

## Structure of Barium Germanium Hydroxide Oxide

BY MITUKO OZIMA

Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

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**Abstract.**  $\text{BaGe}_3\text{O}_6(\text{OH})_2$ ,  $M_r = 485.16$ , monoclinic,  $Cc$ ,  $a = 12.703$  (2),  $b = 4.9047$  (7),  $c = 9.418$  (2) Å,  $\beta = 105.46$  (2)°,  $V = 565.50$  (15) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 5.696$  g cm<sup>-3</sup>,  $\text{Ag K}\alpha$ ,  $\lambda = 0.56087$  Å,  $\mu = 124.59$  cm<sup>-1</sup>,  $F(000) = 872$ ,  $T = 300$  K,  $R = 0.044$  for 843 independent reflections. Eight anions and one Ba cation define a regular h.c.p. layer parallel to the (201) plane. Ge atoms occupy octahedral interstices and a sheet made of three Ge octahedra is formed in the (100) plane by edge sharing. The Ge(1) octahedron shares four edges and the Ge(2) and Ge(3) octahedra share three. Ba is coordinated by twelve anions.

**Introduction.** Studies of high-pressure and high-temperature phases in the system BaO–GeO<sub>2</sub> have been carried out by Ozima, Susaki, Akimoto & Shimizu (1982) and by Kobayashi, Ozima, Shimizu & Akimoto (1983). Ozima *et al.* (1982) found three high-pressure phases in the system BaO–GeO<sub>2</sub>, *i.e.* BaGe<sub>2</sub>O<sub>5</sub> II, BaGe<sub>2</sub>O<sub>5</sub> III, and Ba<sub>2</sub>Ge<sub>5</sub>O<sub>12</sub>. Kobayashi *et al.* (1983) reported two phases of perovskite-like BaGeO<sub>3</sub>, *i.e.* 9R-BaGeO<sub>3</sub> and 6H-BaGeO<sub>3</sub>. 'BaGe<sub>3</sub>O<sub>7</sub>' has not been reported at atmospheric pressure or at high pressures, while the hydroxide oxide, Ba<sub>3</sub>Ge<sub>9</sub>O<sub>20</sub>(OH)<sub>2</sub>, was reported to be obtained under hydrothermal conditions (1000 atm and 770 K) by Malinovskii, Pobedimskaya & Belov (1976). As has already been pointed out (Ozima *et al.*, 1982), the BaO component migrates from the sample through the graphite or platinum capsule during the high-pressure and high-temperature treatments. Hydrogen, on the other hand, which is contained in the pyrophyllite pressure medium, comes into the sample through the capsule. Accordingly, Ozima *et al.* (1982) also obtained Ba<sub>3</sub>Ge<sub>9</sub>O<sub>20</sub>(OH)<sub>2</sub> from the high-pressure and high-temperature run product of BaGeO<sub>3</sub> at 3 GPa and 1020 K. In these experiments, BaGe<sub>3</sub>O<sub>6</sub>(OH)<sub>2</sub> was found on the outer shell of the high-pressure and high-temperature run products of BaGe<sub>2</sub>O<sub>5</sub> at 4 GPa and 1120 K.

In this paper, the structure of BaGe<sub>3</sub>O<sub>6</sub>(OH)<sub>2</sub> is reported and compared with that of Ba<sub>3</sub>Ge<sub>9</sub>O<sub>20</sub>(OH)<sub>2</sub> by Malinovskii *et al.* (1976).

**Experimental.** Parallelogram-plate crystal formed by {201}, {101} and {111}, volume 0.30 × 10<sup>-7</sup> cm<sup>3</sup>; Rigaku automated four-circle diffractometer, graphite-monochromated AgK $\alpha$  radiation; unit-cell parameters

