O(3)–3(U) bond is 2·06. In a similar manner, we find a total bond strength of 1·95 for O(1)–2U and 1·80 for O(2)–2U. For the uranium atom, bond distances vary from 1·80 Å to 2·56 Å, but the total bond strength becomes 5·83 for U–7(O).

The deviations of the total bond strengths from the valences 2 and 6 are probably not significant because of the errors in the coordinate positions. However, it is observed that a number of U–O 'interactions' as low as 3·2 Å are found, and these may contribute to the total bond strength. The accuracy of intensity measurement is not sufficiently high to establish this point.

The temperature factor for O(3) is substantially lower than for the remaining oxygen atoms. This seems reasonable, for the O(3) atom forms three uranium bonds.

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The Crystal Structure of Calcium Beryllate, $Ca_{12}Be_{17}O_{29}$*

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Calcium beryllate crystallizes in the cubic system with $a_0 = 14{\cdot}023 \pm 0{\cdot}005$ Å. Its crystal structure has been determined by standard three-dimensional Patterson and difference Fourier methods. Refinement of the structure in the acentric space group $F\bar{4}3m$ by iterative structure-factor least-squares calculations gave a final error index $R = 0{\cdot}066$. The ideal composition of the compound was found to be $Ca_{12}Be_{17}O_{29}$ (4 formula weights per unit cell) as a result of this analysis.

The structure is described as composed of rods of close atom packing running parallel to ⟨110⟩ crystal directions and intersecting at 4(*b*) sites of $F\bar{4}3m$. As the rods diverge from the 4(*b*) sites, large (5·4 Å free diameter) holes are left centered at 4(*a*) positions.

Two types of calcium-oxygen coordination are found; one has eight oxygen atoms in the form of a rectangular prism about a calcium atom while the other is a sixfold grouping similar to that reported in cubic rare-earth oxides. Of the 68 beryllium atoms per unit cell, twenty have nearly normal tetrahedral oxygen atom coordinations. Thirty-two beryllium atoms have three close and one long oxygen atom contact; the remaining sixteen have an unusual trigonal oxygen atom coordination.

Introduction

The formation of a compound near 60 mole % BeO in the binary system BeO–CaO was first reported by Ader & Bingle (1956), but a later study of the phase equilibria in this system by Potter & Harris (1962) suggested that the compound might be metastable. The growth of single crystals of calcium beryllate permitted Harris, Potter & Yakel (1962) to determine preliminary crystallographic data for the material.

The purpose of this paper is to present results of an X-ray crystal structure analysis of calcium beryllate.

Experimental

Single crystals of calcium beryllate were obtained by melting in air a powdered mixture of 60 mole % BeO, 40 mole % CaO on the platinum strip of a resistance furnace, and then quenching. The quenched product readily yielded water-clear optically isotropic fragments which were found to be single crystals in most cases. A typical crystal had the general form of an elongated plate with a {110} type plane parallel to the plate face and with a direction between a ⟨110⟩-type and a ⟨111⟩-type direction parallel to the elongated crystal axis.

The diffraction symbol $m3mF\ldots$, which embraces space groups $F432$, $F\bar{4}3m$, and $Fm3m$, was indicated by diffraction data obtained from rotation, Weissenberg, and precession photographs (Cu $K\alpha$ radiation, $\lambda = 1{\cdot}54178$ Å) as well as selected intensity measurements of reflection pairs of the type $hk0$, $kh0$ and hkl, hlk. An X-ray density of $2{\cdot}64 \pm 0{\cdot}01$ (g.cm^{-3}) was computed on the basis of 4 formula weights of $Ca_{12}Be_{17}O_{29}$ per cell – the composition suggested by the results of the structure analysis to be described. The lattice parameter was determined from high-angle reflections on a calibrated zero layer Cu $K\alpha$ Weissenberg film about a [110] lattice direction.

Initial intensity data were collected from a plate-shaped crystal having dimensions $0{\cdot}039 \times 0{\cdot}057 \times 0{\cdot}200$

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mm. The long direction of this crystal was approximately parallel to a [110] direction, and this lattice direction was aligned with the rotation axis of a Weissenberg goniometer. Intensity measurements were made with a Geiger counter and Cu $K\alpha$ radiation for zero, first, and second layers ($h, \bar{h}, l$: $1+h, 1-h, l$; $2+h, 2-h, l$ zones, respectively). Data were also obtained from a second crystal of nearly identical shape, size, and orientation by visual intensity estimation from multiple-film equi-inclination Weissenberg photographs of layers zero through eight exposed with Cu $K\alpha$ radiation. A total of 749 reflections were recorded, of which 190 were independent.

