096$. Yttrium atoms lie within distorted square oxygen antiprisms and silicon atoms in isolated SiO₄ tetrahedra. Beryllium atoms occupy distorted tetrahedra linked at one corner to form double Be₂O₇ pyramids oriented upward or downward relative to the c axis. Y₂SiBe₂O₇ is isostructural with silicate minerals of the melilite family, such as Ca₂SiAl₂O₇ and Ca₂MgSi₂O₇. The M₂O₇ group is capable of accepting various small ions of different valence, giving this structural arrangement a remarkable versatility.

Introduction

A new complex oxide of Y, Si, and Be was first observed during studies on the BeO-Y₂O₃ binary phase diagram. Its composition was determined by crystallographic analysis and by analogy with isostructural minerals to

be Y₂SiBe₂O₇. It often coexisted with Y₂BeO₄ whose crystal structure has recently been determined by Harris & Yakel (1967).

Melilite is a complex silicate mineral which varies in composition from äkermanite, Ca₂MgSi₂O₇, to gehlenite, Ca₂SiAl₂O₇. Its crystal structure was first eluci-

dated by Warren (1930) and Raaz (1930); a more accurate determination was made later by Smith (1953). There are many other natural and synthetic members of this family. It is the purpose of this paper to establish the structural relationship of $Y_2SiBe_2O_7$ to these minerals and to compare its metal coordination polyhedra with similar compounds.

Experimental

Single crystals of $Y_2SiBe_2O_7$ found on the surfaces of extruded $BeO-Y_2O_3$ rods after firing in a Globar furnace insulated with silica brick were apparently formed by the vapor transport of SiO_2 . The composition of these pale yellow crystals was determined by direct synthesis. A pellet containing the correct proportion of yttrium, silicon, and beryllium oxides was heated in air for 100 hours at $1350^\circ C$; this heat treatment was repeated after grinding and re-pressing. X-ray powder diffraction analysis of the sintered product indicated the formation of $Y_2SiBe_2O_7$ along with slight traces of Y_2O_3 , Y_2BeO_4 , and cristobalite SiO_2 .

A few small crystals scraped from the surfaces of a sintered rod were rather poorly developed and had rounded edges. A suitable crystal approximately $0.15 \times 0.15 \times 0.02$ mm was found to be oriented with the [001] direction perpendicular to the plate. Three-dimensional intensity data were obtained from multiple film equi-inclination photographs about the b axis ($k=0$ to 4), using a non-integrating Weissenberg camera with $Cu K\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$). Intensities were visually estimated by comparison with a calibrated gray scale. Additional intensity data were obtained from a second crystal of similar size for the zero, first, and second layers during rotation about [001] and also layers zero through four during rotation about [101]. Out of 198 possible independent reflections, 158 were recorded several times on different photographs. The observed intensities were corrected for Lorentz and polarization effects, correlated and averaged.

The high linear absorption coefficient ($\mu=351 \text{ cm}^{-1}$) made it necessary to apply a correction. A computer program for anisotropic corrections was not available, so the crystal volumes were assumed to be spherical and an arbitrary correction was applied using Bond's spherical values for $\mu R=1.7$ (*International Tables for X-ray Crystallography*, 1959).

Table 1. *Crystallographic and optical* data for $Y_2SiBe_2O_7$*

Tetragonal – space group $P\bar{4}2_1m$
$a=7.283 \pm 0.002 \text{ \AA}$
$c=4.755 \pm 0.001 \text{ \AA}$
$Z=2$
$D_{calc}=4.42 \text{ g.cm}^{-3}$
Volume = 252.29 \AA^3
Uniaxial negative
$n_o=1.83, n_E=1.80$
* McVay (1961).

