JOURNAL OF SOLID STATE CHEMISTRY 3, 75–82 (1971)

Ternary Sulfide Compounds AB_2S_4: The Crystal Structures of $GePb_2S_4$ and $SnBa_2S_4$*

K. SUSA AND H. STEINFINK

Materials Science Laboratories, Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712

Received July 24, 1970

Syntheses of compounds with the stoichiometry AB_2S_4 were carried out where A included group IV elements and tetravalent Ti, V, and Mo, and B were alkaline earths and divalent Pb, Sn, Ge, and Cd. The crystal structures were predicted to be of the K_2SO_4 and olivine type, and $SiBa_2S_4$, $GeBa_2S_4$, and $TiBa_2S_4$ were found to have the former structure while $SiCa_2S_4$, $GeCa_2S_4$, and $SnCa_2S_4$ have the latter. Two new structures, related to K_2SO_4, were found for $GePb_2S_4$ and $SnBa_2S_4$. $GePb_2S_4$ is monoclinic, $P2_1/c$, $a = 7.9742(6)$ Å, $b = 8.9255(8)$ Å, $c = 10.8761(8)$ Å, $\beta = 114.171(9)°$, $Z = 4$. The structure consists of isolated GeS_4 tetrahedra and Pb^{2+} ions are in six- and sevenfold coordination. The Ge–S bond lengths are 2.20 Å and the tetrahedron is nearly perfect. The Pb–S bond lengths vary 2.81–3.37 Å. $SnBa_2S_4$ is orthorhombic, $Pna2_1$, $a = 17.823(3)$ Å, $b = 7.359(1)$ Å, $c = 12.613(2)$ Å, $Z = 8$. The structure consists of isolated, distorted SnS_4 tetrahedra and Ba^{2+} ions are in eight- and sixfold coordination. Sn–S bond lengths vary 2.32–2.41 Å and Ba–S distances vary 3.05–3.47 Å. The formation of the K_2SO_4-type structure is favored when the A atom has a large electronegativity value and a small ionic radius and the B atom has a small electronegativity and a large ionic radius. B site occupancy by atoms which fit into the octahedral voids formed by close packing of sulfur ions from AS_4 tetrahedra favor the formation of olivine structure types. When some of these conditions are not favorable distorted structures related to K_2SO_4 are observed.

Introduction

Recently, Kugimiya and Steinfink (*1*) have used a plot of radius ratio, r_A/r_B, versus a force constant, K_{AB}, to provide a map in which the various crystal structures for compounds of stoichiometry AB_2X_4, where A, B are cations and X is a group VI anion, are separated into different regions. This approach was particularly successful for compounds in which the anion was O^{-2}. The superposition of the structure boundaries obtained from a plot for oxide compounds, after suitable scaling for the differences in anionic size, on a plot for chalcogenides should predict structure types for such compounds if the correspondence between oxides and chalcogenides holds. A diagram for sulfide systems was constructed for a number of compounds which have been reported in recent years (*1*). The main structures found for these compounds are spinel, calcium ferrite, thorium phosphide, and Ag_2HgI_4, which on the map fall in the region where the radius ratio exceeds 0.7. Although several of the crystal structure types observed in sulfides do not occur in the AB_2O_4 compounds, e.g., Th_3P_4, it was nevertheless observed that the boundaries transferred from the oxide structures delineated regions of a given structure type for the chalcogenides.

A striking feature of the map was the scarcity of compounds for the region in which the olivine (*2, 3*), K_2SO_4 (*4, 5*), and K_2MgF_4 structure types exist for oxides. In order to explore the validity of predicted structures for various combinations of metal ions in the sulfur system we decided to synthesize and determine the crystal structures of compounds which, on the basis of their radius ratios and force constants, lie in these areas.

The syntheses were carried out for compounds whose analogous oxides had been reported, e.g., $GeBa_2S_4$, whose oxide has the olivine structure type. Other A, B combinations were selected on the basis of similarities of valence states to compounds whose oxide forms are known. Table I shows the com-

* This research was supported by the Robert A. Welch Foundation, Houston, Texas.

