

The Crystal Structures of Two Forms of BaBi₂S₄

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Two forms of BaBi₂S₄ have been prepared on reacting BaS and Bi₂S₃ at 640 °C, and their crystal structures have been determined. Both forms crystallize in the space group *P6₃/m*. *Z*=9 for 9-BaBi₂S₄ and 12 for 12-BaBi₂S₄. 9-BaBi₂S₄ contains a slight excess of Bi₂S₃ and 12-BaBi₂S₄ a slight excess of BaS in relation to the stoichiometric formula. A compound SrBi₂S₄ was prepared and was found to be isotypic to 12-BaBi₂S₄. The intensity data were collected by means of Weissenberg photographs. The cell dimensions for 9-BaBi₂S₄ and 12-BaBi₂S₄ are in turn: *a*=21.705(7) Å, *c*=4.158(3) Å and *a*=25.272(8) Å, *c*=4.1825(3) Å. The corresponding *R*-factors and numbers of independent reflections are 0.0952(608) and 0.1079(1085), respectively. Comparisons are made to other structures of formula AB₂S₄.

Compounds in the systems CaS-Bi₂S₃, SrS-Bi₂S₃ and BaS-Bi₂S₃ have been discussed by Schenk.¹ He showed that an equilibrium MeS+Bi₂S₃⇌MeBi₂S₄ exists for Me=Sr,Ba in the temperature range 456-706 °C and concluded the existence of the compounds SrBi₂S₄ and BaBi₂S₄. Bok and de Wit² reacted BaS, Bi and S at 600 °C for 3 days and obtained a product whose powder photograph was different from those of BaS and Bi₂S₃. The relative intensities and *d* values of the powder photograph were published but no indexing was made. The present author found that the lines could be interpreted with a hexagonal unit cell with *a*=25.14(1) Å and *c*=4.170(2) Å. A systematic study of the systems SrS-Bi₂S₃ and BaS-Bi₂S₃, using X-ray methods, was started and the present paper reports the results.

EXPERIMENTAL

Preparation and composition. In most experiments SrS or BaS was reacted with Bi₂S₃ in evacuated pyrex tubes at 640, 680 or 780 °C for various lengths of time. Bi₂S₃, 99.999 % (metals basis) and SrS 98 % both from Alfa Division and BaS 98 % from Ventron were used for these experiments. Another way of synthesis was also tried. To prepare Ba₂Bi₂Se₅ which later proved to have the composition BaBiSe₃,³ Gattow⁴ reacted Bi, BaAc₂ and Se in the weight ratio 1:5:5 in closed crucibles at 550 °C. A similar procedure was used here substituting Se by S and in some cases BaAc₂ by SrAc₂. Powder photographs were taken for all samples. In spite of many efforts, single crystals could not be obtained for the Sr compound. It was, however, noticed that whisker-like crystals were sometimes formed in the BaS-Bi₂S₃ samples and reaction times, temperatures and compositions were therefore varied. Small thread-like single crystals were obtained when BaS·1.25Bi₂S₃ was heated for 7 days at 640 °C. Intensity data could be collected by means of the Weissenberg method. The unit cell was found to be hexagonal with *a*=21.705(7) and *c*=4.158(3) Å. Thus the single crystals so obtained had not the same cell dimensions as could be deduced from the data of Bok and de Wit.² Inspection of all the powder photographs taken indicated that the two hexagonal phases generally coexisted but with different proportions. Single crystals of the other hexagonal phase were obtained on heating BaS·Bi₂S₃ for 10 days at 670 °C and the Weissenberg photographs taken indicated a cell with *a*=25.3 and *c*=4.18 Å. The corresponding powder photographs gave *a*=25.272(8) and *c*=4.1825(3) Å. 90 % of the lines present could be indexed by the phase. Making reasonable assumptions starting from the cell volumes, *Z*=9 and *Z*=12 were obtained for the two phases.

They will hereafter be denoted 9-BaBi₂S₄ and 12-BaBi₂S₄. To elucidate the relations between the two phases, series of measurements were made on samples with ratios BaS–Bi₂S₃ 4:1, 2:1, 1:1, 1:1.25, 1:1.50, 1:1.75, 1:2 and 1:4. The samples were first prepared on heating the components to 640 °C for 24 h. They were then recrystallized for 2 h at 420, 680 and 780 °C. 4 batches of BaS were used with different ages from the openings of the bottles. The corresponding powder photographs were indexed using the unit cells of 9-BaBi₂S₄, 12-BaBi₂S₄ and Bi₂S₃. The fraction $Q(1)$ of indexed lines corresponding to each unit cell was calculated. Due to the fact

that a certain line may be indexed in more than one way, the sums of the $Q(1)$ values are larger than 1. Thus pure Bi₂S₃ shows the fractions 0.49, 0.56 and 1.00 for 9-BaBi₂S₄, 12-BaBi₂S₄ and Bi₂S₃, respectively. The corresponding values for 9-BaBi₂S₄ and 12-BaBi₂S₄ are in turn 1.00, 0.40, 0.36 and 0.37, 1.00, 0.25. An alternative way of treating the data is as follows. For each phase the fractions, $Q(2)$, of the lines that could solely be indexed by that specific phase was calculated. The fractions so obtained for the pure compounds 9-BaBi₂S₄, 12-BaBi₂S₄ and Bi₂S₃ are in turn 0.41, 0, 0; 0, 0.52, 0; 0, 0, 0.27. Two of the 4 batches were fresh or nearly so and two were aged. The two groups differed somewhat in

