JOURNAL OF SOLID STATE CHEMISTRY 54, 84–88 (1984)

# New $SbS_2$ Strings in the $BaSb_2S_4$ Structure

GERHARD CORDIER, CHRISTOPH SCHWIDETZKY,
AND HERBERT SCHÄFER

*Eduard-Zintl-Institut der Technischen Hochschule Darmstadt, D-6100 Darmstadt, Federal Republic of Germany*

Received January 9, 1984; in revised form March 20, 1984

The new compound $BaSb_2S_4$ crystallizes in the monoclinic system (space group: $P2_1/c$, No. 14) with $a = 8.985(2)$ Å, $b = 8.203(3)$ Å, $c = 20.602(5)$ Å, $\beta = 101.36(3)°$. $SbS_3$ $\psi$ tetrahedra and $\psi$-trigonal $SbS_4$ bipyramids are connected by common corners and edgers to infinite strings. These are arraged crosswise in sheets perpendicular to the $c$ axis.

## Introduction

The alkali thioantimonates(III) show a surprising variation of stoichiometries and structures (*1–7*). The latter ones can be derived from three basic Sb–S units hitherto found in anionic sublattices; the $\psi$-$SbS_3$ tetrahedron, the $\psi$-$SbS_4$ bipyramid, and the $\psi$-$SbS_5$ octahedron. So far, the factors which determine the kind of polyhedra as well as the connecting principles are not understood. For studying the influence of the charge of the cations involved, we started recently to include the alkaline earth compounds in our research (*8–10*). The present paper describes the synthesis and the crystal structure of the new compound $BaSb_2S_4$.

## Experimental Section

### *Preparation and Analysis*

$BaSb_2S_4$ was synthesized directly from the elements. Stoichiometric amounts of barium, coarsely granulated antimony, and oxygen-free sulfur were sealed under dry argon at $\sim 10^{-1}$ Torr into a silica ampoule. The extremely exothermic reaction remains under control if the ampoule is heated slowly at a rate of 50 K/hr to 420 K, kept 12 hr at this temperature, and then brought to 970 K, at the same heating rate. At this temperature, the reaction product was stirred by rotation of the ampoule for 4 hr, slowly cooled to 770 K, annealed for another 4 hr at this temperature, and then cooled to room temperature. The homogenous reaction product consists of dark-red platelets. These decompose in wet air to a dark amorphous powder of unknown stoichiometry, generating $H_2S$ as well. To determine the composition, well-crystallized parts of the regulus were selected under a microscope. The sulfur was determined gravimetrically as $BaSO_4$, barium, and antimony by atomic absorption spectroscopy (results (wt%): Ba theor. 26.98, exp. 26.5; Sb: theor. 47.83, exp. 47.7; S: theor. 25.19, exp. 25.1). An average density of 4.47 g/cm$^3$ was measured by the pycnometer method under dry toluene using selected crystals.

0022-4596/84 $3.00

TABLE I

SUMMARY OF CRYSTAL DATA AND INTENSITY COLLECTION FOR $BaSb_2S_4$

| | |
|---|---|
| Mol. formula | $BaSb_2S_4$ |
| Mol wt | 509.07 |
| Space group | $P2_1/c$ (No. 14) |
| $a$ | 8.985(2) Å |
| $b$ | 8.203(3) Å |
| $c$ | 20.602(5) Å |
| $\beta$ | 101.36(3)° |
| $V$ | 1488.70 $Å^3$ |
| Temp | 24 ± 1°C |
| $d$ (obsd) | 4.47 $g/cm^3$ |
| $d$ (calcd) | 4.54 $g/cm^3$ |
| $Z$ | 8 |
| Abs. coeff. | 134.49 $cm^{-1}$ |
| Color | Red |
| Habit | Platelets |
| Dimensions | .5 × .3 × .1 $mm^3$ |
| $\lambda$ (Mo$K\alpha$) | .7107 Å |
| Method | $\omega$-scan |
| Scan/speed | .02 deg · $sec^{-1}$ |
| Monochromator | Graphite |
| Bkgd time/scan time | 1.0 |
| Standard refl. | 10,0,0; 0,0,−2; −10,0,0; every 8 hr |
| Range of data | $5° \leq 2\Theta \leq 60°$ |
| No. of reflections | 4340 |
| No. of reflections less than 1 $\sigma$ | 0 |
| No. of variables | 87 |
| $R \triangleq \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$ | 0.054 ($R_w$ = 0.053) |
| Counter aperture width | 1° |
| Incident-beam collimator diameter | 0.8 mm |