TABLE I

COMBINATIONS OF A, B ELEMENTS AND THEIR PREDICTED STRUCTURES FOR AB_2S_4[a]

	B						
A	Ba	Sr	Ca	Pb	Sn	Ge	Cd
Si	K_2SO_4	U	U	U	U	IS	U
Ge	U	O	O	U	U	IS	U
Sn	O	K_2MgF_4, O	O	O	—	—	O
Pb	K_2MgF_4	—	—	O	—	—	—
V	O	K_2MgF_4, O	K_2MgF_4, O	O	IS	—	O
Ti	O	K_2MgF_4	K_2MgF_4	O	O	—	O
Mo	O	K_2MgF_4	K_2MgF_4	O	—	—	O

[a] Key: O = Olivine, IS = Inverse Spinel, U = Unpredictable, dash = r_A/r_B exceeds 0.7. Where two structures are shown, either one could be predicted.

binations of A and B metals selected for the synthesis of the AB_2S_4 stoichiometry and the predicted structures based on the map of r_A/r_B versus K_{AB} with the boundaries from the oxide phases (Fig. 1).

Sample Preparation

After various trials, it was found that the most successful results for the synthesis of ternary sulfides were achieved when starting with elemental A, powdered sulfur, and powdered monosulfides of B. The starting materials for the syntheses were obtained frcm commercial sources and had stated purities of 99.9% or better. Stoichiometric ratios of the A and B elements with sulfur or of the appropriate metal sulfide were mixed, sealed under vacuum in vycor tubing, and prereacted at temperatures ranging 200–400°C for 2–4 hr. The temperature was then raised and kept in the range 600–800°C for about 12 hr. After cooling, the vial was examined visually to see whether some of the starting materials had remained unreacted. If the sample looked homogeneous, the vial was opened and the material was further examined by X-ray powder diffraction techniques. If some of the original phases were detected in the sample, it was resealed in a vycor tube and fired at the same or at higher temperatures until it appeared to have completely reacted. In some cases the temperature was raised to 1330°C after first placing the material in a graphite crucible which was then sealed in a vycor tube. If the materials did not react after a maximum of 10 days at about 800°C, it was assumed that no compound exists or cannot be obtained by the solid state reaction under the described experimental conditions.

Sample Identification

Initially the phases were identified by X-ray powder diffraction techniques. Single crystal studies were made whenever it was felt that an ambiguity existed in the assignment of a known structure on the basis of the powder pattern. When a powder pattern indicated that the reaction had produced a new single phase material, then a single crystal was selected to determine the space group and lattice constants. All the lines which appeared in the powder pattern were indexed on the basis of that unit cell, and if the compound was isostructural with one of the known predicted structures an intensity calculation was carried out assuming the same atomic coordinates as those for the known compound. The structure was considered as confirmed when qualitative agreement was obtained between calculated and observed intensities. If the crystal structure of the phase was new, a complete analysis was carried out. The conditions for sample preparation and the resultant phases are summarized in a table which is available on demand.[1] Table II summarizes the crystallographic results for those materials for which single phases were observed. Generally, the observed structure is indeed the same as the predicted one or else it is closely related to it. Several phases crystallized with unknown structures and the crystal structures for $GePb_2S_4$ and $SnBa_2S_4$ were determined and are described below. The structure of $GeCd_4S_6$ will be reported elsewhere since it has a different stoichiometry. The newly synthesized compounds, together with some previously reported (*2–7*), are plotted in Fig. 1, which also shows the structural regions as obtained from the AB_2O_4 map.

Crystal Structure of $GePb_2S_4$

This phase formed a glassy material if the initial mixture was reacted and quenched at temperatures in excess of 600°C. Slow cooling from 600°C produced well-crystallized single-phase material and from it a single crystal was selected for the structure analysis. A series of Weissenberg and

[1] For detailed paper, extended version, or supplementary material, order NAPS Document 01217 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th Street, New York, New York 10001; remitting $2.00 for microfiche or $5.00 for photocopies.

TABLE II

CRYSTALLOGRAPHIC RESULTS FOR SINGLE-PHASE MATERIALS

Phase	Predicted structure	Oxide form	Observed structure	Space group	Cell constants a (Å)	b (Å)	c (Å)	β (°)	$V(z=4)$ Å^3
$SiBa_2S_4$	K_2SO_4	K_2SO_4	K_2SO_4	*Pnma*	8.84	6.76	11.93		712.5
$GeBa_2S_4$ [a]	Unknown	Olivine	K_2SO_4	*Pnma*	8.96	6.89	12.23		755.2
$SnBa_2S_4$	Olivine	K_2MgF_4	Modif. K_2SO_4	$Pna2_1$	17.82	7.36	12.61		827.7
$TiBa_2S_4$	Olivine	Modif. K_2SO_4	K_2SO_4	*Pnma* [b]	9.04	6.85	12.31		762.7
$SiCa_2S_4$ [c]	Unknown	Olivine	Olivine	*Pnma* [b]	13.46	8.14	6.17		676.5
$GeCa_2S_4$ [c]	Olivine	Olivine	Olivine	*Pnma* [b]	13.61	8.19	6.30		702.1
$SnCa_2S_4$ [c]	Olivine	$P2_12_12$	Olivine	*Pnma*	13.88	8.18	6.51		738.8
$SnSr_2S_4$	K_2MgF_4	K_2MgF_4	$SnBa_2S_4$ [d] (low temp)						
$GePb_2S_4$	Unknown		Modif. K_2SO_4	$P2_1/c$	7.97	8.93	10.88	114.17	706.2
$SiCd_4S_6$	Unknown		$GeCd_4S_6$	*Cc*	11.99	7.02	12.12	110.2	
$GeCd_4S_6$	Unknown		New structure	*Cc*	12.35	7.08	12.38	110.2	1016.0