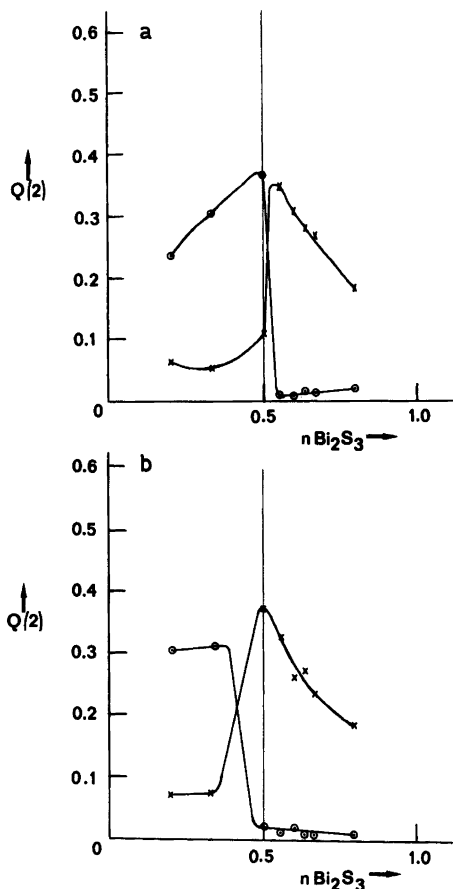


Fig. 1. The fractions $Q(2)$, see the text, for 9-BaBi₂S₄ (×) and 12-BaBi₂S₄ (○) are plotted against the mol fraction of Bi₂S₃ in the samples. Average values are taken for samples prepared at 420, 640 and 680 °C. a. Average values of two nearly fresh batches of BaS. b. Average values of two aged batches of BaS.

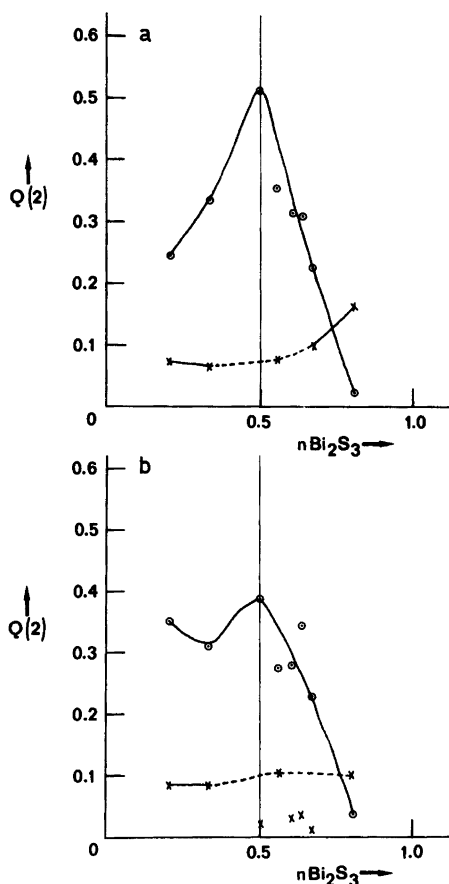


Fig. 2. The fractions $Q(2)$ for 9-BaBi₂S₄ (×) and 12-BaBi₂S₄ (○) are plotted against the mol fraction of Bi₂S₃ in the samples. Temperature of synthesis is 780 °C. a. Average values for two nearly fresh samples of BaS. b. Average values for two aged samples of BaS.

behaviour. $Q(2)$ was plotted against the mol fraction of Bi₂S₃ in the samples in Figs. 1 and 2. Figs. 1a and 1b show the averaged results for measurements made at 420, 640 and 680 °C for fresh and aged samples respectively. It is seen that 12-BaBi₂S₄ is formed for compositions $(1+\varepsilon_{12})\text{BaS}\cdot\text{Bi}_2\text{S}_3$ and 9-BaBi₂S₄ for $\text{BaS}\cdot(1+\varepsilon_9)\text{Bi}_2\text{S}_3$, where $\varepsilon_9, \varepsilon_{12} \geq 0$. Figs. 2a and 2b show the corresponding behaviour for samples recrystallized at 780 °C. The equilibria have shifted drastically and 12-BaBi₂S₄ is the predominant phase. The syntheses according to Gattow⁴ always led to 12-BaBi₂S₄.

SrS and Bi₂S₃ were reacted at 640 °C in the molar ratios 4:1, 3:1, 2:1, 1:1, 1:2 and 1:3. In all cases the powder photographs could be explained by the 12-phase in combination with SrS and/or Bi₂S₃. The same result was obtained in the syntheses according to Gattow.⁴ The $Q(1)$ values, see above, for 12-SrBi₂S₄ seemed to have maximum for the 1:1 samples. The cell dimensions of 12-SrBi₂S₄ prepared on reacting SrS and Bi₂S₃ for 15 min at 640 °C are $a=24.925(2)$ Å, $c=4.0954(8)$ Å. The 9-phase does not seem to exist in the system SrS–Bi₂S₃. Efforts to prepare CaBi₂S₄ either on reaction of CaS with Bi₂S₃ or using the method of Gattow have hitherto failed.