from least-squares fit for 29 reflections with 30 ≤ 2θ ≤ 45°; integrated intensities measured by 2θ-ω scans; 1079 measured, 843 independent reflections ( $|F_o| > 3\sigma|F_o|$ ) within 0 < 2θ ≤ 50°, 236 unobserved;  $(\sin\theta/\lambda)_{\text{max}} = 0.7535$  Å<sup>-1</sup>, -18 ≤ h ≤ 18, 0 ≤ k ≤ 7, 0 ≤ l ≤ 14; four standard reflections every fifty reflections; corrections for Lorentz-polarization, no absorption correction; heavy-atom method; full-matrix least-squares refinement on  $F$  using *RADIEL* (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979); anisotropic thermal parameters for all atoms; fully ionized scattering factors for Ge<sup>4+</sup> and Ba<sup>2+</sup> and  $f'$ ,  $f''$  for Ge, Ba and O from *International Tables for X-ray Crystallography* (1974), scattering factor for O<sup>2-</sup> from Tokonami (1965);  $R = 0.044$ ,  $wR = 0.047$ ,  $S = 1.3906$ ,  $w = 1$ ; max.  $\Delta/\sigma = 1.22$ ;  $\Delta\rho$  in final difference map = -1.3 ~ + 1.8 e Å<sup>-3</sup>.\*

**Discussion.** Final atomic parameters are given in Table 1. The *ORTEP* plot (Johnson, 1965) of the structure along the  $b$  axis of BaGe<sub>3</sub>O<sub>6</sub>(OH)<sub>2</sub> is shown in Fig. 1. In Table 2, bond distances and bond angles are listed. As shown, Ba and Ge atoms are coordinated by 12 and 6 oxygens or hydroxide oxygens, respectively.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42700 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates (× 10<sup>4</sup>; × 10<sup>3</sup> for O and OH) and equivalent isotropic thermal parameters (Å<sup>2</sup> × 10<sup>2</sup>; × 10 for O and OH) with *e.s.d.*'s in parentheses for BaGe<sub>3</sub>O<sub>6</sub>(OH)<sub>2</sub>

$$B_{\text{eq}} = \frac{1}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	$x$	$y$	$z$	$B_{\text{eq}}$
Ba	2508 (8)	6622 (2)	-38 (11)	65 (2)
Ge(1)	5000	2480 (16)	2500	40 (3)
Ge(2)	4407 (7)	7291 (10)	3673 (9)	29 (8)
Ge(3)	5560 (7)	7603 (10)	1241 (9)	50 (9)
O(1)	480 (3)	436 (7)	55 (4)	7 (7)
O(2)	376 (3)	424 (8)	270 (5)	10 (7)
O(3)	569 (3)	583 (6)	317 (4)	15 (7)
O(4)	430 (2)	921 (6)	178 (4)	10 (6)
O(5)	522 (3)	64 (9)	437 (5)	20 (8)
O(6)	621 (3)	77 (8)	218 (4)	17 (7)
OH(1)	689 (3)	635 (8)	112 (5)	11 (7)
OH(2)	313 (3)	869 (10)	391 (5)	19 (8)

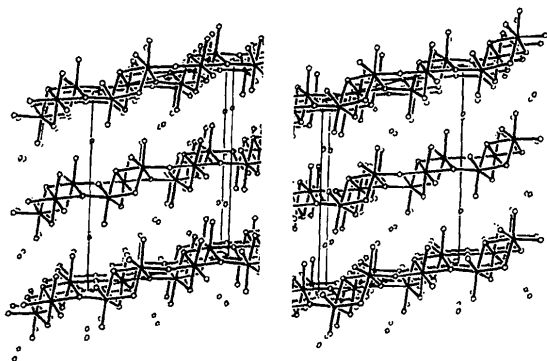


Fig. 1. Stereoscopic projection along the  $b$  axis of the structure of  $\text{BaGe}_3\text{O}_6(\text{OH})_2$ . The  $a$  axis is vertically downwards. Ba and Ge atoms are represented by thermal ellipsoids with a probability of 50%. Anions are represented by a sphere of radius 0.1 Å. Bonds between Ba and anions are not drawn.