Observed intensities were corrected for Lorentz and polarization effects, but not for absorption. If cylindrical symmetry is assumed, μR for the crystals used is about 1·0 for Cu $K\alpha$ radiation. At these small values of μR, the absorption correction may be adequately approximated as $A_0 \exp(-\alpha \sin^2\theta)$, and failure to apply this correction should therefore be equivalent to an underestimation of the overall temperature factor in the refinement. Relative $|F|^2$ values were placed on an absolute scale after the method of Wilson (1942) and statistical tests for symmetry elements were applied (Howells, Phillips & Rogers; 1949, 1950). A centric distribution was found but the result was considered tentative owing to the relatively large contribution of the calcium atoms in the structure to the net scattering in an average reflection.

Structure determination

A preliminary choice of the space group *Fm*3*m* was made on the basis of the data given above. The 48 calcium atoms in the unit cell were located in positions 24(*d*) and 24(*e*)($x \simeq 0{\cdot}25$) of that group by comparing the largest peaks in a three-dimensional Patterson synthesis with calculated interatomic vectors for various possible arrangements of these atoms.

A remaining moderately large peak which was not associated with Ca–Ca vectors was observed on the zero-level Patterson section at a distance from the origin consistent with a Ca–O separation. After several false starts, the oxygen atoms involved in this interaction were placed in the 96(*k*) positions of *Fm*3*m* with $x \simeq 0{\cdot}11$ and $z \simeq 0{\cdot}25$. Structure-factor and least-squares calculations in which only the scale and overall temperature factors were varied gave a measure of agreement $R = 0{\cdot}18$ (where $R = \Sigma|F_o - F_c|/\Sigma|F_o|$) for the partial structure. Atomic scattering factors for these and subsequent calculations were taken from Cromer & Waber (1964) (for Be^{2+} and Ca^{2+}) and from *International Tables for X-ray Crystallography* (1962) (for O^-). The weighting scheme proposed by Hughes (1941) was used throughout the refinement.

The search for other atoms in the structure was pursued by Fourier techniques. Three-dimensional difference Fouriers with 48 calcium and 96 oxygen atoms removed suggested likely positions for 68 beryllium atoms and 20 additional oxygen atoms. A summary of atom positions found at this stage of the analysis is given in Table 1. It will be noted that 32 beryllium and 20 oxygen atoms are disordered in the centric trial structure and that, by virtue of their close proximity, it seems unlikely that the occupation probabilities for the two sets of 16 beryllium atoms in 32(*f*) positions would be independent.

Repeated structure-factor least-squares refinement cycles brought the agreement factor for this trial structure to 0·115. No additional atoms appeared in difference maps at any stage of the refinement (or of the acentric refinement described below) so that the chemical content of the unit cell is $Ca_{48}Be_{68}O_{116}$, or 58·6 mole % BeO rather than 60 mole % as assumed earlier.

Several factors suggested that the centric trial structure, while nearly correct, was not as adequate a description of the true structure as it might be. These factors included: (*a*) The poor agreement between observed and calculated structure factors for a half dozen reflections which was never significantly improved at any stage of the refinement; and (*b*) the high correlation between occupation probabilities which, as noted above, must exist if unlikely or impossible atomic configurations are to be avoided. Removal of the center of symmetry from the space group *Fm*3*m* yields either the octahedral group *F*432 or the tetrahedral group $F\bar{4}3m$. In the absence of sufficient *hhl* data for meaningful statistical tests, the latter group was chosen for refinement since it contains 16-fold positions (16*e*) while *F*432 does not. All atoms deduced for the centric space group could thus be accommodated in $F\bar{4}3m$ in a fully ordered arrangement as indicated in Table 1.

Table 1. *Preliminary atomic positions for calcium beryllate based on the space groups Fm3m and $F\bar{4}3m$*

		*Fm*3*m*			
Atom	Position	occupation	*x*	*y*	*z*
Ca(I)	24(*d*)	24	0·00	0·25	0·25
Ca(II)	24(*e*)	24	0·29	0·00	0·00
Be(I)	4(*b*)	4	0·50	0·50	0·50
Be(II)	32(*f*)	16	0·36	0·36	0·36
Be(III)	32(*f*)	16	0·33	0·33	0·33
Be(IV, V)	32(*f*)	32	0·16	0·16	0·16
O(I, II)	96(*k*)	96	0·11	0·11	0·248
O(III)	8(*c*)	4	0·25	0·25	0·25
O(IV)	32(*f*)	16	0·43	0·43	0·43

		$F\bar{4}3m$			
Atom	Position	occupation	*x*	*y*	*z*
Ca(I)	24(*g*)	24	0·00	0·25	0·25
Ca(II)	24(*f*)	24	0·29	0·00	0·00
Be(I)	4(*b*)	4	0·50	0·50	0·50
Be(II)	16(*e*)	16	0·64	0·64	0·64
Be(III)	16(*e*)	16	0·33	0·33	0·33
{ Be(IV)	16(*e*)	16	0·16	0·16	0·16
{ Be(V)	16(*e*)	16	0·84	0·84	0·84
{ O(I)	48(*h*)	48	0·11	0·11	0·25
{ O(II)	48(*h*)	48	0·88	0·88	0·75
O(III)	4(*c*)	4	0·25	0·25	0·25
O(IV)	16(*e*)	16	0·57	0·57	0·57