Crystal data

Approximate cell dimensions from single-crystal rotation photographs were subsequently refined by recording the high-angle reflections with a powder diffractometer and copper radiation. Forty-one resolved lines in the 2θ region from 102° – 165° were used to calculate the lattice parameters ($Cu K\alpha_1=1.54050 \text{ \AA}$, $Cu K\alpha_2=1.54434 \text{ \AA}$) with the computer program of Mueller, Heaton & Miller (1960). These results and other physical constants for $Y_2SiBe_2O_7$ are given in Table 1.

Structure determination

The only systematic absences were odd $h00$ reflections; this limits the possible space groups to $P42_12$ and $P\bar{4}2_1m$ with four yttrium atoms occupying special positions. Since all fourfold sites in $P42_12$ give rise to additional absences which were not observed, $P\bar{4}2_1m$ was chosen. This choice was verified later in the structure determination. All computations were made using the X-ray 63 crystallographic computing system by Stewart & High (1964).

To begin with, the heavy yttrium atoms were located by means of a three-dimensional Patterson synthesis in the $4(e)$ sites at $x, \frac{1}{2}+x, z$, where $x \approx \frac{1}{2}$ and $z=0$ or $\frac{1}{2}$. A three-dimensional Fourier synthesis was calculated by letting the yttrium atoms in these positions determine the signs of the $|F_o|$ values. At this point, the agreement index was $R=0.35$. Atomic scattering factors for this and all subsequent calculations were taken from Cromer & Waber (1964) for Y^{3+} , Si^{4+} , and Be^{2+} and from Tokonami (1965) for O^{2-} .

From the electron density maps and a consideration of the Y–O bond lengths, all fourteen oxygen atoms were located in the following approximate positions:

	x	y	z
O(1) in $8(f)$	0.083	0.167	0.750
O(2) in $4(e)$	0.333	0.833	0.750
O(3) in $2(c)$	0.000	0.500	0.750

Structure-factor and least-squares calculations reduced R to 0.22 when the scale factor, positional parameters and isotropic temperature factors were allowed to vary.

When the structural relationship between $Y_2SiBe_2O_7$ and the melilite minerals was recognized, the silicon and beryllium atoms were placed in the Zn^{2+} and Si^{4+} sites, respectively, given by Warren & Trautz (1930) for $Ca_2ZnSi_2O_7$. Refinement was carried out with the X-ray 63 system version of the Busing, Martin & Levy (1962) full-matrix least-squares *ORFLS* program and proceeded smoothly to an R value of 0.108. A final refinement was made with the yttrium atoms fixed, but the thermal parameters of Y^{3+} and Si^{4+} as well as the positional and thermal parameters of Be^{2+} and O^{2-} were allowed to vary. Five of the strongest reflections appeared to be affected by extinction and were given zero weight. All others were weighted according to the scheme $w=50/F_o$ when $F_o > 50$ and $w=1$ when

$F_0 \leq 50$. Unobserved reflections were omitted from the refinement when the calculated structure factors were less than the minimum observable value.

The results from the last least-squares cycle are presented in Table 2. The average shift/error ratio was 0.003 for this cycle. The structure factors calculated from these parameters are compared with the observed values in Table 3. The final R value, omitting unobserved reflections, was 0.096. A three-dimensional difference Fourier computed with the final parameters was essentially featureless except for small residual peaks of about 0.8 electrons at the yttrium positions.

Discussion

The interatomic distances and bond angles for the coordination polyhedra in $Y_2SiBe_2O_7$ are listed in Table 4. A drawing of the structure projected down the c axis is shown in Fig. 1. This clearly shows its structural similarity to $Ca_2ZnSi_2O_7$ and other materials of the melilite family. The most interesting feature about $Y_2SiBe_2O_7$ is the fact that Be^{2+} ions occupy the Si^{4+} sites to form a $[Be_2O_7]^{10-}$ double pyramid linked

