Crystal Structure of BaGe[Ge₃O₉] and Its Relation to Benitoite

C. Robbins, A. Perloff, and S. Block

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234

BaGe[Ge₃O₉] is trigonal, space group P3, with lattice constants $a = 11.61$, $c = 4.74$ Å, and $Z = 3$.

The structure was established by three-dimensional Patterson and electron density syntheses. Three-dimensional least-squares refinement resulted in a final R value of 6.8 percent (observed data only).

The previously proposed structural relationship of this compound with benitoite, BaTiSi₃O₉, has been confirmed. The structure can be considered as composed of Ge₃O₉ rings, in which the Ge is tetrahedrally coordinated, linked through octahedrally coordinated Ge atoms to form a three-dimensional Ge-O network. All Ge polyhedra are linked by corner sharing. The Ba ions occupy positions in channels of the network.

Key Words: Barium tetragermanate, structure, benitoite, crystal, x-ray.

1. Introduction

The synthesis of three germanates of formula type MeGe₄O₉ (Me = Sr, Pb, Ba) was reported by Robbins and Levin [1].[1] A comparison of indexed powder patterns suggested that the compounds were isostructural. This was later confirmed by Eulenberger, Wittman, and Nowotny [2]. In addition, they reported the synthesis of two forms of CaGe₄O₉ designated α and β, and found the α form was isostructural with (Sr, Pb, Ba) Ge₄O₉.

Crystal chemical considerations (Robbins and Levin [1]) suggested a structural relationship with the mineral benitoite, BaTiSi₃O₉, whose structure was determined by Zachariasen [3]. Comparison of patterns of 1:4 germanates with indexed benitoite powder data supported this view. From these observations and a consideration of unit cell dimensions, a trial structure for the tetragermanates was obtained (Robbins and Levin [1]). To test the validity of the proposed model, the structure of BaO·4GeO₂ was determined.

2. Experimental Data

Single crystals in the form of needles elongated along [001] were obtained by slowly cooling a melt of composition BaGe₄O₉ from slightly above the congruent melting point of 1392 ± 5 °C.

Unit cell dimensions, density measurements, and optical data for this compound were reported by Robbins and Levin [1]. Their data plus the space group information are:

$$a = 11.61 \text{ Å} \qquad \omega = 1.797 \pm 0.003$$
$$c = 4.74 \text{ Å} \qquad \epsilon = 1.783 \pm 0.003$$
$$S.G. = P3 \qquad \rho \text{ (obs)} = 5.1 \text{ gcm}^{-3}$$
$$Z = 3 \qquad \rho \text{ (calc)} = 5.12 \text{ gcm}^{-3}$$

No systematic absences were observed. Precession films were consistent with space groups P3m1 or P̄3m1. No satisfactory structure could be derived in these space groups. The possible space groups P3 or P̄3 were then considered. The centrosymmetric choice could be eliminated on the basis of packing considerations because of the short c dimension. The assumption that the space group is P3 was confirmed by the final structure.

Integrating Weissenberg films of levels h k l with $l = 0, 1, 2, 3, 4$ were taken with Zr-filtered MoKα radiation ($\lambda = 0.7107$ Å) using the multiple film technique. Intensities were measured with a densitometer comparator. Very weak reflections were estimated visually. The intensity data were obtained from a crystal approximately rectangular in cross section with dimensions of 0.043 mm, 0.066 mm, and a length of 0.189 mm. The linear absorption coefficient for molybdenum radiation is 222.41 cm⁻¹.

Lorentz and polarization factor corrections were applied. Since the main objective of the study was the determination of positional parameters, no corrections for absorption errors were made. The latter would be expected to affect, primarily, the thermal parameters. The data consisted of 327 observed and 435 unobserved independent reflections.