Single crystal work. On reaction in pyrex tubes 9-BaBi₂S₄ and 12-BaBi₂S₄ sintered to rods and single crystals were formed on their surfaces. The 12-BaBi₂S₄ single crystal had a length of 0.7 mm. Its cross-section was slightly elliptical with an average diameter of 0.008 mm. The single crystal of 9-BaBi₂S₄ was lost before measuring but had about the same dimensions. Both single crystals were mounted along their needle axes (4 Å) in Weissenberg cameras and the layers 0–3 were registered using CuK α radiation. The multiple film technique was used and the intensities were estimated visually by the aid of a calibrated scale. The intensities were corrected for $(Lp)^{-1}$ but not for the absorption. The Laue symmetry was found to be $6/m$. The absence of the reflections 001 and 003 in the powder photographs gave the condition limiting possible reflections: $00l:l=2n$ which is characteristic of the space groups $P 6_3$ and $P 6_3/m$. A sample of composition BaBi₂S₄ with $Q(1)=0.90$ for the 9-phase had an observed density of 5.88 Mg m⁻³, whereas the calculated value for $Z=9$ was 6.02 Mg m⁻³. The sample from which the single crystal of 12-BaBi₂S₄ was picked out had $Q(1)=0.90$ and its observed density was 5.71 Mg m⁻³ in good agreement with the calculated value 5.89 Mg m⁻³. Using the observed intensity data and the Z -values derived, three-dimensional Patterson functions were utilized to find the positions of the bismuth atoms. Space group $P6_3/m$ was assumed. Assuming the formula

to be BaBi₂S₄ or close to it the structures were then worked out in the conventional way. Refinements in space group $P6_3$ were not tried. In both cases isotropic temperature factors were used for all atoms, the weighting scheme of Hughes was applied and the restriction $0.3 < |F_o/F_c| < 3$ was made. For the 9-phase the final R -factor was 0.0952 for all 608 reflections and 0.0906 for 602 reflections. For the 12-phase the corresponding values were 0.1079(1085) and 0.1040(1080). In this last case, however, the Fourier maps showed the presence of an "extra" metal atom at the position 0, 0, $\frac{1}{4}$; 0, 0, $\frac{3}{4}$. This extra atom was more or less arbitrarily assumed to be Ba. Positional and thermal parameters are summarized in Table 1. Observed and calculated structure amplitudes are available on request.

Table 1. Final positional parameters and isotropic temperature factors in 9-BaBi₂S₄ and 12-BaBi₂S₄. Standard deviations are given within parentheses.

Atom	x	y	z	B (Å ²)
9-BaBi ₂ S ₄				
Bi(1)	0.8821(2)	0.4426(2)	$\frac{1}{4}$	1.69(8)
Bi(2)	0.6273(2)	0.9696(2)	$\frac{1}{4}$	1.73(8)
Bi(3)	0.1933(2)	0.2011(2)	$\frac{3}{4}$	1.92(9)
Ba(1)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	0.9(2)
Ba(2)	0.2376(3)	0.8215(3)	$\frac{1}{4}$	1.8(1)
Ba(3)*	0	0	$\frac{1}{4}$	4.8(7)
S(1)	0.2995(13)	0.2347(13)	$\frac{1}{4}$	1.7(4)
S(2)	0.0470(12)	0.4414(12)	$\frac{1}{4}$	1.5(4)
S(3)	0.5407(11)	0.3145(11)	$\frac{1}{4}$	0.9(4)
S(4)	0.0969(14)	0.1577(14)	$\frac{1}{4}$	2.0(5)
S(5)	0.3488(11)	0.5203(11)	$\frac{1}{4}$	1.1(4)
S(6)	0.3509(11)	0.1045(11)	$\frac{1}{4}$	0.6(3)
12-BaBi ₂ S ₄				
Bi(1)	0.2743(1)	0.9414(1)	$\frac{1}{4}$	1.28(6)
Bi(2)	0.6488(1)	0.1448(1)	$\frac{1}{4}$	1.09(6)
Bi(3)	0.4596(1)	0.0500(1)	$\frac{1}{4}$	1.27(6)
Bi(4)	0.8449(1)	0.0236(1)	$\frac{1}{4}$	1.52(6)
Ba(1)	0.3226(2)	0.5546(2)	$\frac{1}{4}$	0.61(7)
Ba(2)	0.2279(2)	0.3495(2)	$\frac{1}{4}$	1.00(8)
Ba(3)*	0	0	$\frac{1}{4}$	4.5(6)
S(1)	0.1770(9)	0.4490(9)	$\frac{1}{4}$	1.1(3)
S(2)	0.4529(8)	0.1483(7)	$\frac{1}{4}$	0.6(3)
S(3)	0.0940(9)	0.5479(9)	$\frac{1}{4}$	1.2(3)
S(4)	0.2474(8)	0.0324(8)	$\frac{1}{4}$	0.7(3)
S(5)	0.6344(8)	0.0017(8)	$\frac{1}{4}$	0.9(3)
S(6)	0.6566(8)	0.2495(8)	$\frac{1}{4}$	0.6(3)
S(7)	0.3069(8)	0.1918(8)	$\frac{1}{4}$	0.8(3)
S(8)	0.0623(12)	0.1351(12)	$\frac{1}{4}$	2.7(5)

* The site is half-occupied.