[a] Preparation reported in Ref. (*6*).
[b] Identified from powder pattern only.
[c] Compounds also reported in Refs. (*2, 3, 7*).
[d] The phase gave a similar powder pattern to the low-temperature phase of $SnBa_2S_4$.

precession films showed the diffraction symmetry to be $2/m$ with systematic absences $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, so that the space group is uniquely $P2_1/c$. A tabular crystal with approximate dimensions of $0.03 \times 0.15 \times 0.10$ mm was mounted on a quarter circle goniostat and the lattice parameters were determined by a least-squares refinement based

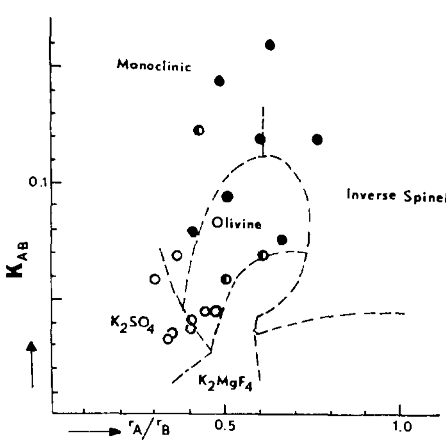

FIG. 1. Plot of K_{AB} versus r_A/r_B for sulfide compounds. Open circles denote K_2SO_4-type structures and full circles olivine type. Half-filled circles are structures which have neither structure but are closely related to K_2SO_4. The regions outlined by the dashed lines are based on a mapping of structures observed for oxides, AB_2O_4.

on $2\theta°$ measurements of 60 reflections between $28° \leqslant 2\theta \leqslant 50°$ peaked on MoK_{α_1}, $\lambda = 0.70926$ Å, and MoK_{α_2}, $\lambda = 0.71354$ Å, with the goniostat at a 1° takeoff angle and a 0.02° receiving slit. The lattice constants are $a = 7.9742(6)$ Å, $b = 8.9255(8)$ Å, $c = 10.8761(8)$ Å, $\beta = 114.171(9)°$, $Z = 4$, $\rho_x = 5.79$ g/cm^3.

For the three-dimensional data collection, Zr-filtered molybdenum radiation, with the goniostat at a 5° takeoff angle, was used to collect about 1200 reflections to a maximum value of $2\theta = 54°$. The stationary counter-stationary crystal method was used to obtain the peak intensity and background was measured at $\pm 2°$ 2θ from the peak. A standard reflection was checked after every 100 measurements to determine instrument drift and possible changes in the alignment of the crystal. Lorentz, polarization and an absorption correction ($\mu = 524$ cm^{-1}) were applied to the data. The transmission factors varied 0.12–0.70.

The structure was solved from the three-dimensional Patterson function from which the two independent Pb atoms were located. Phases based on the heavy atom positions were used to calculate a three-dimensional electron density map which showed all atoms. The structure was refined by a least-squares procedure using a modification of the program ORFLS (*8*); unit weights were used in the refinement and the final R with anisotropic

TABLE III

ATOMIC PARAMETERS AND THEIR STANDARD DEVIATIONS IN PARENTHESES ($\times 10^4$) FOR $GePb_2S_4$[a]