	x	σ(x)	Y	σ(Y)	z	σ(z)	B	σ(B)
Ba	0.3341	0.0004	0.3334	0.0005	0.0		1.0265	0.0526
Ge(1)	.0		.0		−.0928	0.0034	0.3509	.2221
Ge(2)	.6667		.3333		.0062	.0038	.5501	.1798
Ge(3)	.3333		.6667		.1024	.0031	.2158	.1867
Ge(4)	.8148	.0007	.8200	.0006	.4111	.0025	.3859	.1570
Ge(5)	.6674	.0007	.5131	.0006	.5051	.0034	.1402	.0864
Ge(6)	.5160	.0006	.6719	.0007	.5929	.0025	.3680	.1275
O(1)	.8459	.0032	.9286	.0035	.1195	.0075	−.4341	.4651
O(2)	.5843	.0046	.4074	.0047	.2158	.0106	1.1598	.7527
O(3)	.7746	.0033	.6524	.0055	.3101	.0078	−0.1996	.5040
O(4)	.5508	.0035	.3561	.0035	.6965	.0080	.0655	.5479
O(5)	.4743	.0056	.7350	.0058	.8978	.0127	2.2502	.9361
O(6)	.9264	.0038	.8428	.0036	.6430	.0082	0.0008	.5266
O(7)	.6650	.0069	.8081	.0068	.4927	.0175	3.0732	1.2087
O(8)	.4059	.0043	.5880	.0041	.3274	.0091	1.0006	0.6433
O(9)	.7525	.0048	.4844	.0046	.7472	.0103	1.1328	.7087

[a] The standard deviations are derived from the full-matrix least-squares refinement.

3. Structure Determination

Similarities in the x-ray powder patterns and unit cell dimensions of benitoite ($BaTiSi_3O_9$) and $BaO \cdot 4GeO_2$ led Robbins and Levin [1] to suggest that barium germanate probably exists as $BaGeGe_3O_9$ in a structural arrangement closely related to that found for benitoite by Zachariasen [3]. The large number of unobserved reflections obtained in the present study was consistent with the proposed relationship provided the Ba and Ge atoms had x and y parameters near $1/3$ and $2/3$ and z parameters near 0 or $1/2$ in the germanate cell. In benitoite Ba, Ti, and the Si_3O_9 rings all are on, or around threefold axes. The lower symmetry of the germanate permits, at most, only one of the corresponding atoms or groups to be on a threefold axis.

A three-dimensional Patterson function was computed and peaks corresponding to Ba-Ba and Ge-Ge vectors were identified and related to the proposed model. On the basis of the trial structure and space group P3, three choices of origin were possible i.e., at the center of a Ge_3O_9 group, at a Ba atom or at an octahedrally coordinated Ge atom. Using coordinates of Ba and Ge from the model, three cycles of Fourier refinement were calculated for each choice of origin. Only the model with a Ge atom at the origin on a threefold axis refined satisfactorily. Using phases based on Ba and Ge positions from the Fourier refinement, a 3-dimensional electron density map was calculated which yielded the oxygen coordinates.

The structure was refined by a full-matrix least-squares analysis of the 327 observed and 435 unobserved reflections. The final conventional R value based on the 327 observed independent reflections was 0.068. The total number of parameters varied was 62 which included x, y, and z, an isotropic temperature factor for each atom and a scale factor for each level. The final parameters from this refinement are listed in table 1. The temperature factors are not considered meaningful, primarily because of absorption. The correlation matrix from this refinement indicated that many of the variables were correlated to a moderate degree (correlation coefficients on the order of 0.5 to 0.6). The possibility that this was the source of the unrealistic temperature factors was considered. A second least-squares refinement was made in which, alternately, scale and position parameters were varied for 2 cycles with fixed temperature factors and then temperature factors were varied for 2 cycles with fixed scale and position parameters. This was repeated for a total of eight cycles. The result was identical with the first refinement to within one standard deviation. Therefore, only the parameters from the first refinement are given in this paper. Observed and calculated structure factors are reported in table 2.

Atomic scattering factors for neutral Ge and O^{-1} were taken from *International Tables for X-ray Crystallography* (1962). Values for Ba^{+2} were taken from Thomas and Umeda [4]. The barium and germanium form factors were corrected for dispersion (International Tables for X-ray Crystallography, 1962).

4. Structure Description

A projection of the structure of $BaO \cdot 4GeO_2$ along [001] is shown in figure 1. Numbering of the atoms of the asymmetric unit is consistent with table 1. The structure is made up of rings of three GeO_4 tetrahedra linked together by GeO_6 octahedra. Barium atoms are located in channels of the network. Germanium atoms 1, 2, and 3 are octahedrally coordinated and lie on threefold axes. Germanium atoms 4, 5, and 6, in tetrahedral coordination, make up the Ge_3O_9 ring. Six rings are linked through a germanium octahedron to form the germanium-oxygen network. The two nonring oxygens of each of three equivalent GeO_4 tetrahedra are bonded to germanium atoms above and below the ring to form GeO_6 groups. Every germanium polyhedron shares all of its corners; GeO_4 tetrahedra share only corners with other polyhedra with the exception of Ge (6), which shares one edge with a barium polyhedron; each germanium octahedron shares three edges with three different barium polyhedra.