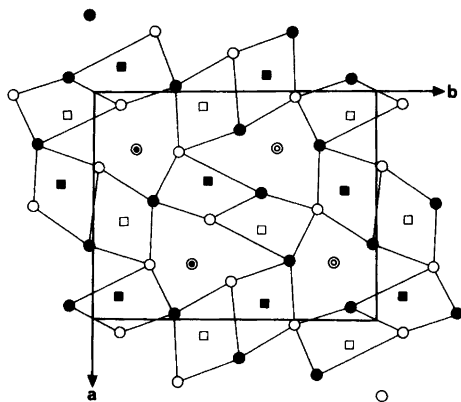


Fig. 3. Projection of the structure of galenobismutite on the ab -plane. The Bi-S octahedra are indicated. Single empty circles, squares and double circles indicate S, Bi and Pb at $z=1/4$. Filled circles and squares indicate the respective atoms at $z=3/4$.

DESCRIPTION AND DISCUSSION OF THE STRUCTURES

Architecture. The building principles of lead bismuth sulfosalts and of heavy metal sulfides in

general have recently been elaborately discussed by Makovicky⁵ and by Makovicky and Hyde.⁶ The present discussion will be limited and starts from the octahedral Bi-S or Sb-S skeletons of the compounds. Thus the Ba(Pb) atoms will be omitted at this stage. Comparisons will be made to compounds of related stoichiometry, e.g. PbBi_2S_4 , galenobismutite,⁷ $6\text{PbS}\cdot 7\text{Sb}_2\text{S}_3$, zinckenite,^{8,9} BaSb_2Se_4 ¹⁰ and PbCr_2Se_4 .¹¹ To describe the octahedral blocks of the compounds, use will be made of layers H and T cut out from the $\text{PbS}(\text{NaCl})$ structure parallel to (111) and (100), respectively.⁵ Use will also be made of the concept of chemical twinning¹² though in a slightly modified form. In galenobismutite⁷ Bi(1) is coordinated by 6 sulfur atoms and Bi(2) by 7. In the following description the contact $\text{Bi}(2)\text{-S}(1)=3.10 \text{ \AA}$ is somewhat arbitrarily neglected. It is seen from Fig. 3 that the octahedral skeleton consists of pairs of edge-sharing octahedra extending to rows in the c -axis direction. These rows could be cut out from single layers H . The rows are formed through the action of centre of symmetry at $0, 0, 0; 1/2, 0, 0; 0, 1/2, 0; 1/2, 1/2, 0$ and each row contains either Bi(1) or Bi(2). 4 rows are joined by corner-sharing which

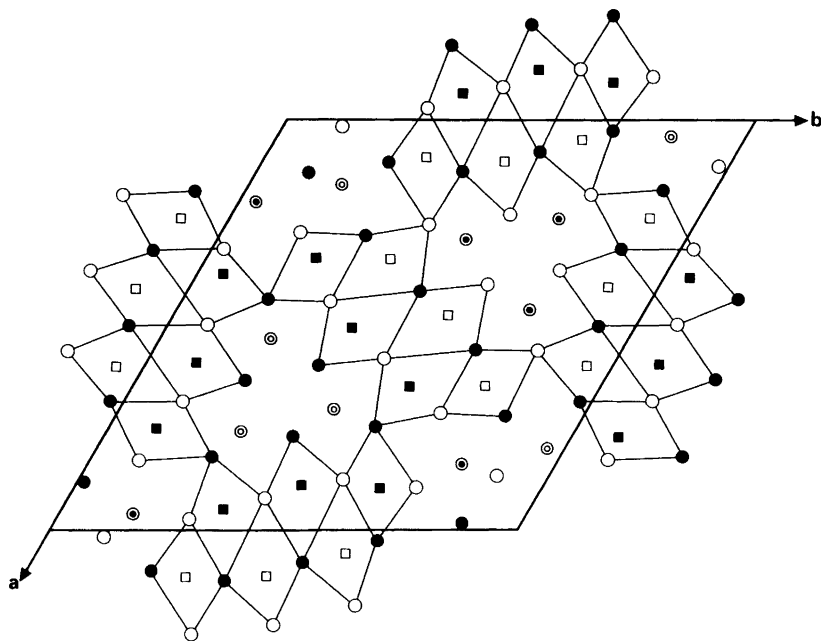


Fig. 4. Projection of the structure of zinckenite according to Takeda and Horiuchi on the ab -plane. The Sb-S octahedra are indicated. Single empty circles, squares and double circles indicate S, Sb, Pb or (Pb,Sb), respectively, at $z=1/4$. Filled circles and squares indicate the respective atoms at $z=3/4$.

