

Phase Relations in the System Ag-Sb-S at 400° C

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The coexisting phases in the three-phase fields of the system Ag-Sb-S at 400°C within the region $\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3-\text{Sb}-\text{Ag}$ have been determined by means of X-ray identification in samples annealed at 400°C and quenched to room temperature. In addition, the reactions between pellets of silver-antimony alloys and silver-antimony sulfides at 400°C have been investigated. The results are in agreement with the isothermal section of the ternary phase diagram deduced from X-ray investigations.

In conjunction with kinetic investigations on solid state reactions in the quasi-binary system $\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3$, it was found desirable to reexamine the isothermal section of the phase diagram of the ternary system Ag-Sb-S at 400°C. Previously this ternary system was investigated by Schenck, Hoffmann, Knepper and Vögler¹ with the help of measurements of the $\text{H}_2\text{S}/\text{H}_2$ ratio during the reduction of sulfides of the quasi-binary system $\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3$ with H_2 at 400°C. From the obtained staircase curves the boundaries of two-phase and three-phase fields were deduced. As the $\text{H}_2\text{S}/\text{H}_2$ ratios for some of the steps of the staircase curves were close together, the reality of some steps may be questioned. The composition of the silver-antimony sulfide phases was given as $\text{Ag}_2\text{S}\cdot\text{Sb}_2\text{S}_3$, $4\text{Ag}_2\text{S}\cdot\text{Sb}_2\text{S}_3$, and $2\text{Ag}_2\text{S}\cdot\text{Sb}_2\text{S}_3$. This is in disagreement with thermal studies by Jaeger and van Klooster² and by Jensen³ where only the phases $\text{Ag}_2\text{S}\cdot\text{Sb}_2\text{S}_3$ and $3\text{Ag}_2\text{S}\cdot\text{Sb}_2\text{S}_3$ were observed. The work was confined to the region Ag-Sb- $\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3$ of the system Ag-Sb-S. The nature of the coexisting phases was ascertained by the following methods.

1) Samples whose compositions were presumably in three-phase fields were prepared from the elements, annealed at 400°C, and quenched. In addition, two samples in two-phase fields were investigated. The phases present were identified by means of X-ray powder diagrams with the help of a General Electric diffraction unit with Cu-radiation and Ni-filter.

2) Pressed and sintered pellets of Ag_2S , Ag_3SbS_3 , AgSbS_2 and Sb_2S_3 and pellets of Ag, Ag_3Sb , and Sb solidified from melts were prepared. Two pellets

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of different composition 2–3 mm thick were pressed together and heated at 400°C for several days in a N₂ atmosphere. Observation of a reaction zone involving new phases indicates that the phases initially present do not coexist under equilibrium conditions.

The following informations on the crystal structures and homogeneity ranges of the phases in the binary systems were used.

1) The binary system Ag–Sb

By means of metallographic examination and X-ray diffraction identification, Weibke and Effinger⁴ studied the system Ag–Sb in detail. Their results agree in principle with previous X-ray diffraction investigations by Broderick and Ehret⁵ and by Westgren, Hägg, and Eriksson⁶. At 400°C, the following phases exist:

α-Phase. Homogeneity range 0–6.2 atom % Sb⁴. Face-centered cubic structure with a lattice constant increasing from $a = 4.086 \text{ \AA}$ for pure silver to $a = 4.121 \text{ \AA}$ ⁶. Lattice constant for pure silver is given on the ASTM data card⁷ as $a = 4.0862 \text{ \AA}$ at 27°C.

ζ-Phase. Homogeneity range 9.4–14.9 atom % Sb⁴. Hexagonal close-packed structure with lattice constants increasing from $a = 2.927 \text{ \AA}$, $c = 4.784 \text{ \AA}$, $c/a = 1.634$ ⁶ to $a = 2.961 \text{ \AA}$, $c = 4.797 \text{ \AA}$, $c/a = 1.620$ ⁴.