The Ge_3O_9 ring, projected along [001], is shown in figure 2. Interatomic distances, angles and standard deviations for the three germanium atoms in tetra-
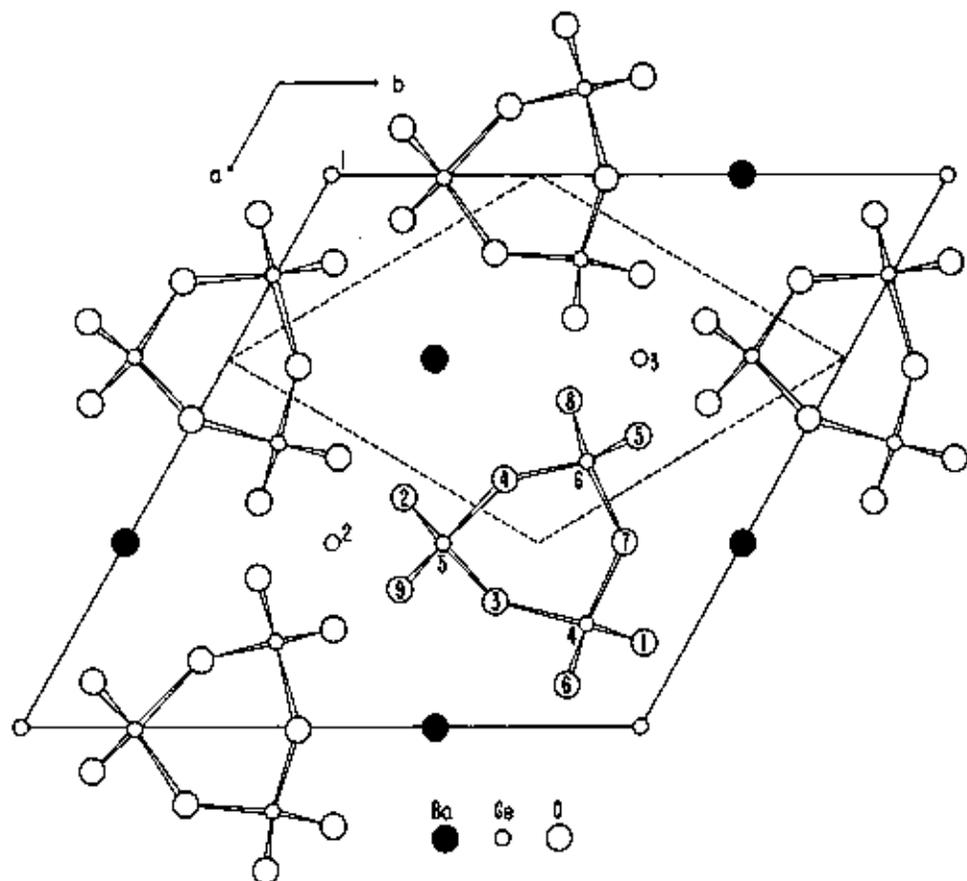
FIGURE 1. [001] *Projection of the* BaGe [Ge₃O₉] *structure.*
The numbering is that of table 1.
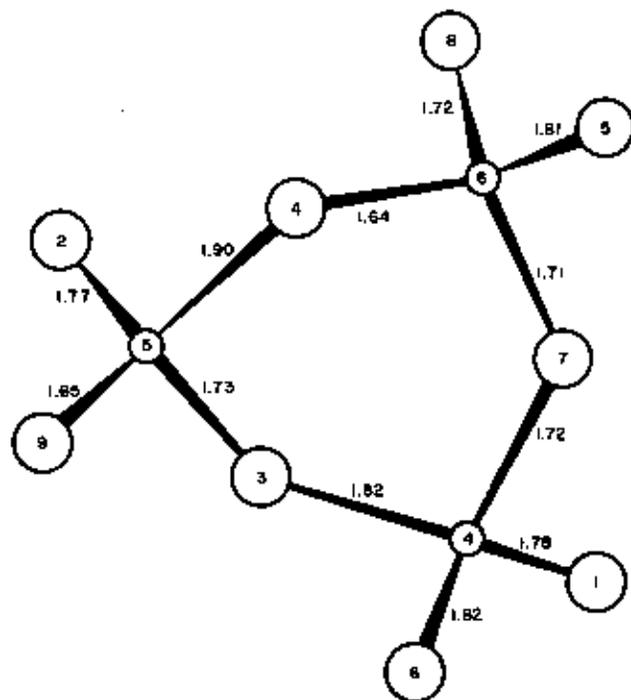
FIGURE 2. [001] *Projection of the* Ge₃O₉ *ring.*
The numbers identify atoms in table 1. Bond distances are in Å.