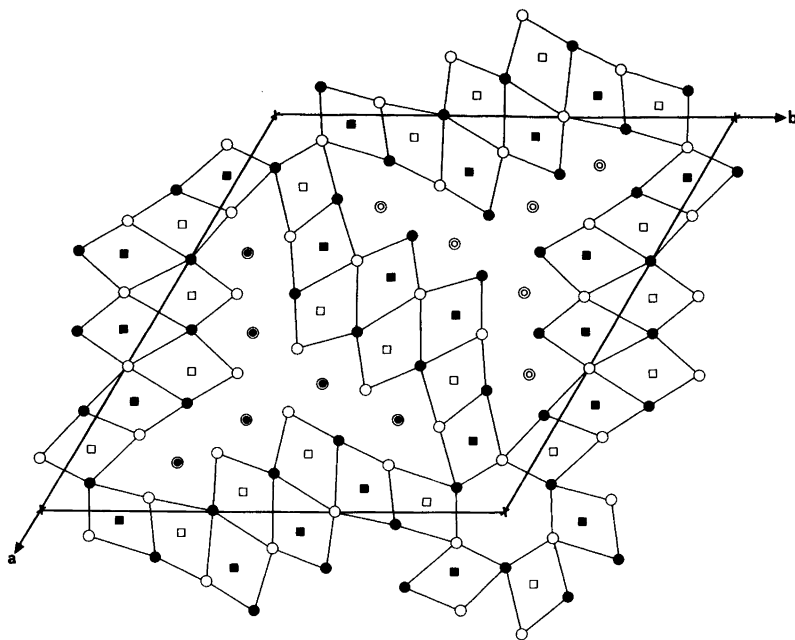


Fig. 5. Projection of the structure of $12\text{-BaBi}_2\text{S}_4$ on the ab -plane. The Bi-S octahedra are indicated. Single empty circles, squares and double circles indicate S, Bi and Ba, respectively, at $z=1/4$. Filled circles and squares indicate the respective atoms at $z=3/4$. The Ba and/or Bi atoms at $0, 0, 1/4$; $0, 0, 3/4$ are denoted by crosses.

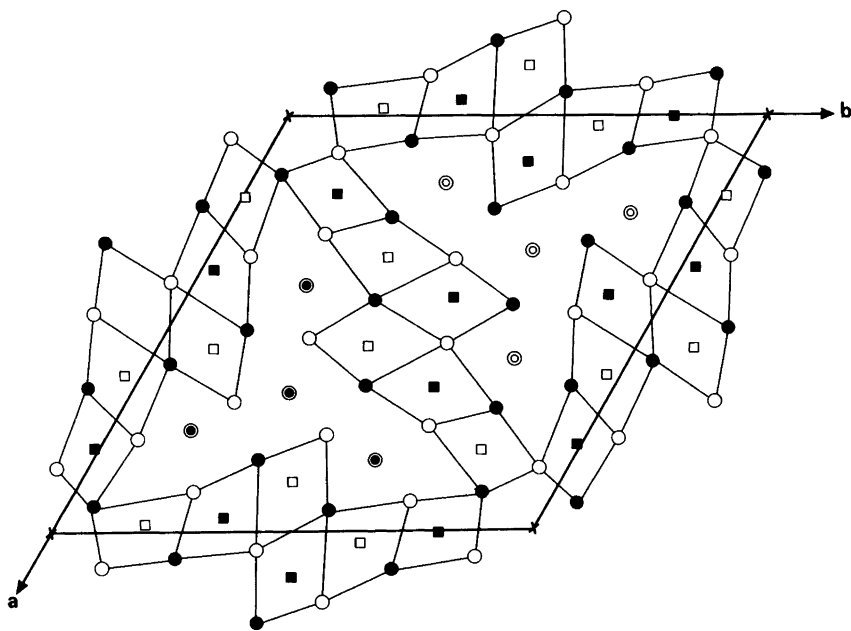


Fig. 6. Projection of the structure of $9\text{-BaBi}_2\text{S}_4$ on the ab -plane. Bi-S octahedra are shown and the notations of the atoms are the same as in Fig. 5.