Refinement of this structure by structure factor-least squares iterative calculations using the computer program of Busing, Martin & Levy (1962) gave a final value for $R(=\Sigma||F_o|-|F_c||/|F_o|)$ of 0·066, with one overall scale factor and one overall temperature factor. Attempts toward additional refinement through introduction of anisotropic or isotropic individual atom temperature factors proved unsuccessful when the thermal parameters of one or more light atoms tended to negative values. A final three-dimensional difference Fourier synthesis with all atoms removed showed no peak containing more than 0·2 electron. Atomic and thermal parameters computed in the penultimate least-squares cycle are presented in Table 2 and a comparison of observed $F^2(hkl)$ with those computed from the final parameters is given in Table 3.

Description of the structure

Table 4 lists important interatomic distances and angles, with their standard deviations, derived from the parameters of Table 2 with the ORFFE program (Busing, Martin & Levy, 1964).

The crystal structure of calcium beryllate may be described as built up of rods of relatively close atom-packing running parallel to ⟨110⟩ crystal directions. The rods intersect at the 4(*b*) sites of the space group $F\bar{4}3m$ ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ and all symmetry-related positions). As the rods diverge from 4(*b*) sites, large holes are left centered about neighboring 4(*a*) sites (0, 0, 0 and all related positions). The diameter of these holes is about 5·4 Å measured between van der Waals radii of opposing oxygen atoms. We shall return to a discussion of them after considering atom coordination in detail.

Table 2. *Final atomic parameters for* $Ca_{12}Be_{17}O_2$ *given by least-squares refinement based on the space group* $F\bar{4}3m$

Atom	Position	*x*	e.s.d.	*y*	(e.s.d.)	*z*	e.s.d.	*B*	e.s.d.
Ca(I)	24(*g*)	−0·00404	0·00028	0·25000		0·25000		0·41679*†	0·06278
Ca(II)	24(*f*)	0·29318	0·00020	0·00000		0·00000			
Be(I)	4(*b*)	0·50000		0·50000		0·50000			
Be(II)	16(*e*)	0·63616	0·00123	0·63616		0·63616			
Be(III)	16(*e*)	0·32609	0·00101	0·32609		0·32609			
Be(IV)	16(*e*)	0·16316	0·00136	0·16316		0·16316			
Be(V)	16(*e*)	0·84346	0·00124	0·84346		0·84346			
O(I)	48(*h*)	0·11211	0·00045	0·11211		0·24745	0·00085		
O(II)	48(*h*)	0·88569	0·00044	0·88569		0·74819	0·00086		
O(III)	4(*c*)	0·25000		0·25000		0·25000			
O(IV)	16(*e*)	0·56856	0·00062	0·56856		0·56856			

* This parameter could be raised to about 0·6 if the neglected absorption correction were made.
† Overall isotropic temperature factor.