In this crystal, anions together with Ba form a closest-packed layer consisting of  $(8 \times \text{O}/\text{OH} + \text{Ba})$  parallel to the (201) plane. This layer stacks to form a hexagonally close-packed structure. The repetition occurs along [201] at every sixth layer with the packing sequence  $(abcdef)$ , where  $a, b, c, d, e, f$  represent the six different phases of the closest-packed layer. Ge atoms occupy octahedral interstices and an undulating sheet of Ge octahedra is formed in the (100) plane. This sheet of Ge octahedra is made from an infinite  $\{\text{Ge}_3\text{O}_{10}\}_\infty$  chain along the  $b$  axis, which is comprised of three edge-sharing Ge octahedra. The parallel chains are interconnected by corner sharing of O(1) and O(5). Fig. 2(a) shows this sheet of Ge octahedra projected along the  $a$  axis and in Fig. 2(b) a schematic view of the sheet in the (201) plane is shown normal to this plane. It can be easily seen in Fig. 2(b) that the Ge(1) octahedron shares four edges and Ge(2) and Ge(3) octahedra three. The two sets of shared edges, O(1)–O(3), O(2)–O(3) and O(5<sup>ii</sup>)–O(4), O(6<sup>ii</sup>)–O(4), are combined with each other *via* another shared edge, O(3)–O(4).

Table 2. Interatomic distances (Å) and interbond angles (°) with *e.s.d.*'s in parentheses for  $\text{BaGe}_3\text{O}_6(\text{OH})_2$

Distance		Angle	
O–M–O		O–M–O	
<b>Ge(1) octahedron</b>			
Ge(1)–O(1)	2.01 (4)		
–O(2)	1.85 (4)		
–O(3)	1.89 (3)		
–O(4 <sup>i</sup> )	1.87 (3)		
–O(5)	1.93 (4)		
–O(6)	1.84 (5)		
O(1)–O(2)	2.70 (6)	88.6 (16)	
–O(3)	2.53 (5)	80.8 (14)	
–O(4 <sup>i</sup> )	2.92 (5)	97.4 (14)	
–O(6)	2.68 (5)	88.0 (17)	
O(5)–O(2)	2.74 (5)	92.5 (18)	
–O(3)	2.91 (5)	99.3 (16)	
–O(4 <sup>i</sup> )	2.51 (5)	82.5 (16)	
–O(6)	2.69 (7)	90.9 (19)	
O(3)–O(2)	2.50 (5)	83.9 (15)	
–O(6)	2.79 (5)	96.8 (17)	
O(4 <sup>i</sup> )–O(2)	2.77 (5)	95.9 (15)	
–O(6)	2.47 (5)	83.2 (17)	
<b>Ge(2) octahedron</b>			
Ge(2)–O(1 <sup>i</sup> )	1.89 (4)		
–O(2)	1.83 (4)		
–O(3)	1.95 (4)		
–O(4)	1.99 (3)		
–OH(2)	1.83 (4)		
–O(5 <sup>ii</sup> )	1.96 (4)		
O(2)–O(1 <sup>i</sup> )	2.74 (5)	95.1 (16)	
–O(3)	2.50 (5)	82.7 (16)	
–O(4)	2.74 (5)	91.4 (15)	
–OH(2)	2.68 (6)	94.0 (17)	
O(5 <sup>ii</sup> )–O(1 <sup>i</sup> )	2.80 (6)	93.5 (16)	
–O(3)	2.75 (5)	89.5 (16)	
–O(4)	2.51 (5)	79.0 (15)	
–OH(2)	2.75 (5)	93.0 (17)	
O(1 <sup>i</sup> )–O(3)	2.77 (6)	92.2 (15)	
–OH(2)	2.72 (5)	94.1 (17)	
O(4 <sup>i</sup> )–O(3)	2.52 (4)	79.3 (15)	
–OH(2)	2.82 (6)	94.8 (16)	
<b>Ge(3) octahedron</b>			
Ge(3)–O(1)	1.88 (3)		
–O(3)	1.98 (4)		
–O(4)	1.96 (3)		
–OH(1)	1.83 (4)		
–O(5 <sup>iii</sup> )	1.91 (4)		
–O(6 <sup>iii</sup> )	1.86 (4)		
O(1)–O(3)	2.53 (5)	81.8 (14)	
–O(4)	2.79 (5)	93.0 (14)	
–OH(1)	2.74 (5)	95.2 (16)	
–O(5 <sup>iii</sup> )	2.80 (6)	95.2 (17)	
O(6 <sup>iii</sup> )–O(3)	2.74 (5)	90.9 (16)	
–O(4)	2.47 (5)	80.2 (16)	
–OH(1)	2.62 (6)	90.7 (18)	
–O(5 <sup>iii</sup> )	2.69 (6)	91.3 (18)	
O(3)–O(4)	2.52 (4)	79.4 (14)	
–OH(1)	2.77 (6)	93.2 (17)	
O(5 <sup>iii</sup> )–O(4)	2.81 (6)	93.1 (16)	
–OH(1)	2.75 (5)	94.8 (19)	
<b>Ba polyhedron</b>			
Ba–O(1)	3.03 (4)		
–O(2)	2.89 (4)		
–O(2 <sup>iii</sup> )	3.01 (5)		
–O(3 <sup>iii</sup> )	2.77 (3)		
–O(4)	2.77 (3)		
–OH(1 <sup>iv</sup> )	2.77 (4)		
–OH(1 <sup>v</sup> )	2.99 (4)		
–OH(2 <sup>iii</sup> )	2.97 (5)		
–OH(2 <sup>iv</sup> )	2.71 (5)		
–O(5 <sup>iii</sup> )	3.02 (4)		
–O(6 <sup>iii</sup> )	3.02 (5)		
–O(6 <sup>iii</sup> )	2.95 (4)		