leads to tunnels where the Pb atoms are situated. Zinckenite will be described here according to Takeda and Horiuchi⁹ and its real composition $6\text{PbS}\cdot 7\text{Sb}_2\text{S}_3$ will be approximated to PbSb_2S_4 and the correct space group $P6_3^8$ to $P6_3/m$. The *ab*-projection is shown in Fig. 4. The octahedral skeleton is built up from blocks of edge-sharing octahedra, 6 octahedra wide, which can be cut out from two consecutive layers *T*. The blocks are joined by corner-sharing which leads to tunnels where Pb or (Pb,Sb) and extra S atoms are situated. The blocks of octahedra are generated from the positions of the atoms in the asymmetric part of the unit cell through the action of centre of symmetry at $\frac{1}{2}, 0, 0; 0, \frac{1}{2}, 0; \frac{1}{2}, \frac{1}{2}, 0; \frac{1}{2}, 0, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. The joining of 3 blocks by corner-sharing is accomplished by the threefold axes at $\frac{2}{3}, \frac{1}{3}, z; \frac{1}{3}, \frac{2}{3}, z$. The architectures of $12\text{-BaBi}_2\text{S}_4$ and $9\text{-BaBi}_2\text{S}_4$ are closely related to that of zinckenite. Both compounds crystallize in $P6_3/m$. The *ab*-projection of $12\text{-BaBi}_2\text{S}_4$ is shown in Fig. 5. As seen, the central parts of the blocks are identical to those of zinckenite. Each block contains $2Z/3=8$ octahedra. Added to the zinckenite parts of the blocks are on each side single rows of edge-sharing octahedra. The octahedral skeleton is built up from the atoms of the asymmetric part of the unit cell in the same way as for zinckenite, namely by means of centre of symmetry and of 3-fold axes. The *ab*-projection of $9\text{-BaBi}_2\text{S}_4$ is shown in Fig. 6. The central part of the octahedral blocks contain here only 4 octahedra instead of 6 as found in $12\text{-BaBi}_2\text{S}_4$ and in zinckenite. Added to the 4-membered blocks are on each side single rows of edge-sharing octahedra as in $12\text{-BaBi}_2\text{S}_4$. Totally the blocks contain $2Z/3=6$ octahedra. Since BaBi_2S_4 occurs in two forms with $Z=9$ and $Z=12$ one might ask if samples with $Z=3$ or 6 could be prepared. Spatial considerations show that this is impossible. Higher polymorphs with $Z=15\dots$ may exist but there is hitherto no experimental proof that such phases could be formed.

BaSb_2Se_4 ¹⁰ is a layer structure. The unit cell is monoclinic, $P2_1/n$ with the general point position x, y, z (1); $\bar{x}, \bar{y}, \bar{z}$ (2); $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ (3); $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$ (4). 2 of the 4 Sb atoms of the asymmetric part of the unit cell are coordinated by 3 S and 2 by 4 S. To accomplish a comparison to BaBi_2S_4 all Sb atoms have, however, been regarded as formally 6-coordinated. Starting

Table 2. Distances Sb-S in the deformed Sb-S octahedra assumed here for BaSb_2Se_4 .¹⁰ Values above the horizontal lines are from [10], those below are calculated here.

Sb(11)-Se(84)	2.59	Sb(21)-Se(21)	2.56
Sb(11)-Se(13)	2.58	Sb(21)-Se(33)	2.65
Sb(11)-Se(62)	2.60	Sb(21)-Se(51)	2.85
		Sb(21)-Se(84)	2.92
Sb(11)-Se(33)	3.41		
Sb(11)-Se(51)	3.49	Sb(21)-Se(62)	3.31
Sb(11)-Se(52)	3.66	Sb(21)-Se(34)	3.95
Sb(31)-Se(53)	2.55	Sb(41)-Se(71)	2.61
Sb(31)-Se(42)	2.67	Sb(41)-Se(41)	2.70
Sb(31)-Se(31)	2.67	Sb(41)-Se(63)	2.80
		Sb(41)-Se(72)	2.85
Sb(31)-Se(71)	3.10		
Sb(31)-Se(81)	3.30	Sb(41)-Se(53)	3.12
Sb(31)-Se(41)	3.51	Sb(41)-Se(31)	3.72

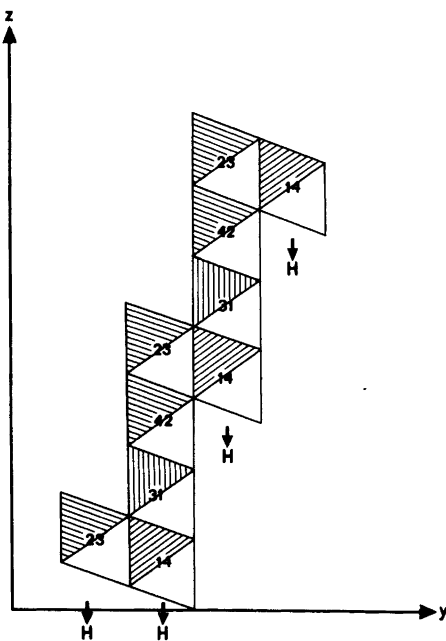


Fig. 7. A slightly idealized projection of one octahedral Sb-S layer with $0.35 < y < 0.65$ in BaSb_2Se_4 . The two-membered figures indicate Sb atoms within the octahedra. The first number is the number of the respective Sb atom as it occurs in the list of coordinates in [10], the second number refers to the general point position in $P2_1/n$ in the order $x, y, z; \bar{x}, \bar{y}, \bar{z}; \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z; \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$. The different slabs of type *H*, see the text, are marked out.