Table 3. *Comparison of observed and calculated* $F^2(hkl)$

h	k	*l*	F²(obs.) × 10⁻²	F²(calc.) × 10⁻²	h	k	*l*	F²(obs.) × 10⁻²	F²(calc.) × 10⁻²	h	k	*l*	F²(obs.) × 10⁻²	F²(calc.) × 10⁻²	h	k	*l*	F²(obs.) × 10⁻²	F²(calc.) × 10⁻²
1	1	1	506	498	8	6	2	160	129	10	8	4	21	14	11	11	3	122	112
2	0	0	357	239	9	5	1	278	306	12	6	2	358	443	11	9	7	12	11
2	2	0	275	342	7	7	3	332	352	13	3	3	191	195	16	0	0	1285	1281
3	1	1	54	43	10	2	2	171	162	9	9	5	221	192	15	5	3	54	46
2	2	2	759	806	6	6	6	469	492	8	8	8	412	404	13	9	3	27	30
4	0	0	1756	1895	9	5	3	101	83	13	5	1	32	34	16	2	0	24	24
3	3	1	171	191	10	4	0	607	533	11	7	5	16	16	14	8	0	146	160
4	2	0	276	221	8	6	4	4	0	14	0	0	20	20	12	10	4	186	144
4	2	2	386	416	10	4	2	66	51	12	6	4	124	107	16	2	2	247	242
3	3	3	638	784	11	1	1	24	18	14	2	0	46	63	14	8	2	49	54
5	1	1	205	184	7	7	5	118	105	10	10	0	154	114	10	10	8	5	3
4	4	0	1641	2210	8	8	0	2025	2509	10	8	6	51	40	13	7	7	134	135
5	3	1	51	42	11	3	1	60	43	13	5	3	6	10	11	11	5	18	14
6	0	0	471	384	9	7	1	31	24	11	9	1	29	19	14	6	6	285	246
4	4	2	1028	1154	9	5	5	309	332	14	2	2	192	196	16	4	0	354	319
6	2	0	123	117	10	4	4	263	274	10	10	2	348	330	12	8	8	24	21
5	3	3	38	40	8	8	2	556	584	12	8	0	97	78	15	7	1	7	4
6	2	2	173	184	10	6	0	7	2	11	9	3	0	0	15	5	5	240	257
4	4	4	4816*	7469	8	6	6	38	37	9	9	7	7	5	13	9	5	105	98
7	1	1	108	87	11	3	3	115	115	14	4	0	136	116	16	4	2	78	68
5	5	1	603	703	9	7	3	98	78	12	8	2	291	260	14	8	4	6	2
6	4	0	215	181	10	6	2	527	670	14	4	2	55	53	12	10	6	58	48
6	4	2	192	184	12	0	0	1142	1077	12	6	6	61	57	15	7	3	64	69
7	3	1	271	218	8	8	4	70	59	10	10	4	312	320	11	9	9	80	52
5	5	3	178	175	11	5	1	74	79	13	7	1	62	82	16	4	4	310	376
8	0	0	5155*	5252	7	7	7	519	523	13	5	5	102	95	12	12	0	135	123
7	3	3	522	586	12	2	0	64	76	11	7	7	198	199	17	1	1	13	18
8	2	0	576	568	12	2	2	432	431	12	8	4	90	88	13	11	1	4	6
6	4	4	6	11	10	6	4	68	49	15	1	1	1585	1671	11	11	7	46	33
8	2	2	998	1164	11	5	3	18	23	13	7	3	96	93	16	6	0	71	106
6	6	0	614	819	9	7	5	19	15	11	9	5	90	73	12	12	2	593	563
7	5	1	51	53	12	4	0	253	227	14	4	4	89	90	16	6	2	91	105
5	5	5	594	704	9	9	1	153	155	10	8	8	58	46	14	10	0	44	36
6	6	2	297	319	12	4	2	536	442	14	6	0	162	170	14	8	6	80	77
8	4	0	615	649	10	8	0	34	31	15	3	1	12	8	17	3	1	60	51
9	1	1	90	84	8	8	6	673	618	14	6	2	183	197	15	7	5	48	48
7	5	3	15	11	10	8	2	194	138	10	10	6	859	858	13	9	7	0	0
8	4	2	78	71	13	1	1	17	17	15	3	3	23	21	14	10	2	468	447
6	6	4	192	173	11	7	1	43	43	13	7	5	1	1	10	10	10	386	350
9	3	1	1	0	11	5	5	173	166	11	11	1	12	12	12	12	4	219	186
8	4	4	487	562	9	9	3	49	46	9	9	9	147	136	17	3	3	99	106
9	3	3	41	33	10	6	6	509	556	12	10	0	6	4	15	9	1	43	48
7	7	1	95	107	12	4	4	1073	1246	12	8	6	178	150	16	6	4	6	0
7	5	5	65	60	13	3	1	14	11	14	6	4	4	3	14	10	4	5	20
10	0	0	155	109	11	7	3	112	106	12	10	2	44	31	17	5	1	6	5
8	6	0	389	356	9	7	7	74	60	15	5	1	94	91	15	9	3	5	19
10	2	0	14	15	12	6	0	22	0	13	9	1	16	15	13	11	5	5	7
															16	8	0	466	467
															17	5	3	3	22

*Affected by extinction. F²(obs.) has been arbitrarily set equal to F²(calc.)

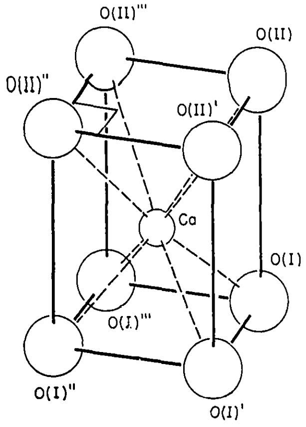
Rod configuration

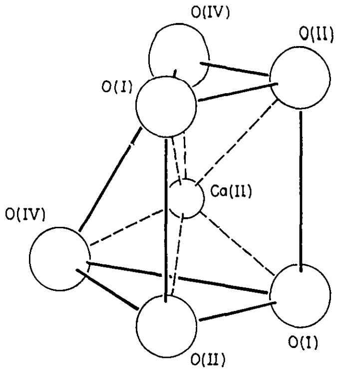
The structure of a typical rod may be appreciated by beginning at an intersection point (say $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), which is the location of a beryllium atom [Be(I)] about which four oxygen atoms [O(IV)] form a regular tetrahedron (Fig. 1). The Be–O separation in this group (1·67 ± 0·02 Å) is comparable to the distances 1·659 and 1·645 Å reported for the wurtzite form of BeO (Smith, Newkirk & Kahn, 1964).