h	k	l	Fo	aFc	h	k	l	Fo	aFc	h	k	l	Fo	aFc
0	15	0	97	88	3	5	1	55	68	2	8	2	124	121
1	4	0	184	187	3	6	1	178	170	-2	8	2	74	81
1	-5	0	111	108	-3	-6	1	190	184	-2	10	2	124	120
1	7	0	55	58	3	-7	1	81	73	3	0	2	136	133
1	-8	0	53	50	-5	7	1	43	46	3	-1	2	103	95
1	10	0	94	94	-5	-9	1	156	153	3	-2	2	62	60
1	-11	0	92	95	3	9	1	165	155	3	2	2	72	54
2	5	0	60	49	-5	9	1	176	173	3	4	2	55	39
2	-7	0	60	57	-3	12	1	168	160	3	5	2	53	53
2	8	0	169	171	4	0	1	34	36	3	-6	2	107	109
-2	10	0	169	176	4	-1	1	43	58	3	6	2	84	88
2	11	0	46	49	4	1	1	147	146	3	-7	2	99	98
-2	13	0	42	50	4	-2	1	82	94	-3	9	2	90	95
2	14	0	53	56	-4	-4	1	75	80	4	0	2	115	105
-2	16	0	54	56	4	4	1	72	81	4	1	2	73	68
3	0	0	123	115	-4	5	1	145	150	4	-2	2	223	224
3	3	0	116	111	4	7	1	92	80	4	4	2	164	148
3	-6	0	132	138	-4	7	1	82	83	4	6	2	60	56
3	-9	0	134	134	4	9	1	50	58	-4	-7	2	72	74
3	9	0	80	85	5	0	1	92	83	5	0	2	62	66
3	12	0	82	77	5	2	1	139	130	5	-1	2	61	66
4	4	0	208	230	5	-3	1	56	59	5	1	2	156	146
4	7	0	85	75	5	3	1	39	37	5	2	2	73	72
4	10	0	120	115	5	5	1	108	106	5	-2	2	60	57
4	13	0	43	50	-5	-5	1	114	104	5	5	2	72	76
5	5	0	155	156	5	8	1	103	94	5	7	2	76	79
5	11	0	100	97	-5	-8	1	86	87	6	-1	2	150	150
5	-16	0	87	90	-5	13	1	111	95	6	1	2	37	47
6	6	0	189	194	6	3	1	193	188	6	-3	2	104	106
6	9	0	90	84	7	1	1	175	171	6	3	2	66	67
7	4	0	81	87	-7	-4	1	77	76	6	-5	2	96	83
7	10	0	64	65	7	7	1	134	125	6	5	2	109	110
8	8	0	79	68	-7	-7	1	134	125	6	6	2	157	150
9	0	0	108	107	7	-9	1	69	88	-6	-6	2	215	224
9	3	0	79	85	8	1	1	56	55	7	0	2	74	77
9	6	0	93	90	8	-5	1	59	66	7	-2	2	63	64
9	9	0	93	80	8	5	1	103	91	7	-3	2	107	104
10	7	0	54	60	-8	8	1	72	66	7	3	2	73	67
10	10	0	50	52	9	0	1	140	128	7	4	2	69	70
12	0	0	185	179	9	-1	1	41	60	8	1	2	51	59
12	3	0	79	75	9	-2	1	56	60	8	-2	2	118	121
12	6	0	113	93	-9	-6	1	84	89	8	-4	2	167	170
12	9	0	51	50	9	6	1	89	74	8	-5	2	67	61
12	-10	0	86	82	9	-7	1	62	78	9	0	2	108	93
13	4	0	49	54	10	1	1	81	81	9	-1	2	51	53
14	-7	0	36	45	10	3	1	42	48	9	3	2	66	67
14	-10	0	116	105	11	-1	1	90	87	9	-3	2	68	65
15	3	0	52	65	-12	-5	1	103	98	9	-10	2	72	65
0	3	1	274	286	-12	9	1	170	157	10	1	2	50	50
0	4	1	92	89	13	-3	1	51	52	-10	-1	2	92	82
0	5	1	35	42	0	2	2	56	33	10	-2	2	135	125
0	9	1	109	130	0	3	2	114	100	10	-3	2	62	64
1	2	1	85	80	0	4	2	37	40	10	-5	2	51	60
1	3	1	29	31	0	5	2	188	190	10	-6	2	51	56
1	4	1	127	128	0	6	2	229	233	10	-9	2	54	63
-1	5	1	129	125	0	9	2	76	71	-10	10	2	95	89
-1	7	1	164	160	0	11	2	94	103	-11	1	2	82	77
-1	-7	1	171	166	1	1	2	62	63	11	1	2	69	74
-1	8	1	171	169	1	3	2	99	97	11	-1	2	77	60
1	13	1	79	94	1	4	2	83	75	11	2	2	64	56
2	1	1	105	100	-1	4	2	107	99	11	-5	2	105	107
2	-1	1	206	216	1	5	2	86	85	12	6	2	119	116
2	2	1	97	94	-1	5	2	79	83	12	-1	2	87	73
-2	3	1	107	94	-1	6	2	104	96	-12	-3	2	89	79
-2	-3	1	72	66	-1	7	2	106	96	12	-3	2	78	65
2	3	1	70	64	1	9	2	54	65	12	-6	2	149	143
-2	-5	1	132	127	1	10	2	65	77	12	-7	2	71	80
2	5	1	146	143	2	0	2	40	54	12	-9	2	89	77
2	6	1	37	44	2	-1	2	79	78	0	2	2	38	42
-2	7	1	141	136	2	-2	2	198	214	0	3	3	145	147
-2	8	1	40	43	2	4	2	66	61		5	3	89	95
2	11	1	47	55	2	5	2	47	57		6	3	63	60
3	0	1	239	253	-2	6	2	54	58		8	3	88	90
3	2	1	68	66	2	7	2	78	80	1	1	3	97	106
3	4	1	39	57	-2	7	2	45	39	1	3	3	148	145