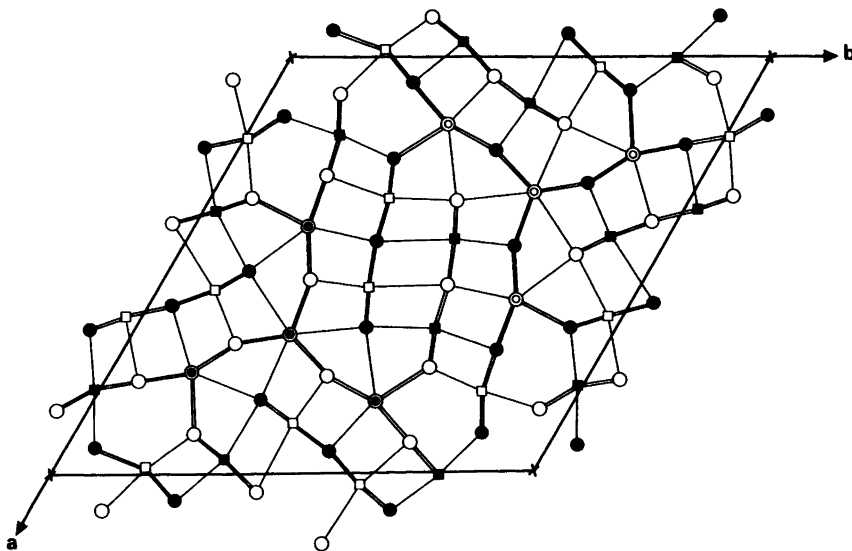


Fig. 8. The bonding scheme in 9- BaBi_2S_4 . The notations of the atoms are the same as in Fig. 5.

from the coordinates given in Ref. 10 as x , y , z and using the numbering of the atoms in the general point position as given above as subscripts the 6-coordination of the Sb atoms was obtained as shown in Table 2. Fig. 7 shows a slightly idealized projection of the Sb-S layer with $0.35 < y_{\text{Sb}} < 0.65$ on the y, z -plane. As seen,

the layer is built up from 4-membered strips of type H which are joined stepwise. At each junction the arrangements of the octahedra are the same as in two consecutive layers of type H . Thus even if formal octahedra are introduced there is very little similarity between BaSb_2Se_4 and the hexagonal compounds BaBi_2S_4 and

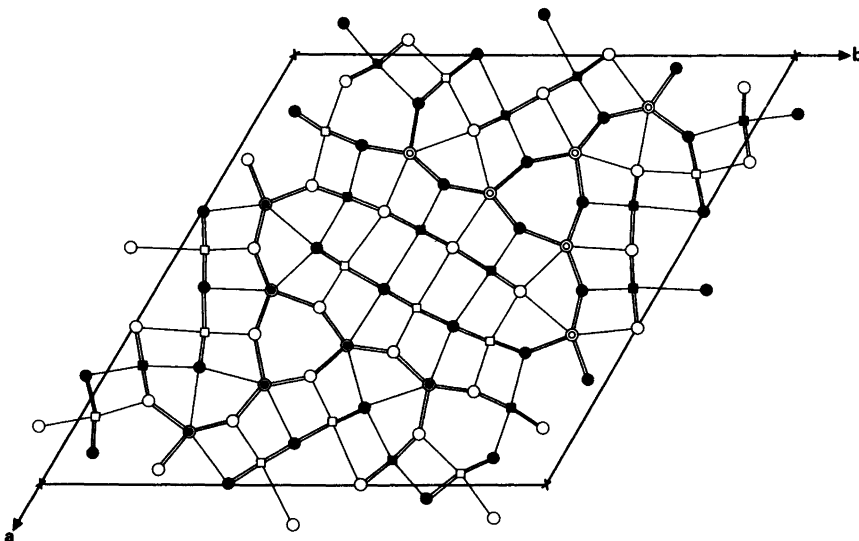


Fig. 9. The bonding scheme in 12- BaBi_2S_4 . The notations of the atoms are the same as in Fig. 5.

Table 3. Selected distances (Å) with standard deviations in parentheses of 9-BaBi₂S₄ and 12-BaBi₂S₄. Average values are calculated for the bismuth-sulfur distances within each octahedron and the sums of the squares of the departures from these values are also given.