Coordinated to each edge of this tetrahedron and lying on a [100] direction relative to its center is a Ca(II) atom. One such calcium atom is shown about each tetrahedron in Fig. 1; the rest are omitted for clarity. An approximately square group of oxygen atoms [O(I) and O(II)] completes the sixfold coordination around a Ca(II) atom. The arrangement, which can be described as a severely distorted octahedron, is similar to that about rare-earth ions in cubic rare-earth

Table 4. *Interatomic distances and angles for the coordination polyhedra in calcium beryllate*

Coordination polyhedra	Interatomic distances (Å)		Interatomic angles (°)	
A Tetrahedron about Be(I)	(4) Be(I)–O(IV)	1·66 ±0·01		
	(6) O(IV)–O(IV)	2·71 ±0·02		
B Tetrahedron about Be(II)	(3) Be(II)–O(II)	1·62 ±0·01	(3) O(II)–Be(II)–O(II)	109·1 ± 1·1
	(1) Be(II)–O(IV)	1·64 ±0·03	(3) O(II)–Be(II)–O(IV)	109·8 ± 1·1
	(3) O(II)–O(II)	2·65 ±0·02		
	(3) O(II)–O(IV)	2·68 ±0·02		
C Tetrahedron about Be(III)	(3) Be(III)–O(I)	1·65 ±0·01	(3) O(I)–Be(III)–O(I)	115·3 ± 0·6
	(1) Be(III)–O(III)	1·85 ±0·02	(3) O(I)–Be(III)–O(III)	102·7 ± 0·9
	(3) O(I)–O(I)	2·78 ±0·02		
	(3) O(I)–O(III)	2·73 ±0·01		
D Tetrahedron about Be(IV)	(3) Be(IV)–O(I)	1·55 ±0·01	(3) O(I)–Be(IV)–O(I)	119·1 ± 0·4
	(1) Be(IV)–O(III)	2·11 ±0·03	(3) O(I)–Be(IV)–O(III)	95·3 ± 1·3
	(3) O(I)–O(I)	2·68 ±0·02		
	(3) O(I)–O(III)	2·73 ±0·01		
E Triangle about Be(V)	(3) Be(V)–O(II)	1·58 ±0·01	(3) O(II)–Be(V)–O(II)	119·7 ± 0·3
	(3) O(II)–O(II)	2·73 ±0·02		
F Rectangular Prism Ca(I)	(4) Ca(I)–O(I)	2·528 ± 0·003	O(I)–Ca(I)–O(I)′	66·8 ± 0·5
	(4) Ca(I)–O(II)	2·452 ± 0·003	O(I)–Ca(I)–O(I)‴	64·1 ± 0·5
	(4) O(I)–O(II)	3·17 ±0·01	O(I)–Ca(I)–O(I)″	99·8 ± 0·4′
	O(I)–O(I)″	2·78 ±0·02	O(II)–Ca(I)–O(II)′	67·6 ± 0·5
	O(I)–O(I)′	2·68 ±0·02	O(II)–Ca(I)–O(II)‴	65·6 ± 0·5
	O(II)′–O(II)″	2·65 ±0·02	O(II)–Ca(I)–O(II)″	101·8 ± 0·4
	O(II)–O(II)′	2·73 ±0·02		
G Sixfold coordination about Ca(II)	(2) Ca(II)–O(IV)	2·368 ± 0·002	O(IV)–Ca(II)–O(IV)	70·1 ± 0·7
	(2) Ca(II)–O(I)	2·314 ± 0·009	O(I)–Ca(II)–O(II)	86·1 ± 0·1
	(2) Ca(II)–O(II)	2·340 ± 0·009	O(I)–Ca(II)–O(I)	147·8 ± 0·6
	(4) O(I)–O(II)	3·17 ±0·01	O(II)–Ca(II)–O(II)	151·3 ± 0·6
	O(IV)–O(IV)	2·71 ±0·02	O(I)–Ca(II)–O(IV)	103·1 ± 0·6
	O(IV)–O(II)	2·68 ±0·02	O(II)–Ca(II)–O(IV)	69·3 ± 0·5
	O(IV)–O(I)	3·67 ±0·01	O(II)–O(I)–O(II)	91·1 ± 0·4
			O(I)–O(II)–O(I)	88·9 ± 0·4
			O(IV)–O(IV)–O(II)	109·8 ± 0·3
			O(IV)–O(IV)–O(I)	68·2 ± 0·2





oxides (*e.g.* Pauling & Shappell, 1930). The two O(II) and two O(IV) atoms of the group are strictly coplanar; O(I) atoms are 0·06 Å below (*i.e.* away from the calcium atom) a {100} plane through O(II) atoms. Ca–O distances vary from 2·31 to 2·37 Å (compare to 2·40 Å in CaO), the shorter involving square-base oxygen atoms. As is evident from Fig. 1, each Ca(II)O_6 group is part of four diverging ⟨110⟩ rods.