ε-Phase. Homogeneity range 21.3–26.2 atom % Sb⁴. Orthorhombic structure which can be considered as a slightly distorted ζ-phase structure. The change in lattice constants within the homogeneity range for alloys annealed at 400°C is from $a = 2.986 \text{ \AA}$, $b = 5.180 \text{ \AA}$, $c = 4.774 \text{ \AA}$ to $a = 2.996 \text{ \AA}$, $b = 5.246 \text{ \AA}$, $c = 4.854 \text{ \AA}$ ⁶.

The lattice constants given by Westgren, Hägg, and Eriksson⁶ for the lower limit of the homogeneity range of the ε-phase are considerably higher than those given by Weibke and Effinger⁴. Only the latter authors give the annealing temperature of the alloys and report differences in lattice constants for alloys annealed at 400°C and 500°C and thus their values are considered to be more accurate.

Sb-Phase. The dimensions of the hexagonal unit cell of pure Sb are given on the ASTM data card⁸ as $a = 4.307 \text{ \AA}$, $c = 11.273 \text{ \AA}$. The solubility of Ag in Sb and its effect on the lattice constants are not yet known.

2) The binary system Sb–S

As shown already by Jaeger and van Klooster², Sb₂S₃ is the only stable compound in the system Sb–S. The compound Sb₂S₃ has been obtained only by precipitation from aqueous solutions. The ASTM data card⁹ gives the following dimensions of the orthorhombic unit cell of Sb₂S₃: $a = 11.229 \text{ \AA}$, $b = 11.310 \text{ \AA}$, $c = 3.839 \text{ \AA}$.

The homogeneity ranges of the Sb phase and the Sb₂S₃ phase must be considered as very limited, but actual data are missing.

3) The binary system Ag–S

There is only one compound Ag₂S, which has a cubic structure at 400°C¹⁰, called α Ag₂S or argentite. Transformation to the low temperature modification, called β Ag₂S or acanthite, takes place spontaneously near 178°C even on rapid quenching. According to Ramsdell¹¹ acanthite is monoclinic, $a = 9.47 \text{ \AA}$, $b = 6.92 \text{ \AA}$, $c = 8.28 \text{ \AA}$, $\beta = 124^\circ$. The homogeneity range of α

Ag₂S was deduced by Wagner¹² at 200° and 300°C from electrochemical measurements and can be given as Ag_{2.000}S to Ag_{2.002}S.

The solubility of S in Ag is negligible.

4) The quasi-binary system Ag₂S—Sb₂S₃

A thermal study of the system Ag₂S—Sb₂S₃ was first made by Jaeger and van Klooster². The most detailed investigation has been made by Jensen³. Two intermediate compounds with a narrow homogeneity range are reported, AgSbS₂ and Ag₃SbS₃.

*α*AgSbS₂. This modification is stable above 380°C. The crystal structure is cubic with a lattice constant $a = 5.653 \text{ \AA}$ according to Graham¹³. The transformation to the low temperature modification *β* AgSbS₂, miargyrite, takes place on slow cooling whereas *α* AgSbS₂ is preserved on quenching.

Ag₃SbS₃, *pyrargyrite*. The structure of this phase was determined by Harker¹⁴. The dimensions of the hexagonal unit cell are $a = 11.06 \text{ \AA}$, $c = 8.74 \text{ \AA}$.

In addition, there have been reported the minerals polyargyrite,

11 Ag₂S·Sb₂S₃, polybasite, 8Ag₂S·Sb₂S₃, pyrostitpnite, 3Ag₂S·Sb₂S₃, and stephanite, 5Ag₂S·Sb₂S₃. Polybasite and pyrostitpnite were prepared by Weil and Hoert¹⁵ by heating the components in glycerol.

IDENTIFICATION OF PHASES BY X-RAY DIFFRACTION

In Fig. 1 the compositions of the samples in the ternary system are indicated in the phase diagram. The exact composition and the phases identified in each sample are given in Table 1.