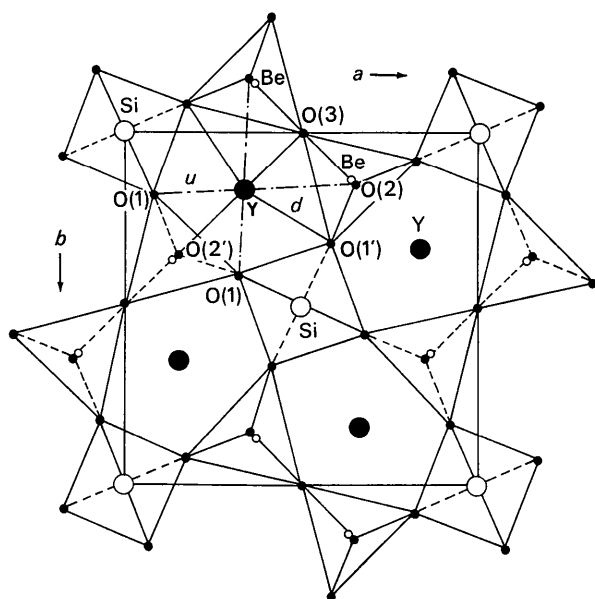


Fig. 1. Projection of the $Y_2SiBe_2O_7$ structure onto the c axis. The Y-O bonds alternate up (u) and down (d). Apical oxygen atoms pointing downward are dashed.

Table 2. Final atomic parameters for $Y_2SiBe_2O_7$ *

Atom	Position	x	y	z	B
Y	4(e)	0.1595 (6)	0.6595 (6)	0.4873 (7)	0.79 (8)
Si	2(a)	0.0000	0.0000	0.0000	0.51 (20)
Be	4(e)	0.363 (13)	0.863 (13)	0.031 (14)	1.94 (97)
O(1)	8(f)	0.0823 (28)	0.1664 (32)	0.7928 (46)	0.94 (31)
O(2)	4(e)	0.3561 (56)	0.8561 (56)	0.7053 (55)	0.54 (40)
O(3)	2(c)	0.0000	0.5000	0.8275 (71)	0.02 (52)

* Numbers in the parentheses in all tables are estimated standard deviations in the least significant digits.

at a corner oxygen. Although the substitution of beryllium for silicon in the M_2O_7 group has been suspected for some time, the results reported here unequivocally demonstrate the existence of this arrangement. It should be mentioned that Cannillo, Giuseppetti & Tazzoli (1967) have reported a $[(Si, Be)O_6F]^-$ double tetrahedron in leucophanite, a mineral closely related to melilite.

The coordination polyhedron around the yttrium ion is a distorted square Archimedean antiprism. There are six close yttrium-oxygen contacts ranging from 2.28 Å to 2.40 Å, plus two longer distances of 2.61 Å. In melilite, $Ca_2MgSi_2O_7$, the Ca-O separations vary from 2.42 Å to 2.75 Å, distances which are 0.14 Å larger than the maximum and minimum Y-O bond lengths found in $Y_2SiBe_2O_7$. The O-Y-O acute angles

Table 3. Observed and calculated structure factors ($\times 10$)