Atom	x	y	z	10^4B_{11}	10^4B_{22}	10^4B_{33}	10^4B_{12}	10^4B_{13}	10^4B_{23}
Pb1	0.0356(2)	0.3161(1)	0.3407(1)	84(2)	84(2)	46(1)	12(1)	22(1)	0(1)
Pb2	0.4124(2)	0.4326(1)	0.1551(1)	108(2)	68(2)	54(1)	−10(1)	38(1)	−10(1)
Ge	0.7137(4)	0.1908(3)	0.0063(3)	65(5)	43(3)	27(3)	−6(3)	18(3)	−0(2)
S1	0.2465(10)	−0.0171(8)	0.1256(7)	68(11)	50(8)	46(7)	−7(8)	17(7)	−17(6)
S2	0.7644(9)	0.0900(8)	0.2027(7)	92(13)	41(8)	44(7)	−6(8)	30(8)	15(6)
S3	0.4437(9)	0.2002(8)	0.3980(7)	69(12)	55(8)	46(7)	12(8)	17(8)	−2(6)
S4	0.9193(10)	0.3691(8)	0.0610(7)	90(9)	57(9)	40(7)	−39(9)	12(8)	−7(7)

[a] The temperature factor is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

temperature factors was 0.0594 for 1148 reflections. The atomic scattering factors, Pb and Ge corrected for the real and imaginary parts of anomalous dispersion, as listed in the International Tables (*9*) were used in the refinement. The standard deviation of an observation of unit weight is 0.750. The final atomic parameters and their standard deviations are shown in Table III and the observed and calculated structure factors are listed in a table which is available on demand (see footnote 1).

Discussion of the Structure. The bond distances and angles are shown in Table IV and a stereoscopic view of the structure is shown in Fig. 2. The Ge atom is in almost perfect tetrahedral coordination to sulfur, with an average Ge–S distance of 2.20 Å. The Pb atoms are in six- and sevenfold coordination, with Pb–S distances ranging 2.81–3.37 Å, and serve to hold the isolated GeS_4 tetrahedra together. The parameters $r_A/r_B = 0.415$ and $K_{AB} = 0.123$ place this compound into a region of the map where no corresponding oxide or sulfide structure was previously known and thus a new structure type is not unexpected.

TABLE IV

BOND DISTANCES AND ANGLES IN $GePb_2S_4$[a]

Distances (Å)			
Ge–S3	2.21(1)	Pb2–S2	2.85(1)
Ge–S4	2.18(1)	Pb2–S3	3.29(1)
Ge–S1	2.22(1)	Pb2–S1	2.82(1)
Ge–S2	2.20(1)	Pb2–S3	2.81(1)
		Pb2–S4	3.25(1)
Pb1–S1	3.37(1)	Pb2–S3	3.14(1)
Pb1–S2	3.06(1)		
Pb1–S4	2.83(1)	Ge–Pb1	3.902(6)
Pb1–S2	2.89(1)	Ge–Pb2	4.785(6)
Pb1–S4	3.34(1)	Pb1–Pb2	4.375(3)
Pb1–S3	3.22(1)		
Pb1–S1	2.84(1)		

Angle (°)	
S3–Ge–S4	106.4(5)
S3–Ge–S1	109.2(5)
S3–Ge–S2	116.7(5)
S1–Ge–S4	113.3(5)
S1–Ge–S2	108.8(5)
S2–Ge–S4	102.4(5)

[a] Standard deviations are shown in parentheses.

The Crystal Structure of $SnBa_2S_4$

On the plot of K_{AB} versus r_A/r_B, for sulfides (Fig. 1) this compound falls into the olivine region. The compound was first prepared at 800°C and a melted black material was observed adhering to the vycor tube. The powder pattern of the phase showed very diffuse lines which indicated a relationship to a K_2SO_4 structure type. A second preparation, which was heated at 600°C overnight, produced a light yellow single-phase material whose powder pattern differed from the previous one but was still similar to a K_2SO_4 structure type.

The material was considered single phase on the basis of its homogeneous appearance under the microscope and the fact that none of the starting materials could be identified in the X-ray powder pattern. Because of poor crystallinity no single crystals were found in the specimen. This sample was soaked overnight at 1000°C with a resultant color change to light brown and an improvement in crystallinity but its diffraction pattern differed again from the previous two patterns although qualitatively it appeared to have maintained a similarity to K_2SO_4. A single crystal was selected from this preparation and a series of X-ray photographs showed a super cell along one of the axes. It is possible that this is a high temperature phase

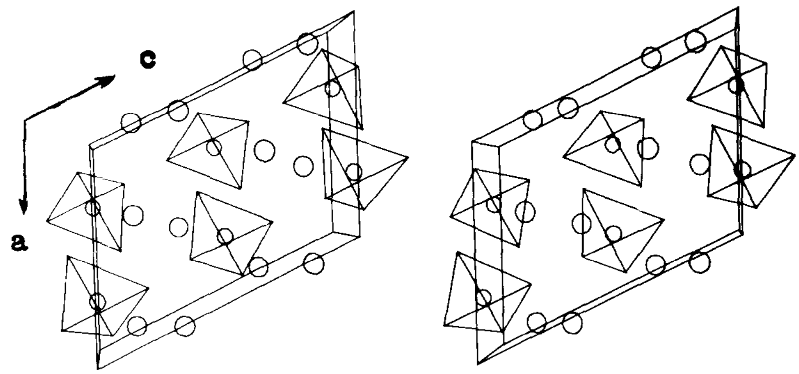

FIG. 2. Stereoscopic view of the structure of $GePb_2S_4$ along the *b* axis. Small circles represent Ge atoms, large circles represent Pb atoms, tetrahedra have sulfur atoms at the corners.

of $SnBa_2S_4$ and the other phase represented a low temperature form.