## *Collection and Reduction of X-Ray Intensity Data*

Weissenberg (Cu$K\alpha$) and precession (Mo$K\alpha$) photographs ensured the crystalline singularity of the platelet, which, covered with dry heavy paraffin oil, was sealed in a Lindemann's glass capillary tube. These photographs show the $2/m$ Laue symmetry; the substance belongs therefore to the monoclinic system. Least-square analysis of the setting angles of 25 precisely centered reflections ($10° \leq 2\theta \leq 30°$, Philips PW 1100 four-circle diffractometer, Mo$K\alpha$ radiation, graphite monochromator) yielded the lattice parameters and the orientation matrix. The observed systematic absences ($h0l$ for $l = 2n + 1$, $0k0$ for $k = 2n + 1$) indicate the space group $P2_1/c$ (No. 14). The details of the intensity data collection are given in Table I. An absorption correction was applied according to the approximate (broken edges) size of the crystal (*11*). Lorentz and polarization effects were corrected as usual.

## *Solution and Refinement of Structure*

The structure was solved via the direct methods routine using SHEL-X-76 (*11*). The antimony and barium atoms were located from the E map based on the phase solution of highest internal consistency. The remaining S atoms were located in subsequent Fourier and difference Fourier syntheses. All parameters were refined by the least-square method to a final $R$ value of 0.054 ($R_w$ = 0.053). Because of the approximate absorption correction only the thermal parameters of the heavy Sb and Ba atoms have been refined anisotropically. Atomic scattering factors for neutral atoms were used and corrections for anomalous scattering but not for extinctions were included. All calculations were performed using the X-ray program system SHEL-X-76 (*11*). The final coordinates of all atoms are given in Table II. Figure 1 includes the atomic distances and angles of the anionic sublattice. In Table III, the Ba–S distances are summarized.

## *Description of Structure*

Two of the four crystallographically different Sb atoms (Sb1 and Sb2) are surrounded by three S atoms. They form distorted trigonal pyramids in which the antimony takes the apex position (Fig. 1). This leads with respect to the free electron pair of the Sb atom to a $\psi$-tetrahedron. The other antimony atoms (Sb3 and Sb4) are surrounded by four S atoms which together with the Sb lone pair form distorted $\psi$-trigo-

TABLE II

POSITIONAL PARAMETERS AND TEMPERATURE FACTORS[a]

| Atom | $x$ | $y$ | $z$ | $U11$ | $U22$ | $U33$ | $U23$ | $U13$ | $U12$ |
|---|---|---|---|---|---|---|---|---|---|
| Ba(1) | 0.0237(1) | 0.0437(1) | 0.8093(<1) | 0.0146(3) | 0.0136(3) | 0.0146(3) | −0.0009(2) | 0.0022(2) | −0.0011(2) |
| Ba(2) | 0.5202(1) | 0.4429(1) | 0.2992(<1) | 0.0136(3) | 0.0178(3) | 0.0109(3) | −0.0045(2) | 0.0031(2) | −0.0028(2) |
| Sb(1) | 0.3023(1) | 0.4781(1) | 0.8753(<1) | 0.0131(3) | 0.0152(3) | 0.0102(3) | 0.0002(3) | 0.0014(2) | −0.0002(3) |
| Sb(2) | 0.8549(1) | 0.1579(1) | 0.0026(<1) | 0.0113(3) | 0.0164(3) | 0.0131(3) | 0.0019(3) | 0.0004(2) | 0.0003(3) |
| Sb(3) | 0.4237(1) | 0.2028(1) | 0.0304(<1) | 0.0152(3) | 0.0143(3) | 0.0129(3) | 0.0002(3) | 0.0018(3) | −0.0000(3) |
| Sb(4) | 0.8473(1) | 0.5000(1) | 0.8852(<1) | 0.0177(3) | 0.0120(3) | 0.0117(3) | −0.0011(3) | 0.0006(3) | 0.0008(3) |
| S(1) | 0.0380(3) | 0.2952(4) | 0.9395(1) | 0.0152(5) | | | | | |
| S(2) | 0.2202(3) | 0.0580(4) | 0.0841(1) | 0.0148(5) | | | | | |
| S(3) | 0.6293(3) | 0.0055(3) | 0.0742(1) | 0.0125(5) | | | | | |
| S(4) | 0.2311(3) | 0.8471(4) | 0.7163(1) | 0.0145(5) | | | | | |
| S(5) | 0.9214(3) | 0.1549(4) | 0.6541(1) | 0.0140(5) | | | | | |
| S(6) | 0.7429(3) | 0.8260(4) | 0.7291(1) | 0.0140(5) | | | | | |
| S(7) | 0.4965(3) | 0.6647(3) | 0.8480(1) | 0.0136(5) | | | | | |
| S(8) | 0.6546(4) | 0.3470(5) | 0.9611(2) | 0.0252(7) | | | | | |