Adjacent oxygen atoms in the square base of a Ca(II)O_6 group combine with corresponding atoms of a neighboring Ca(II)O_6 group to form the base of an eightfold coordination polyhedron about Ca(I) atoms. One such polyhedron, which approximates a rectangular prism, is shown in Fig. 1. Ca–O distances are 2·45 and 2·53 Å; reported Ca–O separation in compounds containing eightfold calcium coordinations include 2·40 to 2·70 Å (average 2·50 Å) in herderite ($CaBePO_4F$) (Pavlov & Belov, 1960), 2·42 to 2·75 Å (average 2·57 Å) in melilite ($Ca_2MgSi_2O_7$) (Warren, 1930), and 2·35 to 2·73 Å (average 2·51 Å) in CaB_2O_4 (Marezio, Plettinger & Zachariasen, 1963). The coordination polyhedra in herderite and melilite approximate cubic antiprisms while those in calcium metaborate approximate cubic prisms. Additional interatomic distances and angles of Ca(I)O_8 and Ca(II)O_6 groups in calcium beryllate appear in Table 4.

To the extent that a pseudo-center of symmetry may be considered to exist at the Ca(I) atom position, the structure of the rod is inverted through that center and continues *via* adjoining Ca(II)O_6 groups to another Be(I)O_4 tetrahedron centered at, for example, 1, 1, $\frac{1}{2}$.

Inter-rod configuration

The remaining atoms of the structure are found in regions where the rods begin to branch apart. In a [100] direction, we have already noted the Ca(II)O_6 group which ties together rods diverging in the four ⟨110⟩ directions at 45° to the [100]. In a [111] direction, the situation is more complicated and Figs. 2, 3, and 4 aid in the description. Only those atoms of one unit cell which immediately surround what we shall choose to call the [111] lattice direction are shown in Fig. 2; a few calcium atoms are added in Fig. 4 to indicate particular coordinations. The reader must remember that the configurations are repeated by the operations of the group $F\bar{4}3m$ about any suitable origin.

Consider ⟨110⟩ rods radiating from the intersection at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. O(II) and O(I) atoms from rods at 35·26° to [111] and [$\bar{1}\bar{1}\bar{1}$], respectively, form the triangular groups O(II)$_B$ and O(I)$_C$ shown in Fig. 2. The former group, by sharing an apex O(IV)$_A$ atom of the central tetrahedron, T_A, forms a virtually regular tetrahedron T_B in which Be(II) atoms are centrally located. The latter group, with the other O(IV)$_A$ atoms of T_A, forms an octahedral interstice (free diameter = 1·4 Å) which is empty.

The triangular groups labelled O(I)$_D$ and O(II)$_E$ consist of oxygen atoms of rods radiating from neighboring intersections (*e.g.* $\frac{1}{2}$, 0, 0 and $\frac{1}{2}$, 1, 1, respectively). With O(I)$_C$ and O(II)$_B$ groups, and with other oxygen atoms of rods radiating from $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, they form nearly spherical pockets centered at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ and $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$ whose free diameters are 2·67 and 2·59 Å. The latter are empty but the former pockets contain an oxygen atom O(III) at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$. The tetrahedra formed by an O(III) atom with surrounding O(I) atoms, T_C and T_D, contain beryllium atoms Be(III) and Be(IV) (Fig. 2). While the tetrahedra are nearly regular, the beryllium atoms in them are displaced away from O(III). In T_C this results in three normal Be–O contacts (1·65 Å) and one long