388

TABLE 2. *Comparison of observed and calculated structure factors* $S(hk0) = 1.97$, $S(hk1) = 2.68$, $S(hk2) = 3.09$, $S(hk3) = 3.25$, $S(hk4) = 4.44$ —Continued

h	k	l	Fo	aFc	h	k	l	Fo	aFc	h	k	l	Fo	aFc
1	4	5	93	67	8	−1	3	82	80	4	−3	4	90	60
1	7	3	82	76	8	−2	3	79	82	4	4	4	64	68
−1	8	3	82	82	8	−4	3	41	47	5	1	4	131	128
2	0	3	17	26	9	0	3	93	87	5	−2	4	35	35
2	−1	3	112	107	9	−1	3	122	121	5	4	4	74	74
2	1	3	186	172	9	3	3	49	61	5	−4	4	90	80
2	2	3	53	51	9	−3	3	100	106	5	5	4	73	69
2	5	3	93	90	9	−9	3	78	82	7	1	4	67	55
2	7	3	157	144	10	1	3	77	67	7	3	4	68	64
2	−7	3	79	79	10	3	3	98	96	7	4	4	45	58
−2	7	3	96	89	10	−3	3	109	105	7	−5	4	65	61
−2	9	3	141	143	10	−5	3	85	77	7	−8	4	67	73
3	0	3	99	98	11	−1	3	80	63	8	1	4	93	76
3	−1	3	170	175	11	−4	3	41	48	8	−1	4	67	58
3	2	3	127	115	11	−5	3	75	67	8	−4	4	52	65
3	3	3	108	106	11	−7	3	86	71	9	−1	4	72	68
3	5	3	103	104	12	−3	3	62	70	9	−6	4	49	54
3	−7	3	167	159	12	−4	3	86	93	9	−7	4	86	90
−3	8	3	105	105	0	2	4	57	54	10	−2	4	44	52
−3	9	3	80	74		3	4	83	81	10	−3	4	74	65
3	−9	3	98	97		5	4	158	153	10	−5	4	73	71
4	1	3	125	125		6	4	54	64	10	−6	4	95	85
4	−2	3	51	43	3	0	4	67	69					
4	−3	3	160	145	4	0	4	86	83					
4	4	3	33	42	6	0	4	42	54					
4	9	3	121	108	7	0	4	83	75					
5	−1	3	122	123	9	0	4	68	69					
5	−2	3	124	117	1	1	4	107	95					
5	−4	3	91	93	1	3	4	97	94					
5	5	3	80	77	1	4	4	90	79					
−6	2	3	57	55	1	6	4	95	85					
6	−2	3	76	81	−1	7	4	64	81					
6	−3	3	103	106	1	7	4	91	73					
6	−4	3	50	53	−1	8	4	80	72					
6	5	3	64	61	2	1	4	98	97					
7	1	3	83	78	2	2	4	59	66					
7	−2	3	76	71	3	2	4	45	53					
7	3	3	112	98	3	6	4	45	53					
7	−3	3	164	151	3	−6	4	59	66					
8	1	3	130	119	4	1	4	99	83					