A series of Weissenberg and precession photographs showed an orthorhombic diffraction symmetry with systematic absences $0kl$, $k + l = 2n + 1$, $h0l$, $h = 2n + 1$, yielding the diffraction symbol *mmmPna* consistent with space groups $Pna2_1$ or *Pnma*. A flat crystal in the shape of a trigonal prism with dimensions $0.05 \times 0.10 \times 0.10$ mm was mounted on a quarter circle single-crystal orienter on which it was aligned along the c^* axis. The 2θ values for about 50 strong reflections in the range 20–60° were measured using MoK_{α_1} and K_{α_2} radiation under the same fine conditions as previously described, to determine the precise unit cell dimensions by a least-squares procedure. The unit cell parameters are $a = 17.823(3)$ Å, $b = 7.359(1)$ Å, $c = 12.613(2)$ Å, $Z = 8$, $\rho_x = 4.18$ g/cm³.

For the three-dimensional data collection, Zr-filtered MoK_α radiation was used to measure about 1900 reflections to a 2θ limit of 60° and about 1200 reflections were accepted as statistically nonzero. The basis for accepting an intensity as statistically nonzero was a value of $\Delta I/I \leqslant 0.1$, where $\Delta I/I = (T + t^2 B)^{1/2}/(T - tB)$, T = total peak count in time t_T, B = total background count on each side of peak, $t = t_T/t_1 + t_2$, t_1 and t_2 are background counting intervals (*10*). The expression

$$\sigma(|F_0|) = \left\{\left(\frac{F_0}{2I}\right)^2 \left[I + B\frac{t}{2} + 0.0004I^2\right]\right\}^{1/2}$$

was used to estimate the standard deviation for the observed structure factor. The experimental conditions for data collection were the same as previously described. Lorentz, polarization and absorption corrections were made ($\mu = 139$ cm^{-1}) and a three-dimensional Patterson function was calculated from the resultant structure factors. From an interpretation of the Patterson map the Sn and Ba atoms could be located and also it was evident that the space group was $Pna2_1$. A three-dimensional electron density map calculated with phases based on the heavy atom positions revealed the locations of the sulfur atoms.

The atomic parameters were refined by a least-squares procedure using $1/\sigma^2$ to weight the structure factors (*8*). Anisotropic temperature factors and atomic scattering factors, Ba and Sn corrected for the real ($\Delta f'$) and imaginary contributions ($\Delta f''$), were used in the calculation (*9*). The conventional R coefficient for 1176 reflections greater than $3\sigma(|F_0|)$ is 0.0744 using the parameters shown in Table V and is 0.0746 when $\bar{x}\bar{y}\bar{z}$ are used. The hypothesis that the correct structure has the negative parameter values can be rejected at the 0.025 significance level using Hamilton's test (*11*), $R_{1,1020,0.025} = 1.0028$. A table which lists the observed and calculated structure factors is available on demand (see footnote 1).

Discussion of the Structure of $SnBa_2S_4$. The structure is a modified K_2SO_4 type in which the unit cell is doubled along the *a* axis. The two Sn atoms in fourfold coordination are tightly bonded to the sulfur tetrahedron with Sn–S bond distances ranging 2.32–2.41 Å, Table VI. Two of the four Ba atoms are in eightfold coordination with Ba–S bond distances ranging 3.06–3.47 Å. The other two Ba atoms are in sixfold coordination with Ba–S distances ranging 3.05–3.37 Å. These values are comparable with the Sn–S bond distance in the compound SnS, 2.4 Å and Ba–S bond distance in the compound BaS, 3.4 Å. The stereoscopic view of the structure (Fig. 3) shows the arrangement of the isolated SnS_4 tetrahedra held together by barium.