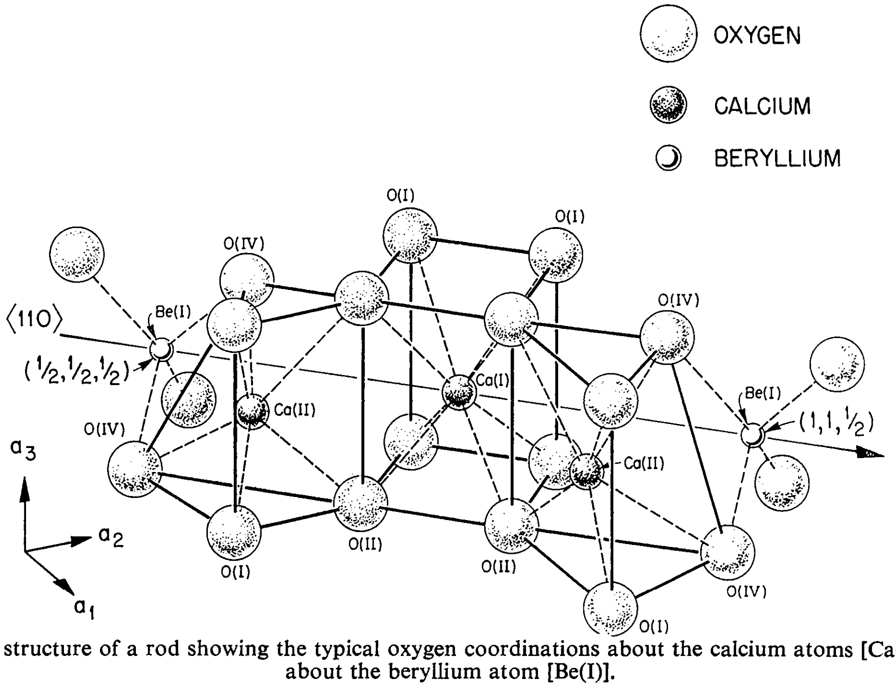


Fig. 1. The partial structure of a rod showing the typical oxygen coordinations about the calcium atoms [Ca(I) and Ca(II)] and about the beryllium atom [Be(I)].

contact (1·85 Å); in T_D we find three abnormally short Be–O distances (1·56 Å) and one abnormally long distance (2·11 Å). The short contacts are comparable to Be–O separations of 1·55 Å in a BeO_3F tetrahedron of hederite (Pavlov & Belov, 1960) and 1·58 Å in Al_2BeO_4 (Farrell, Fang & Newnham, 1963); no precedent for the long contacts has been found.

The reason for these beryllium atom displacements in T_C and T_D is probably twofold. First, $\bar{4}3m$ symmetry about $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ produces a set of four T_C and four T_D tetrahedra from those shown in Fig. 2. All eight tetrahedra have a common apex at O(III) and each T_C tetrahedron shares one edge with a T_D tetrahedron (see *Fig. 3(a) for a schematic representation*). If Be(III) and Be(IV) atoms occupied more symmetrical positions in their respective oxygen tetrahedra (*i.e.* x[Be(III)] = 0·320, x[Be(IV)] = 0·180) the separation between beryllium atoms across the shared edge would be 1·94 Å. Mutual repulsion could thus reasonably displace the beryllium atoms along triad axes to the more comfortable observed atomic separation of 2·29 Å. Sharing of BeO_4 tetrahedra edges also occurs in the high-temperature form of BeO (Smith, Cline & Austerman, 1964); the reported Be–Be separation across an edge is 2·20 Å but equal Be–O contacts were a constraint of the structure refinement.

A second reason for the almost trigonal coordination of Be(IV) atoms may be found in their proximity to large inter-rod holes (*e.g.* that centered at 0, 0, 0). The sides of these holes are formed of negatively charged oxygen atoms [*e.g.* $O(I)_D$ and $O(II)_E$] and, to achieve some charge balance, atoms such as Be(IV) and Ca(II) may be attracted toward the sides and away from more symmetric sites in $Be(IV)O_4$ and $Ca(II)O_6$ groups.

At the triangular group $O(II)_E$, a unique trigonal coordination is adopted by a Be(V) atom which nests tightly (Be–O distance = 1·58 Å) into the oxygen-atom triangle and faces out into the large inter-rod hole centered at 1, 1, 1. As seen in Fig. 3(*b*), $\bar{4}3m$ symmetry produces three additional trigonal $Be(V)O_3$ groups about the pocket at $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$ which face into large holes centered at $1, \frac{1}{2}, \frac{1}{2}$; $\frac{1}{2}, \frac{1}{2}, 1$; $\frac{1}{2}, 1, \frac{1}{2}$. Again, requirements of charge balance may stabilize this unusual arrangement.

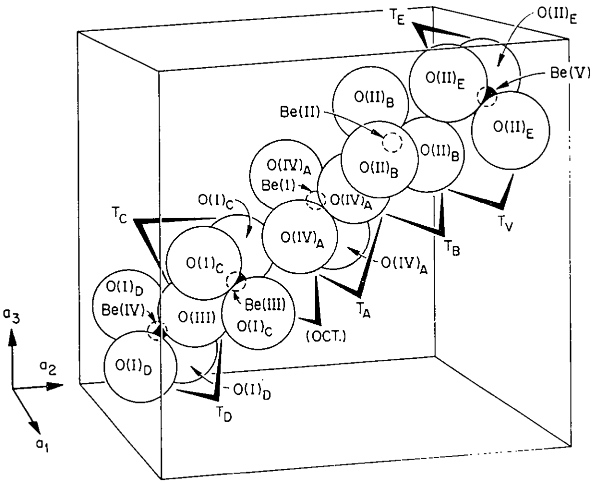


Fig. 2. Packing around a threefold axis showing oxygen coordinations about all crystallographically different beryllium atoms.