Symmetry code: (i)  $+x, -1.0 + y, +z$ ; (ii)  $+x, +1.0 + y, +z$ ; (iii)  $+x, +1.0 - y, -0.5 + z$ ; (iv)  $+x, +2.0 - y, -0.5 + z$ ; (v)  $+x, +1.0 - y, +0.5 + z$ ; (vi)  $-0.5 + x, +0.5 + y, +z$ ; (vii)  $-0.5 + x, -0.5 + y, +z$ ; (viii)  $-0.5 + x, +0.5 - y, -0.5 + z$ ; (ix)  $-0.5 + x, +1.5 - y, -0.5 + z$ .

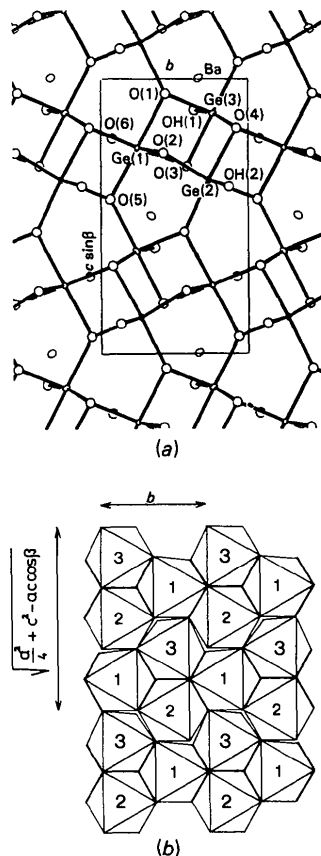


Fig. 2. (a) Projection of a sheet of Ge octahedra along the  $a$  axis of  $\text{BaGe}_3\text{O}_6(\text{OH})_2$ . (b) Schematic projection of the sheet of three Ge octahedra along [201]. Thick lines indicate the shared edges and 1,2,3 indicate the Ge(1), the Ge(2) and the Ge(3) octahedra, respectively.

The two anions which are not shared by Ge octahedra are identified as  $\text{OH}^-$ , because the bond-valence sum is 1.0 for these two. The fact that the distances  $M\text{—O}$  for these two are considerably smaller than those for the others supports this identification. The contribution of the hydrogen atoms to the structure factors, however, was neglected in the structure refinement.

From the fact that the Ge(1) octahedron shares four edges and the Ge(2) and Ge(3) octahedra three, the Ge(1) octahedron is expected to be most distorted. As shown in Table 2, for the Ge(1) octahedron, the spreads of O—O distances and O—M—O angles are in fact larger than those in the Ge(2) and Ge(3) octahedra. Similarly to anatase (Horn, Schwerdtfeger & Meagher, 1972), the lengths of the shared edges are prominently shorter than those of the unshared edges. However, in the case of  $\text{BaGe}_2\text{O}_5$  II (Ozima, 1985), such a tendency was not so distinctive. Three- or four-edge sharing in an octahedron in germanate is unusual but it is often seen in titanate, e.g. brookite,  $\text{TiO}_2$  (Baur, 1961) and anatase,  $\text{TiO}_2$  (Horn *et al.*, 1972). In this respect, the present crystal could be compared to ' $\text{BaTi}_3\text{O}_6(\text{OH})_2$ ', but such a compound has not been reported. Furthermore, three- or four-edge sharing in octahedra in this crystal implies an intensive character for the covalent bonding. The structure was solved on the basis of an ionic model, which resulted in a comparatively large  $\Delta\rho$  in the final difference Fourier map.