E = extinction, L = less than.																
h	k	l	F_o	F_c	A	P	E	h	k	l	F_o	F_c	A	P	E	
1	0	0	318	286	-286	0	0	6	3	L	173	78	35	70	7	1
2	0	0	761	810	-810	0	0	7	3	L	381	370	-366	57	2	1
3	0	0	1051	1052	1052	0	0	8	3	L	157	62	-63	26	2	2
4	0	0	163	163	163	0	0	4	4	L	264	228	-164	263	214	104
5	0	0	255	242	-242	0	0	4	5	L	545	543	534	-99	318	215
6	0	0	571	617	617	0	0	7	4	L	523	545	545	-11	318	215
7	0	0	621	656	656	0	0	7	6	L	362	333	-296	-11	318	215
8	0	0	692	787	-787	0	0	7	8	L	153	94	42	85	323	266
9	0	0	188	40	-40	0	0	5	5	L	228	151	166	-84	323	266
10	0	0	150	92	-92	0	0	6	5	L	259	166	-166	0	323	266
11	0	0	309	289	-289	0	0	7	5	L	235	184	183	20	323	266
12	0	0	272	271	271	0	0	6	6	L	469	451	-460	0	323	266
13	0	0	433	412	-412	0	0	7	6	L	136	99	-85	50	323	266
14	0	0	238	189	-189	0	0	2	2	L	739	750	750	0	323	266
15	0	0	740	844	844	0	0	1	0	L	325	324	0	-324	0	0
16	0	0	460	459	459	0	0	1	0	L	365	316	-316	0	0	0
17	0	0	176	61	-61	0	0	2	2	L	165	122	-107	-57	0	0
18	0	0	357	332	-332	0	0	3	4	L	389	318	-318	0	0	0
19	0	0	237	162	-162	0	0	4	0	L	544	75	0	0	0	0
20	0	0	152	67	-67	0	0	0	0	L	182	0	0	0	0	0
21	0	0	926	1114	-1114	0	0	1	0	L	166	116	0	-116	0	0
22	0	0	740	844	844	0	0	1	0	L	165	122	12	0	0	0
23	0	0	408	367	367	0	0	1	0	L	480	209	-204	47	0	0
24	0	0	174	19	19	0	0	1	0	L	722	943	943	-40	0	0
25	0	0	603	699	699	0	0	1	0	L	801	796	87	0	0	0
26	0	0	158	96	96	0	0	1	0	L	480	-476	-56	0	0	0
27	0	0	722	736	736	0	0	1	0	L	181	61	36	50	0	0
28	0	0	444	430	-430	0	0	1	0	L	307	253	-179	180	0	0
29	0	0	374	332	-332	0	0	1	0	L	442	437	355	152	0	0
30	0	0	400	334	334	0	0	1	0	L	185	155	-155	0	0	0
31	0	0	173	155	155	0	0	1	0	L	330	324	24	0	0	0
32	0	0	171	88	-88	0	0	1	0	L	968	866	366	37	0	0
33	0	0	145	85	85	0	0	1	0	L	243	185	-185	0	0	0
34	0	0	101	101	101	0	0	1	0	L	397	330	-24	-60	0	0
35	0	0	551	583	583	0	0	1	0	L	692	816	815	-42	0	0
36	0	0	145	97	97	0	0	1	0	L	501	25	-25	19	0	0
37	0	0	923	-923	0	0	0	7	8	L	445	445	105	48	0	0
38	0	0	18	18	0	0	0	8	8	L	139	115	105	48	0	0
39	0	0	687	780	780	0	0	2	3	L	614	626	-626	15	0	0
40	0	0	545	567	567	0	0	3	3	L	162	159	168	0	0	0
41	0	0	643	797	797	0	0	6	6	L	180	133	30	-130	0	0
42	0	0	187	98	98	0	0	7	8	L	463	474	474	17	0	0
43	0	0	537	603	-603	0	0	4	4	L	406	341	341	-10	0	0
44	0	0	221	172	172	0	0	5	4	L	506	507	-504	36	0	0
45	0	0	259	206	206	0	0	6	4	L	346	290	-290	3	0	0
46	0	0	142	133	0	-133	0	7	4	L	297	272	270	31	0	0
47	0	0	493	427	-427	0	0	5	1	L	140	156	-176	0	0	0
48	0	0	776	954	-954	0	0	2	3	L	230	173	168	42	0	0
49	0	0	532	528	515	118	0	7	6	L	153	79	23	76	0	0
50	0	0	578	607	588	149	0	6	6	L	669	622	622	-19	0	0
51	0	0	313	260	258	32	0	0	0	L	881	918	-918	0	0	0
52	0	0	268	211	185	101	0	0	0	L	191	86	0	86	0	0
53	0	0	342	364	353	29	0	1	0	L	481	419	419	0	0	0
54	0	0	432	477	-477	10	0	0	0	L	185	22	0	-22	0	0
55	0	0	211	221	-211	-67	0	0	0	L	573	538	538	0	0	0
56	0	0	493	427	-427	0	0	0	0	L	173	0	0	0	0	0
57	0	0	226	140	100	-98	0	0	0	L	173	0	0	0	0	0
58	0	0	191	73	-73	-3	0	0	0	L	504	0	0	0	0	0
59	0	0	719	785	-783	-17	0	0	0	L	160	6	0	-6	0	0
60	0	0	479	476	474	-43	0	0	0	L	231	202	202	164	0	0
61	0	0	414	423	414	-85	0	0	0	L	379	346	346	154	0	0
62	0	0	160	201	198	-36	0	0	0	L	694	757	-752	85	0	0
63	0	0	863	1074	1074	-20	0	0	0	L	184	105	-105	-77	0	0
64	0	0	171	140	-133	0	0	0	0	L	612	607	607	20	0	0
65	0	0	180	130	-132	-53	0	0	0	L	367	350	289	-197	0	0
66	0	0	180	130	-132	-53	0	0	0	L	264	230	194	-123	0	0
67	0	0	317	320	311	75	0	0	0	L	317	320	311	75	0	0
68	0	0	382	493	-492	-32	0	0	0	L	382	493	-492	-32	0	0
69	0	0	259	292	236	214	0	0	0	L	259	292	236	214	0	0
70	0	0	215	193	-110	193	0	0	0	L	215	193	-110	193	0	0
71	0	0	318	318	318	318	0	0	0	L	318	318	318	318	0	0
72	0	0	323	249	85	249	0	0	0	L	323	249	85	249	0	0
73	0	0	323	266	265	-19	0	0	0	L	323	266	265	-19	0	0
74	0	0	760	899	899	21	0	0	0	L	760	899	899	21	0	0
75	0	0	212	142	140	-24	0	0	0	L	212	142	140	-24	0	0
76	0	0	168	102	-101	-2	0	0	0	L	168	102	-101	-2	0	0
77	0	0	238	247	-246	21	0	0	0	L	238	247	-246	21	0	0
78	0	0	215	169	-165	-31	0	0	0	L	215	169	-165	-31	0	0
79	0	0	371	351	368	-44	0	0	0	L	371	351	368	-44	0	0
80	0	0	503	594	594	0	0	0	0	L	503	594	594	0	0	0
81	0	0	169	202	202	0	0	0	0	L	169	202	202	0	0	0
82	0	0	121	122	-93	0	0	0	0	L	121	122	-93	0	0	0