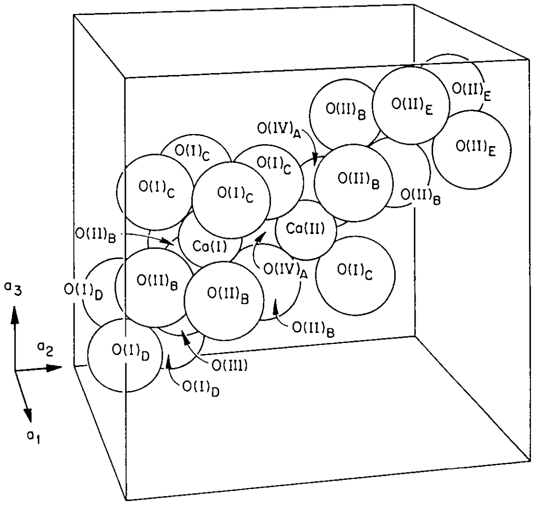
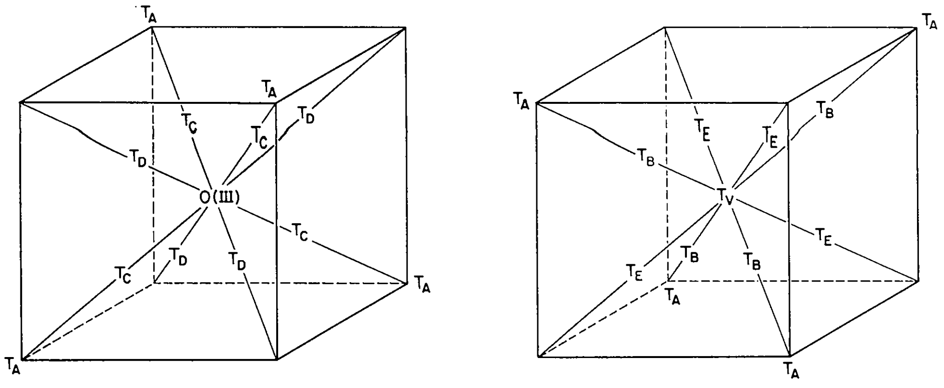


Fig. 4. Packing about a threefold axis with the addition of typical Ca(I) and Ca(II) coordination polyhedra.



(*a*) (*b*)

Fig. 3. Schematic representation of the beryllium–oxygen polyhedral arrangements about (*a*) the oxygen [O(III)] at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ and (*b*) about the hole at $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$.

Groups about Be(III), Be(IV), and Be(V) atoms are the final bits of inter-rod 'glue' encountered along ⟨111⟩ directions before diverging rods leave large (5·4 Å diameter) holes centered at sites such as 0, 0, 0 and 1, 1, 1. Some indication of the manner in which these groups interlock with the rod structure may be seen in Fig. 4.

Hole configuration

The large inter-rod holes are relatively isolated from one another. They are surrounded by the square bases of Ca(II)O_6 groups in ⟨100⟩ directions, by the prism sides of Ca(I)O_8 groups in ⟨110⟩ directions, and by triangular faces of Be(IV)O_4 and Be(V)O_3 groups in ⟨111⟩ directions. The shortest path between them is through a Ca(I)O_8 group; a more devious path lies through a Be(V)O_3 group, into a $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$ pocket, and into an adjoining large hole through another Be(V)O_3 group.

Structural obstacles along either path would seem to dictate low interhole diffusion rates for large guest atoms or molecules. This has been tentatively verified by repeated failures in attempts to introduce argon into the holes by treating calcium beryllate in a 2400-lb.in^{-2} argon atmosphere at 500 to 550°C for periods up to 18 hr. Diffusion rates may be higher for small atoms or molecules (He or H_2), and the possible entrapment of guest atoms during formation of calcium beryllate is worth investigation.

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The Crystal Structure of Bavenite

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Bavenite, a silicate containing aluminum, beryllium, calcium and hydrogen, is orthorhombic, with space group *Cmcm*, $Z=4$, $a=23{\cdot}19$, $b=5{\cdot}005$, $c=19{\cdot}39$ Å. Its crystal structure has been solved from a three-dimensional Patterson synthesis. Final bond lengths and angles were determined from coordinates obtained by the least-squares method applied to three-dimensional data (final over-all R value: 6·6 %). Bavenite displays a framework-like structure in which the dominant motif is a fourfold chain of linked tetrahedra running parallel to **b**. The diadochy between aluminum, tetrahedrally coordinated, and beryllium is discussed. The positions of the hydrogen atoms have been determined and an improved chemical formula has been derived, *i.e.* $Ca_4(BeOH)_{2+x}Al_{2-x}Si_9O_{26-x}$, where $0{\cdot}10 \le x \le 0{\cdot}84$.

Introduction

Bavenite is a silicate containing aluminum, beryllium and calcium, always found in a tardomagmatic environment. After some discussion it has been recognized as orthorhombic. Its probable space group is reported as *Cmcm* and slightly varying lattice constants have been found by different authors who handled different specimens (Berry, 1963). It often occurs in

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* G.F. carried out the differential thermal analysis of bavenite, contributing to the arrangement of the chemical formula.