9-BaBi ₂ S ₄		Average value	ΣΔ ²	12-BaBi ₂ S ₄		Average value	ΣΔ ²
Bi(1)–S(3)	2.55(2)	2.98	0.62	Bi(1)–S(4)	2.70(2)	2.84	0.04
Bi(1)–2S(5)	2.73(1)			Bi(1)–2S(7)	2.79(1)		
Bi(1)–2S(2)	3.03(2)			Bi(1)–2S(5)	2.91(1)		
Bi(1)–S(2)	3.59(2)			Bi(1)–S(1)	2.96(2)		
Bi(2)–S(1)	2.66(3)	2.87	0.12	Bi(2)–S(6)	2.55(2)	2.95	0.48
Bi(2)–2S(6)	2.81(1)			Bi(2)–2S(1)	2.72(1)		
Bi(2)–2S(2)	2.86(2)			Bi(2)–2S(3)	3.07(1)		
Bi(2)–S(5)	3.14(2)			Bi(2)–S(5)	3.45(2)		
Bi(3)–S(4)	2.74(3)	2.82	0.02	Bi(3)–S(2)	2.57(2)	2.98	0.54
Bi(3)–2S(4)	2.76(2)			Bi(3)–2S(3)	2.82(1)		
Bi(3)–S(6)	2.86(2)			Bi(3)–2S(5)	2.94(1)		
Bi(3)–2S(1)	2.91(2)			Bi(3)–S(3)	3.57(2)		
Ba(1)–6S(3)	3.29(2)			Bi(4)–S(8)	2.73(3)	2.83	0.03
Ba(1)–3S(5)	3.36(2)			Bi(4)–2S(8)	2.76(2)		
Ba(2)–2S(3)	3.15(2)			Bi(4)–S(7)	2.89(2)		
Ba(2)–S(2)	3.16(2)			Bi(4)–2S(4)	2.92(1)		
Ba(2)–S(5)	3.23(2)			Ba(1)–2S(2)	3.16(1)		
Ba(2)–2S(1)	3.25(2)			Ba(1)–2S(6)	3.18(1)		
Ba(2)–2S(6)	3.25(2)			Ba(1)–2S(6)	3.24(1)		
Ba(3)*–3S(4)	2.99(3)			Ba(1)–S(1)	3.29(2)		
Ba(3)*–6S(4)	3.64(2)			Ba(1)–S(3)	3.39(2)		
Closest S–S approach				Ba(2)–2S(2)	3.15(1)		
S(1)–S(6)	3.52(3)			Ba(2)–2S(4)	3.21(1)		
				Ba(2)–2S(7)	3.25(1)		
				Ba(2)–S(5)	3.34(2)		
				Ba(2)–S(1)	3.35(2)		
				Ba(3)*–3S(8)	2.96(3)		
				Ba(3)*–6S(8)	3.63(2)		
				Closest S–S approach			
				S(6)–2S(6)	3.47(3)		

zinckenite.

In Eu_{1-p}Cr₂Se_{4-p}¹¹ the Cr–Se skeleton, space group *P* 6/*m*, consists of 5-membered single layers *H* which are fused by face-sharing of the terminal octahedra and there is no similarity to BaBi₂S₄.

Stoichiometry of the BaBi₂S₄ phases. As discussed above, 9-BaBi₂S₄ has the composition BaS·(1+ε₉)Bi₂S₃ for samples prepared at 640 °C and also for those recrystallized at 420 or 680 °C.

12-BaBi₂S₄ has the composition (1+ε₁₂)BaS·Bi₂S₃ for samples prepared in the same way. For both phases the Fourier maps show the presence of atoms, presumably cations in the tunnels around 0, 0, *z*. The composition BaS·(1+ε₉)Bi₂S₃ for 9-BaBi₂S₄ may be attained with the present structure if there are slight vacancies in the cation lattice. The composition (1+ε₁₂)BaS·Bi₂S₃ for 12-BaBi₂S₄ may result if

some extra Ba is inserted at the point position 0, 0, $\frac{1}{4}$; 0, 0, $\frac{3}{4}$ and the charge is compensated by some vacancy in the Bi lattice or in the stoichiometric case if ≤ 1 Ba atom per unit cell is moved from its 6-fold position to a half-occupied site at 0, 0, $\frac{1}{4}$; 0, 0, $\frac{3}{4}$ leaving a vacancy at its former site. The mechanisms proposed here are based on the assumption that the sulfur lattice remains intact. Neither mechanism could, however, be proved by means of the intensity data.

Coordination of the metal atoms. For both polymorphs the cations Ba and/or Bi at the position 0, 0, $\frac{1}{4}$ are coordinated by 9 sulfur atoms in the form of a three-capped trigonal prism, see Table 3, Ba(3)*, and Figs. 8 and 9. The atoms Ba(2) 9-BaBi₂S₄, and Ba(1) and Ba(2) 12-BaBi₂S₄, are 8-coordinated in the form of a bicapped trigonal prism. The coordination polyhedra are fairly regular with distances Ba-S 3.15–3.39 Å, see Table 3 and Figs. 8 and 9. The Ba(1) atom of 9-BaBi₂S₄ is situated at the position $\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{4}$; $\frac{2}{3}$, $\frac{1}{3}$, $\frac{3}{4}$ and its coordination polyhedron is a regular three-capped trigonal prism. The coordination polyhedra of bismuth are as expected irregular octahedra. The Bi-S distances vary between 2.55 and 3.59 Å. The departure from regularity of the octahedra was estimated as follows. Average values of the 4 independent Bi-S distances were calculated for each octahedron and the sums of the squares of the departures $\Sigma\Delta^2$ were derived and used as a measure of the irregularity. The average Bi-S distance and corresponding $\Sigma\Delta^2$ are given for each Bi octahedron in Table 3. It is seen that $\Sigma\Delta^2$ for 9-BaBi₂S₄ grows in the order Bi(3), Bi(2), Bi(1). For 12-BaBi₂S₄ the corresponding order is Bi(4), Bi(1), Bi(2), Bi(3). These orders are, however, the same as when one starts from the outermost of the octahedra in the octahedral blocks shown in Figs. 5 and 6 and moves to the centre of the blocks. Thus in 9-BaBi₂S₄ and 12-BaBi₂S₄ the central octahedra are the most deformed ones. This is contrary to what was found by Makovicky⁵ for bismuth sulfosalts containing other cations e.g. Ag, Cu, Pb.

Finally it ought to be mentioned that all S-S distances are normal though some of them are quite short, see Table 3.

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