vary from 61° to 87° , the mean being 78° , compared to O–Ca–O angles of 59° to 83° , with a mean of 73° .

Very similar calcium and yttrium polyhedra are found in the minerals herderite and gadolinite. Herderite of composition $CaBePO_4F$ is structurally related to $Fe_{1/2}YBeSiO_4O$ (Pavlov & Belov, 1960) by replacing Ca^{2+} with Y^{3+} , PO_4^{3-} with SiO_4^{4-} , and F^- with O^{2-} . In order to satisfy the valence requirements, Fe^{2+} ions occupy sites within rings of YO_8 polyhedra; these are vacant in the herderite structure. Relative bond lengths in the Ca and Y distorted cubic antiprism are shown in Table 5. A comparison of these data with those for $Ca_2MgSi_2O_7$ and $Y_2SiBe_2O_7$ show the close relationship between their structural arrangements. In all of these compounds, the eightfold coordinated Ca or Y antiprisms are linked through oxygen (or F in herderite) atoms to Be or Si tetrahedra.

The nearly ideal SiO_4 tetrahedra in $Y_2SiBe_2O_7$ has four equal Si–O distances of 1.67 \AA ; this is somewhat greater than the average value of 1.61 \AA for silicates. Similar isolated SiO_4 tetrahedra in meliphanite, a mineral of composition $Ca(Na,Ca)BeSi_2O_6F$ (Dal Negro, Rossi & Ungaretti, 1967) have Si–O distances ranging from 1.64 \AA to 1.68 \AA .