In Table 3, the structure of  $\text{Ba}_3\text{Ge}_9\text{O}_{20}(\text{OH})_2$  by Malinovskii *et al.* (1976) is compared with that of  $\text{BaGe}_3\text{O}_6(\text{OH})_2$  by the present author. The former is a low-pressure (probably including atmospheric pressure) phase and the latter is a high-pressure phase. This is consistent with the differences in the density and the structure in these two phases, i.e. in  $\text{Ba}_3\text{Ge}_9\text{O}_{20}(\text{OH})_2$ ,

Table 3. Comparison of  $\text{BaGe}_3\text{O}_6(\text{OH})_2$  (present study) with  $\text{Ba}_3\text{Ge}_9\text{O}_{20}(\text{OH})_2$  (Malinovskii *et al.*, 1976)

	Density ( $\text{g cm}^{-3}$ )	Ge tetrahedron	Ge tetragonal pyramid	Ge octahedron	Coordination number of Ba
$\text{Ba}_3\text{Ge}_9\text{O}_{20}(\text{OH})_2$	5.70	0	0	9	12, 12, 12
$\text{Ba}_3\text{Ge}_9\text{O}_{20}(\text{OH})_2$	4.98	6	1	2	8, 8, 9

only two of the nine Ge atoms are octahedrally coordinated and the mean coordination number of Ba is 8.3. In  $\text{BaGe}_3\text{O}_6(\text{OH})_2$ , on the other hand, all Ge atoms are octahedrally coordinated and the coordination number of Ba is 12.

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#### References

- BAUR, W. H. (1961). *Acta Cryst.* **14**, 214–216.  
 COPPENS, P., GURU ROW, T. N., LEUNG, P., STEVENS, E. D., BECKER, P. J. & YANG, Y. W. (1979). *Acta Cryst.* **A35**, 63–72.  
 HORN, M., SCHWERDTFEGGER, C. F. & MEAGHER, E. P. (1972). *J. Kristallogr.* **136**, 273–281.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)  
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.  
 KOBAYASHI, T., OZIMA, M., SHIMIZU, Y. & AKIMOTO, S. (1983). Program and Abstracts, 24th High-Pressure Conference of Japan, p. 192.  
 MALINOVSKII, YU. A., POBEDIMSKAYA, E. A. & BELOV, N. V. (1976). *Dokl. Akad. Nauk SSSR*, **227**, 1350–1353.  
 OZIMA, M. (1985). *Acta Cryst.* **C41**, 1003–1007.  
 OZIMA, M., SUSAKI, J., AKIMOTO, S. & SHIMIZU, Y. (1982). *J. Solid State Chem.* **44**, 307–317.  
 TOKONAMI, M. (1965). *Acta Cryst.* **19**, 486.

*Acta Cryst.* (1986). **C42**, 515–517

## Structure of Lead(II) Dimercury(II) Diiodide Disulfide

BY R. BLACHNIK

*Anorganische Chemie, Barbarastrasse 7, Universität Osnabrück, 4500 Osnabrück, Federal Republic of Germany*

AND W. BUCHMEIER AND H. A. DREISBACH

*Fachbereich Chemie, Anorganische Chemie, Universität—GH-Siegen, Siegen, Federal Republic of Germany*

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**Abstract.**  $\text{Hg}_2\text{PbI}_2\text{S}_2$ ,  $M_r = 926.31$ , tetragonal,  $P4/mbm$ ,  $a = 13.501$  (1),  $c = 4.593$  (1) Å,  $V = 837.20$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 7.349$  g cm<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) = 0.71069$  Å,

$\mu = 644.9$  cm<sup>-1</sup>,  $F(000) = 1520$ ,  $T = 293$  K. Final  $R = 0.039$  for 489 unique observed reflections. Crystals of  $\text{Hg}_2\text{PbI}_2\text{S}_2$  were grown by annealing the proper

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