*Note*. The isotropic temperature factors are defined as $\exp[-8\pi^2 U \cdot \sin^2 \vartheta/\lambda^2]$, the anisotropic temperature factors are defined as $\exp[-2\pi^2(h^2a^*U_{11} + k^2b^{*2}U_{22} + 1^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$. $U$-values in Å$^2$, estimated standard deviations in parentheses.

[a] All atoms on the sites with Wyckoff notation 4e.

nal bipyramids (Fig. 1). Corresponding to the higher coordination, the Sb–S distances are here larger than the Sb–S distances in the $\psi$-tetrahedra (Fig. 1). These Sb–S polyhedra are connected by common edges and corners forming strings which run crosswise parallel to the (110) and ($\bar{1}$10) direction, respectively, forming sheets perpendicular to the $c$ axis at $z = 0$ and $z = 0.5$ (Figs. 2a,b). In each layer, every second string is shifted along the string axis, relative to the first string, by half of its identity period.

Between the layers the barium atoms are surrounded by 8 and 9 sulfur atoms, respectively. The polyhedra may be described as distorted trigonal prisms, above the rectangular faces there are two or three additional S-atoms (see Fig. 3). Table III shows the interatomic distances. The anionic unit

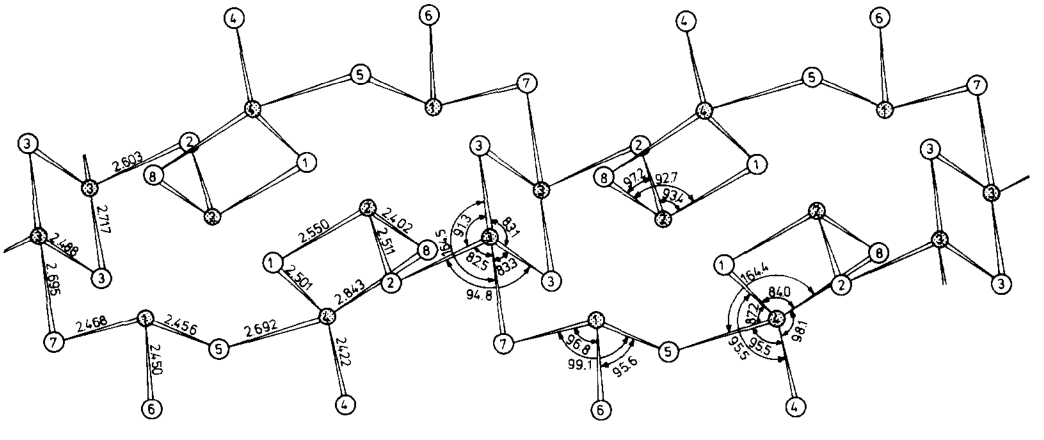

FIG. 1. $SbS_2^-$ string in $BaSb_2S_4$. (Hatched circles = Sb, open circles = S, numbers refer to Table II.) Atomic distances in Å, bonding angles in degrees, maximal estimated standard deviation 0.004 Å and 0.1°, respectively.