The double pyramids of Be_2O_7 are oriented upward and downward relative to the c axis; they are a rather unusual grouping for the known minerals of beryllium. These tetrahedra appear to be distorted with two Be–O distances of 1.55 – 1.56 \AA and two others of 1.71 \AA (average 1.63 \AA). The short contacts are similar to Be–O separations of 1.55 \AA in a BeO_3F tetrahedron in herderite (Pavlov & Belov, 1960) and the 1.56 \AA Be–O distances found by Harris & Yakel (1966) in calcium beryllate. The average Be–O distance of 1.63 \AA is identical with that reported by Farrell, Fang & Newnham (1963) for all Be–O contacts in chrysoberyl $BeAl_2O_4$.

The distortion of the Be_2O_7 double tetrahedra and the short O–O distances of 2.51 \AA and 2.59 \AA can

Table 5. *Relative bond lengths* (\AA)

Herderite		Gadolinite*	
Ca–O(1)	2.40, 2.40	Y–O(1)	2.25, 2.46
Ca–O(2)	2.44	Y–O(2)	2.31
Ca–O(3)	2.61, 2.70	Y–O(3)	2.57, 2.61
Ca–O(4)	2.44	Y–O(4)	2.30
Ca–F	2.58, 2.71	Y–O(5)	2.50, 2.57
Average	2.53 ₅	Average	2.44 ₆

* Calculated from data of Pavlov & Belov (1960).

Table 4. *Interatomic distances and bond angles in $Y_2SiBe_2O_7$*

Interatomic distances (\AA)		Interatomic angles ($^\circ$)	
Distorted square antiprism			
(2) Y–O(1)	2.305 (22)	(1) O(1)–Y–O(1)	68.3 (0.8)
(1) Y–O(2')	2.275 (38)	(2) O(1)–Y–O(1')	149.4 (0.7)
(2) Y–O(2)	2.395 (39)	(2) O(1)–Y–O(1'')	86.6 (0.7)
(1) Y–O(3)	2.306 (24)	(2) O(1)–Y–O(2)	122.2 (0.9)
(2) Y–O(1')	2.612 (22)	(2) O(1)–Y–O(2')	80.7 (1.0)
Average	2.401	(2) O(1)–Y–O(2'')	74.7 (1.0)
(2) O(1')–O(3)	2.51 (2)	(2) O(1)–Y–O(3)	145.8 (0.6)
(1) O(1)–O(1)	2.59 (3)	(1) O(1')–Y–O(1')	110.2 (0.7)
(2) O(1)–O(2')	2.78 (4)	(2) O(1')–Y–O(2)	67.3 (0.9)
(2) O(1')–O(2)	2.78 (4)	(2) O(1')–Y–O(2')	129.0 (1.0)
(2) O(2)–O(3)	2.94 (4)	(2) O(1')–Y–O(2'')	82.3 (1.0)
(1) O(2)–O(2)	2.97 (6)	(2) O(1')–Y–O(3)	61.0 (0.5)
(2) O(1)–O(2)	3.04 (5)	(1) O(2)–Y–O(2)	76.5 (1.4)
(2) O(1')–O(2')	3.22 (5)	(2) O(2)–Y–O(2')	141.7 (1.4)
(2) O(1)–O(1')	3.38 (3)	(2) O(2)–Y–O(3)	77.3 (0.9)
(1) O(2')–O(3)	3.71 (4)	(1) O(2')–Y–O(3)	108.3 (1.0)
Tetrahedron			
(2) Si–O(1)	1.67 (2)	(1) O(1)–Si–O(1)	107.8 (1.1)
(2) Si–O(1')	1.67 (2)	(1) O(1')–Si–O(1')	107.8 (1.1)
(1) O(1)–O(1)	2.70 (3)	(4) O(1)–Si–O(1')	110.3 (1.0)
(1) O(1')–O(1')	2.70 (3)		
(4) O(1)–O(1')	2.75 (3)		
Tetrahedron			
(1) Be–O(2)	1.55 (7)	(1) O(1')–Be–O(1')	98.8 (4.0)
(1) Be–O(3)	1.56 (9)	(2) O(1')–Be–O(2)	118.0 (5.6)
(2) Be–O(1')	1.71 (9)	(2) O(1')–Be–O(3)	100.2 (4.4)
Average	1.63	(1) O(2)–Be–O(3)	118.0 (5.7)
(2) O(1')–O(3)	2.51 (2)		
(1) O(1')–O(1')	2.59 (3)		
(1) O(2)–O(3)	2.67 (4)		
(2) O(1')–O(2)	2.78 (4)		