TABLE V

ATOMIC PARAMETERS AND THEIR STANDARD DEVIATIONS IN PARENTHESES ($\times 10^4$) FOR $SnBa_2S_4$[a]

Atom	x	y	z	10^4B_{11}	10^4B_{22}	10^4B_{33}	10^4B_{12}	10^4B_{13}	10^4B_{23}
Sn1	0.9768(2)	0.7696(4)	0.6081(6)	4(1)	39(5)	26(3)	2(2)	−1(2)	3(4)
Sn2	0.7333(2)	0.7198(4)	0.2705(5)	4(1)	55(6)	21(3)	−1(2)	2(1)	−1(4)
Ba1	0.6264(2)	0.7106(4)	0.	9(1)	78(6)	19(2)	−2(2)	1(1)	1(4)
Ba2	0.8735(2)	0.7008(4)	0.8773(3)	6(1)	66(5)	37(3)	2(2)	0(1)	−3(4)
Ba3	0.6888(2)	0.7015(5)	0.6113(5)	9(1)	176(8)	32(3)	−14(2)	2(2)	−10(5)
Ba4	0.9454(2)	0.7337(6)	0.2638(7)	6(1)	202(9)	88(5)	13(2)	2(2)	43(6)
S1	0.7475(9)	0.9972(19)	0.9044(14)	20(5)	78(27)	40(12)	−6(9)	16(8)	−7(13)
S2	0.4959(10)	0.9677(20)	0.4906(19)	17(5)	66(25)	75(16)	8(9)	15(8)	9(17)
S3	0.7975(8)	0.9886(18)	0.3299(12)	12(4)	67(25)	21(9)	−6(8)	−13(5)	2(12)
S4	0.9644(8)	0.9653(20)	0.0369(18)	7(4)	74(25)	99(18)	−7(9)	−13(8)	−45(18)
S5	0.8506(7)	0.8502(20)	0.6453(14)	2(3)	91(25)	46(11)	−4(8)	6(5)	−4(14)
S6	0.6131(7)	0.8387(20)	0.2404(12)	3(3)	105(26)	25(10)	12(8)	−3(5)	−16(12)
S7	0.5428(8)	0.7890(26)	0.7713(14)	10(4)	294(47)	19(9)	7(11)	−7(6)	−19(21)
S8	0.7999(7)	0.6447(20)	0.1160(14)	12(4)	173(31)	14(8)	−6(9)	3(6)	−3(17)

[a] The temperature factor is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

TABLE VI

BOND DISTANCES AND ANGLES IN $SnBa_2S_4$[a]

Distances (Å)

Ba1–S3	3.06(3)	Ba2–S1	3.15(3)	Sn1–S2	2.32(3)
Ba1–S6	3.16(3)	Ba2–S6	3.18(3)	Sn1–S5	2.37(3)
Ba1–S2	3.17(3)	Ba2–S8	3.31(3)	Sn1–S7	2.41(3)
Ba1–S1	3.20(3)	Ba2–S2	3.23(3)	Sn1–S4	2.39(3)
Ba1–S4	3.23(3)	Ba2–S4	3.24(3)		
Ba1–S5	3.31(3)	Ba2–S5	3.15(3)		
Ba1–S7	3.29(3)	Ba2–S7	3.30(3)		
Ba1–S8	3.47(3)	Ba2–S3	3.48(3)	Sn2–S6	2.35(3)
				Sn2–S3	2.41(3)
Ba3–S5	3.12(3)	Ba4–S6	3.05(3)	Sn2–S1	2.38(3)
Ba3–S3	3.18(3)	Ba4–S7	3.28(3)	Sn2–S8	2.35(3)
Ba3–S1	3.22(3)	Ba4–S8	3.26(3)		
Ba3–S8	3.27(3)	Ba4–S4	3.35(3)		
Ba3–S7	3.36(3)	Ba4–S3	3.34(3)		
Ba3–S4	3.37(3)	Ba4–S2	3.35(4)		

Angles (°)

S2–Sn1–S5	117(1)	S6–Sn2–S3	100(1)
S2–Sn1–S7	110(1)	S6–Sn2–S1	120(1)
S2–Sn1–S4	108(1)	S6–Sn2–S8	115(1)
S5–Sn1–S4	110(1)	S3–Sn2–S1	106(1)
S5–Sn1–S4	107(1)	S3–Sn2–S8	102(1)
S7–Sn1–S4	105(1)	S1–Sn2–S8	111(1)

[a] Standard deviations are shown in parentheses.

Crystal Chemistry of K_2SO_4 and Olivine Structure Types

An examination of the structures that are summarized in Table II and plotted on the diagram of Fig. 1 shows that the K_2SO_4 structure type extends over a larger area than observed for the oxides.