hedral coordination are given in table 3(A). The germanium-oxygen distances range from 1.617 ± 0.044 to 1.895 ± 0.048 Å,[*] with an average value of 1.74_9 Å. This agrees well with the average value of 1.74_9 Å recorded for $Na_4Ge_9O_{20}$ (Ingri and Lundgren [5]) and with individual independent values of 1.737 ± 0.003 Å and 1.741 ± 0.002 Å obtained by Smith and Isaacs [6] from a study of the α-quartz form of germanium dioxide. The O-Ge-O angles vary from $94.0 \pm 3.1°$ to $124.9 \pm 2.1°$ with an average value of $109.3°$.

A GeO_6 group is shown in figure 3, [001] projection. Bond distances and angles for the three independent germanium atoms in sixfold coordination are presented in table 3(B). The mean Ge-O distance is 1.88 Å. This is in agreement with the value of 1.89 Å given by Ondik and Smith [7] for octahedrally coordinated germanium. It is apparent that both tetrahedra and octahedra are somewhat irregular.

Germanium-germanium distances are listed in table 3(C). The average value of 3.15_9 Å is in good agreement with the value of 3.153_4 Å obtained by Smith and Isaacs [6].

The oxygen polyhedron about the barium ion is shown in figure 4 [001] projection. Barium is coordinated to ten oxygen atoms with bond lengths ranging from 2.663 ± 0.029 Å to 3.277 ± 0.087 Å. Bond distances and standard deviations are listed in table 4. The barium ions lie in channels in the germanate network as shown in figure 1.

5. Relation to Benitoite

The structural relationship between $BaGe[Ge_3O_9]$ and $BaTiSi_3O_9$ proposed by Robbins and Levin [1] is essentially correct. In figure 1, the dashed outline of the $BaTiSi_3O_9$ cell [3] is shown on the [001] projection of the germanate cell. Within the dashed lines, Ge(3) in six-fold coordination corresponds to titanium

TABLE 3. *Germanium-oxygen bond lengths and angles* [a]