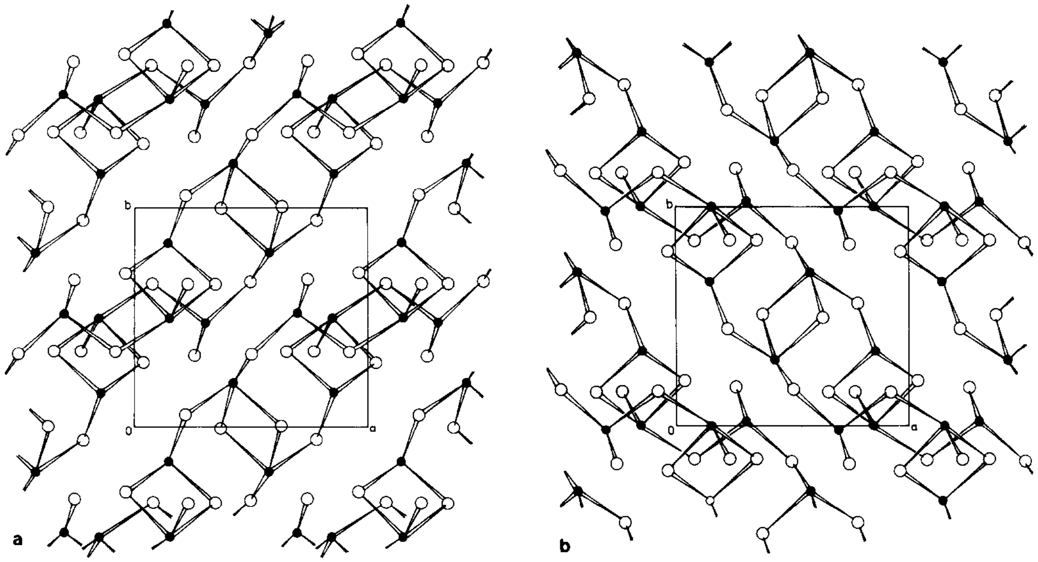

FIG. 2. Arrangement of the $SbS_2^-$ strings in planes perpendicular to the $c$ axis at $z = 0$ (a) and $z = \frac{1}{2}$ (b). (Full circles = Sb, open circles = S.)

observed in this compound is new for the combination Sb–S, but there are equivalent anions in $BaSb_2Se_4$ (*12*). Nevertheless, both compounds are not isotypic. The main difference between both structures is given by the stacking of the strings which in $BaSb_2Se_4$ are all parallel to each other.

## Discussion

Compounds $Me^{II}Me_2^{III}X_4$ with $X$ = S, Se, Te, are structurally known especially for $Me^{III}$ = main group(III) element. With $Me^{II}$ = Mg, Ca, Sr, Ba, the structures of these compounds show characteristic variations depending on the ratio $r$(chalcogenide ion)/

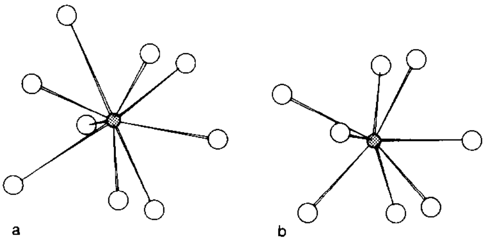

FIG. 3. Coordination polyhedra of the Ba1 (a) and Ba2 (b) ions.

TABLE III

Ba–S Distances (Å) in $BaSb_2S_4$

| | |
|---|---|
| Ba(1)–S(6) | 3.263 |
| –S(5) | 3.277 |
| –S(5) | 3.292 |
| –S(6) | 3.322 |
| –S(4) | 3.338 |
| –S(4) | 3.352 |
| –S(1) | 3.367 |
| –S(2) | 3.496 |
| –S(3) | 3.564 |
| Ba(2)–S(7) | 3.133 |
| – S(2) | 3.147 |
| –S(6) | 3.201 |
| –S(3) | 3.203 |
| –S(6) | 3.290 |
| –S(4) | 3.298 |
| –S(4) | 3.323 |
| –S(7) | 3.391 |

*Note.* The maximal estimated standard deviations are 0.003 Å.