Gattow and Franke (*4*) have investigated a series of compounds of the type Me_2MoS_4 and Me_2WS_4, where Me represents K^+, NH_4^+, Rb^+, and Cs^+, and found that they have the K_2SO_4 structure type. The r_A/r_B and K_{AB} parameters for them lie within the extended K_2SO_4 region of Fig. 1. Gattow and Franke have pointed out that their compounds lie on a straight line in a plot of $\Sigma r = r_A + r_B + r_X$ versus unit cell volume and the K_2SO_4 type phases reported here, including the modified structures of $SnBa_2S_4$ and $GePb_2S_4$, also follow this straight line relationship.

The bond distances between A and X atoms are in good agreement with the covalent tetrahedral radii of Pauling (*12*), while B atoms are bonded ionically to X atoms in sixfold or larger coordination. Thus a large value of electronegativity and small radius for the A ion and, conversely, a small electronegativity and large radius for the B ion help stabilize the structure. These conditions are satisfied if B atoms are alkali or alkaline earth metals and A atoms are from group IV or VI in the periodic chart.

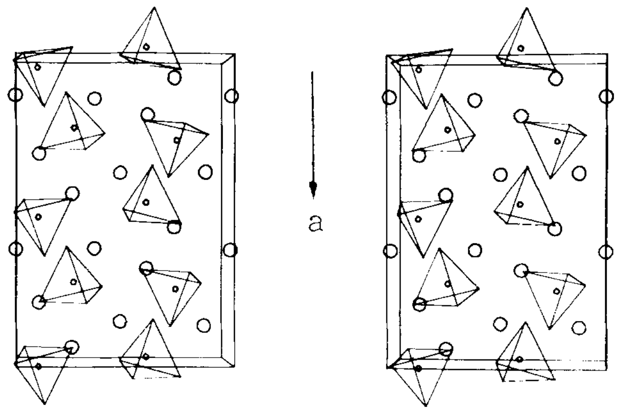

FIG. 3. Stereoscopic view of the structure of $SnBa_2S_4$ as seen along *b* axis. Large circles represent Ba atoms, small circles represent Sn atoms, tetrahedra have sulfurs at the corners.

The experimental results indicate that Si^{4+}, Ge^{4+}, and Ti^{4+} ions meet the requirements very well for the A site and Ba^{2+} for the B site or W^{6+} and Mo^{6+} for the A site and K^+, Cs^+, Rb^+, and NH_4^+ for the B site. If the A ion is as large as Sn^{4+} the radius ratio becomes very unfavorable for tetrahedral coordination and it is not surprising that the $(SnS_4)^{4-}$ tetrahedron is distorted. The removal of the mirror plane in the K_2SO_4 structure and its replacement by the "*a*" glide plane in $SnBa_2S_4$ removes the spatial restrictions on the locations of the atoms and the resultant distortion in the tetrahedron stabilizes this modified structure. As the size of the A atom increases as in Pb^{4+}, the tetrahedron would have to be distorted to such an extent that it no longer can be accommodated in this structural framework. As a result the synthesis of $PbBa_2S_4$ is not successful and only a solid solution of PbS in BaS is observed. If the B ion becomes as small as Ca^{2+}, then the cations tend to be in octahedral coordination and this changes the structure from the K_2SO_4 type to the olivine type.

Olivine Structure Type. Although there are many oxide compounds with the olivine structure there are relatively few sulfide compounds of this type (*2*, *3*). The structure is characterized by the hexagonal close packing of the anions, with the A atom in the tetrahedral site and the B atom in the octahedral site. This differs from the K_2SO_4 structure, which consists of isolated tetrahedra. However, a similarity between the two structures can be seen if the B atom in the K_2SO_4 type is considered together with the anion as part of a close packed framework with the A atom in the tetrahedral interstice. In the olivine structure both A and B atoms go into the interstices of the hexagonal close packed arrangement of anions. This is not unlike the perovskite structure for compounds ABS_3 in which the bigger cation can be considered as part of the anion layer to build the close packing arrangement and the small cation fills the octahedral void.

The olivine structure is predicted and observed for $GeCa_2S_4$ and $SnCa_2S_4$ and that structure is also found for $SiCa_2S_4$. Depending on the reaction temperature $SiCa_2S_4$ shows another structure whose powder pattern is similar to the K_2SO_4 structure type, although the pattern always indicated a poorly crystalline material.