A. Tetrahedrally coordinated germanium

Distances			Angles		
	Å	σ, Å			σ
Ge(4)—O(1)	1.785	0.039	O(1)—Ge(4)—O(5)	113.5°	1.8°
O(5)	1.823	.040	O(1) O(6)	123.3	1.6
O(6)	1.617	.044	O(1) O(7)	94.0	3.1
O(7)	1.719	.088	O(5) O(6)	96.3	2.1
			O(5) O(7)	105.4	2.6
			O(6) O(7)	123.8	3.2
Ge(5)—O(2)	1.770	.048	O(2)—Ge(5)—O(3)	97.0	2.0
O(3)	1.734	.033	O(2) O(4)	109.8	2.2
O(4)	1.895	.048	O(2) O(9)	124.9	2.1
O(9)	1.653	.053	O(3) O(4)	106.5	1.9
			O(3) O(9)	109.6	2.6
			O(4) O(9)	107.5	2.3
Ge(6)—O(4)	1.642	.049	O(4)—Ge(6)—O(5)	108.6	2.8
O(5)	1.805	.069	O(4) O(7)	108.0	3.5
O(7)	1.714	.060	O(4) O(8)	100.0	2.2
O(8)	1.720	.042	O(5) O(7)	101.5	3.3
			O(5) O(8)	121.9	2.7
Average	1.740		O(7) O(8)	116.2	3.1
			Average	109.3	
			Ge(4)—O(7)—Ge(6)	129.5	5.4
			Ge(4)—O(3)—Ge(5)	122.5	2.3
			Ge(5)—O(4)—Ge(6)	124.1	2.1
O(1)—O(3)	3.022	.056			
O(1)—O(6)	2.993	.069			
O(1)—O(7)	2.562	.080			
O(3)—O(6)	2.566	.047			
O(3)—O(7)	2.818	.107			
O(6)—O(7)	2.943	.097			
O(2)—O(3)	2.625	.050			
O(2)—O(4)	3.000	.071			
O(2)—O(9)	2.882	.069			
O(3)—O(4)	2.910	.052			
O(3)—O(9)	2.768	.056			
O(4)—O(9)	2.865	.068			
O(4)—O(6)	2.801	.091			
O(4)—O(7)	2.715	.081			
O(4)—O(8)	2.576	.068			
O(5)—O(7)	2.726	.100			
O(6)—O(8)	3.082	.074			
O(7)—O(8)	2.916	.070			
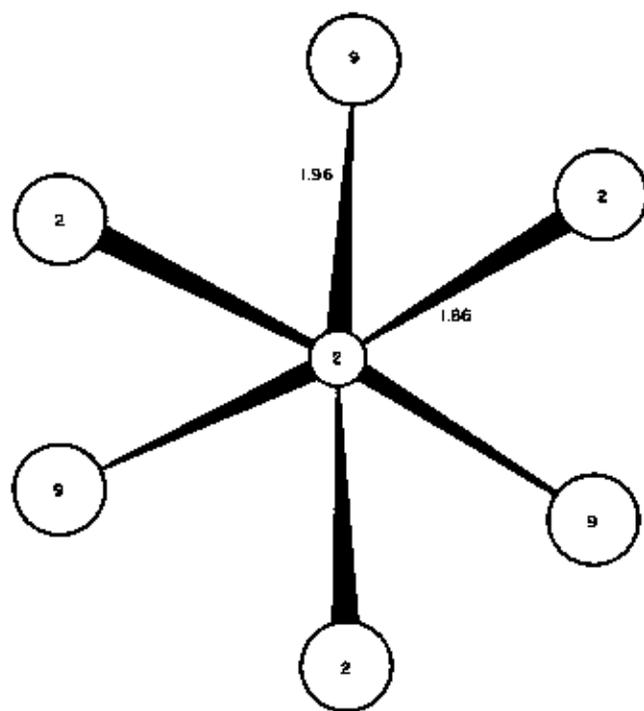
FIGURE 3. *[001] Projection of a GeO₄ group.*
The numbering is consistent with that of table 1. Bond distances are in Å.

B. Octahedrally coordinated germanium

Distances			Angles		
	Å	σ, Å			σ
Ge(1)—O(1)	1.846	0.036	O(1)—Ge(1)—O(6)	88.0°	1.5°
O(6)	2.018	.099	O(1) O(1)'	93.2	1.6
			O(6) O(6)'	85.5	1.8
			O(1) O(6)'	93.1	1.7
Ge(2)—O(2)	1.861	.063	O(2)—Ge(2)—O(2)'	94.1	2.5
O(9)	1.957	.051	O(9) O(9)'	84.8	2.4
			O(2)' O(9)'	94.0	2.0
			O(2)' O(9)'	86.9	2.3
Ge(3)—O(5)	1.717	.058	O(5)—Ge(3)—O(5)'	91.2	2.8
O(8)	1.858	.056	O(8) O(8)'	90.3	2.2
			O(8)' O(5)'	89.4	2.3
Average	1.877		O(8) O(5)'	89.4	2.8
O(1)—O(6)	2.688	.059			
O(1)—O(1)'	2.687	.039			
O(6)—O(6)'	2.740	.068			
O(1)—O(6)'	2.810	.052			
O(2)—O(2)'	2.725	.067			
O(9)—O(9)'	2.640	.089			
O(2)'—O(9)'	2.793	.080			
O(2)'—O(9)'	2.626	.069			
O(5)—O(5)'	2.455	.066			
O(8)—O(8)'	2.634	.080			
O(8)'—O(5)	2.516	.084			
O(8)—O(5)'	2.516	.074			

C. Distances between germanium atoms

	Å	σ, Å
Ge(1)—Ge(4)	3.167	0.017
Ge(1)—Ge(6)	3.194	.017
Ge(2)—Ge(5)	3.151	.019
Ge(2)—Ge(5)	3.159	.019
Ge(3)—Ge(6)	3.143	.015
Ge(3)—Ge(6)	3.210	.015
Ge(4)—Ge(5)	3.119	.011
Ge(4)—Ge(6)	3.106	.012
Ge(5)—Ge(6)	3.127	.014
Average	3.153	