readily be explained on the basis of Pauling's rule which states that shared edges of coordination polyhedra are shortened while unshared edges are correspondingly lengthened. The three short O-O edges are shared by the Be and Y groups.

The melilite structure is remarkably versatile. Theoretical end members of this mineral group are gehlenite, $\text{Ca}_2\text{SiAl}_2\text{O}_7$, and åkermanite, $\text{Ca}_2\text{MgSi}_2\text{O}_7$. When sodium and potassium are substituted for calcium, the charge deficiency is compensated for by the replacement of Al^{3+} with Si^{4+} in gehlenite or the substitution of Al^{3+} for Mg^{2+} in åkermanite. The introduction of Be^{2+} for Mg^{2+} yields the rare mineral gugiaite, $\text{Ca}_2\text{BeSi}_2\text{O}_7$, as reported by Peng, Tsao & Chou (1962). When a trivalent ion such as Y^{3+} occupies the Ca^{2+} positions, the charge balance can be maintained by the introduction of additional Be^{2+} ions. The end result of such substitutions gives rise to the new compound $\text{Y}_2\text{SiBe}_2\text{O}_7$. The transition of the M_2O_7 double tetrahedra from $\text{Si}_2\text{O}_7^{6-}$ to $\text{Al}_2\text{O}_7^{8-}$ to $\text{Be}_2\text{O}_7^{10-}$ and all intermediate combinations of these three indicates the wide latitude of possible compositions.

Many other silicate compounds having the melilite or a closely related structure are known. Brisi & Abbattista (1960) have synthesized $\text{Sr}_2\text{MnSi}_2\text{O}_7$ and $\text{Sr}_2\text{FeSi}_2\text{O}_7$. More recently the new mineral fresnoite of composition $\text{Ba}_2(\text{TiO})\text{Si}_2\text{O}_7$ was shown by Moore & Louisnathan (1967) to have a structure very similar to melilite, except that the Si_2O_7 groups all point in the same direction and the Ti coordination polyhedron is a square pyramid instead of the usual tetrahedron. Recent structural determinations on the minerals leucophanite (Cannillo, Giuseppetti & Tazzoli, 1967) and meliphanite (Dal Negro, Rossi & Ungaretti, 1967) demonstrate their remarkable similarity to melilite.

It seems quite likely that a series of solid solutions exists from $\text{Y}_2\text{SiBe}_2\text{O}_7$ to $\text{Y}_2\text{BeAl}_2\text{O}_7$ as end members, but no attempt has yet been made to prepare the latter compound. At any rate, it is obvious that a wide variety of new compounds can be made by the substitution of

the trivalent rare earth ions for Y^{3+} in $\text{Y}_2\text{SiBe}_2\text{O}_7$. Preliminary experiments indicate that a 1:1 ratio of certain monovalent (Na, K) and trivalent rare earth (Sm, Eu, Dy) ions can be substituted for part of the Ca^{2+} in $\text{Ca}_2\text{ZnSi}_2\text{O}_7$. This development opens the way to the synthesis of innumerable compounds having possible technical applications.

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