The compounds $SnCd_2S_4$, VCd_2S_4, and $SnPb_2S_4$, for which the olivine structure is predicted, could not be synthesized. A phase $TiSn_2S_4$ was produced but appears to have a new structure type, possible related to Mn_3O_4, but we were unable to obtain a single crystal for further structural investigation. The reaction product from the composition VSn_2S_4 could not be identified because of the poor crystallinity of the material. The composition $MoBa_2S_4$ always yielded the two phases MoS_2 and BaS. The composition VBa_2S_4 showed the phase BaS, some form of a vanadium sulfide, and elemental vanadium and sulfur. Several phases were also observed for $SiSr_2S_4$, whose oxide has the K_2SO_4 structure type. Recently (*7*) a monoclinic phase has been reported for $GeSr_2S_4$ and may be identical with the material which we observed in the reaction product and which is labeled $GeSr_2S_3$ (see footnote 1).

The olivine region in Fig. 1 is considerably smaller than observed for the oxide phases. Favorable conditions for the formation of this structure are B site occupancy by atoms which fit into the octahedral voids without unduly distorting the octahedra. Ca^{2+}, Mg^{2+}, and Mn^{2+} are apparently the only atoms which can satisfy this condition with group IV A atoms. The failure to obtain the olivine structure for strontium compounds with Si^{4+} and Ge^{4+} is probably due to the large ionic radius of Sr^{2+}, which is too big to fit into the octahedral site in the olivine structure and is too small to be part of the sulfur layers in the K_2SO_4 structure. The Pb^{2+} ion is intermediate in size between Ba^{2+} and Sr^{2+}, and $GePb_2S_4$ is monoclinic, containing isolated tetrahedra similar to the K_2SO_4 structure type, but the small Pb^{2+} ion can not participate with the anion in close packing and a monoclinic structure is obtained. We have synthesized $SiPb_2S_4$ and $SiPb_2Se_4$ and these structures are also monoclinic, although not isostructural with each other. A detailed discussion of their structures will appear elsewhere.

K_2MgF_4 Structure Type. Attempts to synthesize compounds with this predicted structure type were not successful and multiple phases were always observed, except for the compound $PbBa_2S_4$ which showed a solid solution of PbS in the face centered cubic structure of BaS. Compounds of the type $MgLn_2S_4$, where Ln is a rare-earth element, would fall into this region in Fig. 1, but their known structures are different (*13*).

This crystal structure is characterized by close packing of the B and X atoms, and the A atom is placed in the interstices similar to the K_2SO_4 structure, although the packing of the atoms is much more ordered than for the latter structure. The ionic radii of O^{2-} and F^- are close to the radius of the B^{2+} cation and many oxide and fluoride compounds are known with this structure. However, S^{2-}, Cl^-, or Br^- are considerably larger than the B^{2+} cations, so that the resultant distortion prevents the formation of this structure type and may give rise to the K_2SO_4 type, provided the A atom is small enough to fit into the tetrahedral site.

Conclusion

The olivine- and K_2SO_4-type structures for chalcogenides occupy distinct areas in a map based on a plot of r_A/r_B versus K_{AB}. However, the areas are somewhat modified when compared with those found for oxide compounds with these structure types. The K_2SO_4-type structures occupy a larger region and the olivine-type structures a smaller region. A narrow transition region appears to be present in which structures exist which are related to K_2SO_4 but have lower symmetry.

References

1. K. Kugimiya and H. Steinfink, *Inorg. Chem.* **7**, 1762 (1968).
2. A. Weiss and G. Rocktaschel, *Z. Anorg. Allg. Chem.* **307**, 1 (1960).
3. G. Rocktaschel, W. Ritter, and A. Weiss, *Z. Naturforsch. B* **19**, 958 (1964).
4. G. Gattow and A. Franke, *Naturwissenschaften* **52**, 493 (1965).
5. K. Sasvari, *Acta Crystallogr.* **16**, 719 (1963).
6. M. Maurin and M. Ribes, *C.R.H. Acad. Sci. Ser. C* **265**, 1461 (1967).
7. M. Ribes, E. Philippot, and M. Maurin, *C.R.H. Acad. Sci. Ser. C* **270**, 716 (1970).
8. W. R. Busing, K. O. Martin, and H. A. Levy, USAEC Report ORNL-TM-305 Oak Ridge National Lab., Oak Ridge, Tennessee, 1962.
9. "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962.
10. M. Mack, *Norelco Rep.* **12**, 40 (1965).
11. W. C. Hamilton, *Acta Crystallogr.* **18**, 502 (1965).
12. L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Chaps. 7, 11, 13, Cornell Univ. Press, Ithaca, N. Y., 1960.
13. J. Flahaut, *Acta Crystallogr.* **19**, 14 (1965).