[a] The standard deviations are derived from the diagonal terms of the least-squares matrix.
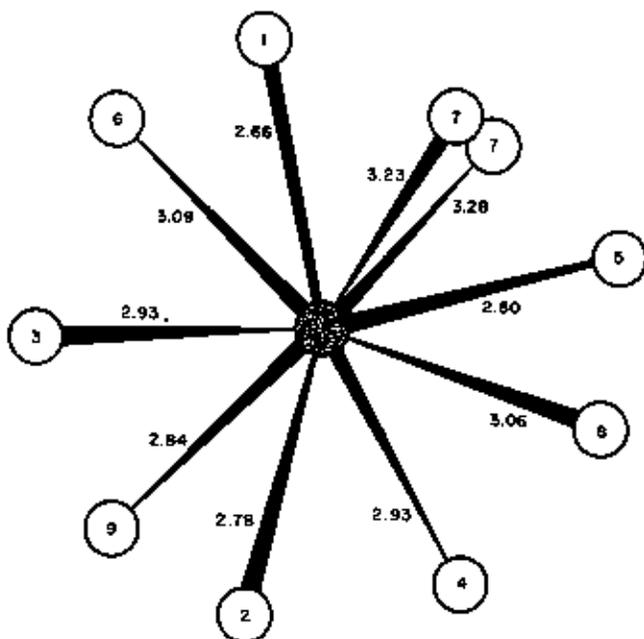
FIGURE 4. *Nearest neighbor barium ion coordination, [001] projection.*
The numbering is consistent with that of table 1. One O(7) atom is shown displaced slightly in x and y. Bond distances are in Å.

TABLE 4. *Bond distances of the barium coordination polyhedron*[a]

	Å	σÅ
Ba—O(1)	2.663	0.029
O(6)	3.088	.035
O(3)	2.929	.049
O(9)	2.836	.063
O(2)	2.760	.055
O(4)	2.927	.032
O(8)	3.063	.047
O(5)	2.802	.079
O(7)	3.277	.087
O(7)	3.227	.087

[a] The standard deviations are derived from the diagonal terms of the least-squares matrix.

TABLE 5. *Crystal data for $BaGe[Ge_3O_9]$ and $BaTiSi_3O_9$*

Compound	a, Å	c, Å	Space group	Calc. density, g cm⁻³	Z
$BaGe[Ge_3O_9]$	11.61 ± 0.02	4.74 ± 0.01	P3	5.12	3
$BaTiSi_3O_9$ [a]	6.60 ± 0.01	9.71 ± 0.01	P6̄c2	3.73	2

[a] Data from Zachariasen [3].

in the silicate compound and the rings to Si_3O_9 groups. In the silicate cell, the origin is on a threefold axis at the center of a ring. The Ba ion also lies on a three-fold axis. In addition, $BaTiSi_3O_9$ has two sheets of rings in the length of the c axis ($c = 9.71$ Å, Zachariasen, [3] whereas $BaGe[Ge_3O_9]$ has one ($c = 4.74$ Å). For discussion, only the first sheet of the silicate structure will be considered.

With the substitution of three germanium atoms for three silicon atoms and one germanium atom for one titanium atom in the formula unit $BaTiSi_3O_9$ (to give BaGe [Ge_3O_9]) the following major structural changes are noted: (1) Unlike the silicon atoms and ring oxygens of Si_3O_9, germanium atoms and ring oxygens of the Ge_3O_9 group are not coplanar and the germanium ring does not have threefold symmetry. (2) While the titanium atom lies on a threefold axis at $z = 0$, three independent octahedrally coordinated germanium atoms lie on threefold axes at $z = -0.44_0$ Å, 0.02_9 Å and 0.48_5 Å.[3] (3) In benitoite, the barium ion is on a three-fold axis surrounded by six oxygen atoms at a distance of 2.74 Å and six other oxygens at a distance of 3.4 Å. In the germanate cell, the barium ion is linked to 10 oxygen atoms at distances ranging from 2.66 Å to 3.28 Å, and no longer lies on a threefold axis. (4) SiO_4 tetrahedra share only corners with other poly-hedra in benitoite. This is true of GeO_4 groups of the tetragermanate with the exception of Ge(6). The latter shares one edge with a barium polyhedron. (5) There are two sheets of rings within the c dimension of benitoite whereas $BaGe[Ge_3O_9]$ has one. Crystal-lographic data for the two compounds are presented in table 5.

[a] Origin chosen at $z = 0$ for Ba in both structures.

Computations were performed utilizing the x-ray 63 system of crystallographic programs developed at the University of Washington and the University of Maryland [8].

6. References

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