*r*(alkaline earth ion). The anions of all Mg compounds form close packings with several stacking sequences and with different distributions of the cations in the octahedral and tetrahedral holes (*13–16*). Such close arrangements of the chalkogenide anions are not possible with the bigger $Ca^{2+}$, $Sr^{2+}$, and $Ba^{2+}$ ions. As basic structure, the TlSe type is realized with several distribution modes of the cations (*17–20*). The only exceptions are $BaAl_2S_4$ and $BaGa_2S_4$ which form a separate structure type with $AlS_4$ and $GaS_4$ tetrahedra, respectively, connected by common corners to a framework (*21*). The substitution of element(III) by Sb(III), despite similar atomic sizes, causes significantly different structures. Apparently, as in the formerly investigated alkali thioantimonates(III), Sb(III) has a $sp^3$ and $sp^3d$ hybridization, respectively. There are $\psi$-$Sb(S,Se)_3$ tetrahedra and $\psi$-trigonal $Sb(S,Se)_4$ bipyramids with steric effective lone pair electrons. These polyhedra, connected by common corners and edges, produce the new structure principles found. They can be interpreted as "salt-like" structures with one-dimensional infinite chain-like $(SbS_2)^-$ and $(SbSe_2)^-$ anions which are variably stacked according to their different atomic sizes.

## Acknowledgments

The authors thank the "Deutsche Forschungsgemeinschaft," the "Fonds der Chemischen Industrie," and the "Vereinigung von Freunden der Technischen Hochschule Darmstadt" for their financial support.

## References

1. H. A. GRAF AND H. SCHÄFER, *Z. Naturforsch. B* **27,** 1308 (1972).
2. H. A. GRAF AND H. SCHÄFER, *Z. Anorg. Allg. Chem.* **414,** 211, 220 (1975).
3. G. DITTMAR AND H. SCHÄFER, *Z. Anorg. Allg. Chem.* **441,** 98, 93 (1978); **437,** 183 (1977).
4. K. VOLK AND H. SCHÄFER, *Z. Naturforsch. B* **34,** 172 (1979); **33,** 827 (1978).
5. B. EISENMANN AND H. SCHÄFER, *Z. Naturforsch. B* **34,** 383 (1979).
6. K. VOLK, P. BICKERT, R. KOLMER, AND H. SCHÄFER, *Z. Naturforsch. B* **34,** 389 (1979).
7. K. VOLK AND H. SCHÄFER, *Z. Naturforsch. B* **34,** 1637 (1979).
8. G. CORDIER, CH. SCHWIDETZKY, AND H. SCHÄFER, *Rev. Chim. Miner.* **19,** 179 (1982).
9. G. CORDIER AND H. SCHÄFER, *Rev. Chim. Miner.* **18,** 218 (1981).
10. W. DÖRRSCHEIDT AND H. SCHÄFER, *Z. Naturforsch. B* **36,** 410 (1981).
11. G. SHELDRICK, "SHEL-X-76 Program System," University of Cambridge, Cambridge, England (not published).
12. G. CORDIER AND H. SCHÄFER, *Z. Naturforsch. B* **34,** 1053 (1979).
13. B. EISENMANN, M. JAKOWSKI, AND H. SCHÄFER, *Mater. Res. Bull.*, in press.
14. C. ROMERS, B. A. BLAISSE, AND D. J. W. IJDO, *Acta Crystallogr.* **23,** 634 (1967).
15. P. DOTZEL, H. SCHÄFER, AND SCHÖN, *Z. Anorg. Allg. Chem.* **426,** 260 (1976).
16. P. DOTZEL, E. FRANKE, H. SCHÄFER, AND G. SCHÖN, *Z. Naturforsch. B* **30,** 179 (1975).
17. W. KLEE AND H. SCHÄFER, *Z. Anorg. Allg. Chem.* **499,** 145 (1983); **479,** 125 (1981).
18. W. KLEE AND H. SCHÄFER, *Z. Naturforsch. B* **33,** 829 (1978).
19. W. KLEE AND H. SCHÄFER, *Rev. Chim. Miner.* **16,** 465 (1979).
20. B. EISENMANN, M. JAKOWSKI, AND H. SCHÄFER, *Rev. Chim. Miner.* **20,** 255 (1983).
21. B. EISENMANN, M. JAKOWSKI, AND H. SCHÄFER, *Mater. Res. Bull.* **17,** 1169 (1982).