The interpretation of the X-ray diffraction diagrams was complicated because overlapping of diffraction lines from different phases often occurred. The *β* Ag₂S, Sb₂S₃ and Ag₃SbS₃ phases give very complex patterns. The complex *β* Ag₂S pattern could have been avoided by using a high temperature camera where the specimen was kept at a temperature above 178°C, but in the present investigation a high temperature camera was not used.

The accuracy of the lattice constants is estimated to be 0.2 % unless otherwise stated.

The lattice constants of the individual phases found in the various samples were compared with values available in the literature with the following results.

Sb₂S₃-Phase. Within the limits of error, complete agreement was found between the Sb₂S₃ phase in sample G and pure Sb₂S₃⁹.

Sb-Phase. Within the limits of error the lattice constants of Sb in the samples G, A, and B agreed with those of pure Sb⁸.

α AgSbS₂-Phase. The samples G, A, B, K, and C contain *α* AgSbS₂ with a lattice constant equal to the value given for pure *α* AgSbS₂¹³.

ε-Phase. The calculated lattice constants in samples B and K are $a = 2.992 \text{ \AA}$, $b = 5.244 \text{ \AA}$, $c = 4.852 \text{ \AA}$. In sample C considerable overlapping from Ag₃SbS₃ interferes with an accurate evaluation of the lattice constants, but they are within a limit of error of $\pm 0.4 \%$ the same as in samples B and K. Upon comparing these values with the lattice constants of the *ε*-phase in the system Ag—Sb⁶ within the homogeneity range, nearly complete agreement with the values for the Sb-rich limit of the *ε*-phase is found. In sample L where

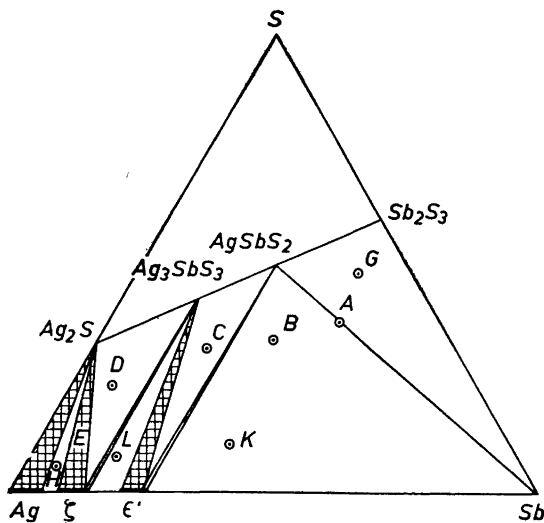


Fig. 1. Isothermal section of the phase diagram of the system Ag-Sb-S at 400°C for the region Ag-Sb-Ag₂S-Sb₂S₃.

both the ϵ -phase and the ζ -phase are present, nearly complete overlapping of the reflections from these phases is observed.

Ag₃SbS₃. Within an estimated error of $\pm 0.4\%$, agreement of the lattice dimensions of the *Ag₃SbS₃* phase in the samples C, L, D with synthetic *Ag₃SbS₃* prepared from *Ag₂S* and *Sb₂S₃* was obtained.

ζ -Phase. The following lattice constants were obtained:

Sample L:	$a = 2.965 \text{ \AA}$,	$c = 4.783 \text{ \AA}$
Sample D:	$a = 2.963 \text{ \AA}$,	$c = 4.780 \text{ \AA}$
Sample E:	$a = 2.940 \text{ \AA}$,	$c = 4.792 \text{ \AA}$
Sample H:	$a = 2.924 \text{ \AA}$,	$c = 4.763 \text{ \AA}$

Table 1.

Alloy	Ag	Atom % Sb	S	Phases present
G	9.4	41.9	48.7	<i>Sb₂S₃</i> , <i>Sb</i> , α <i>AgSbS₂</i>
A	18.8	43.8	37.4	<i>Sb</i> , α <i>AgSbS₂</i>
B	33.3	33.3	33.3	<i>Sb</i> , α <i>AgSbS₂</i> , ϵ
K	55.0	35.0	10.0	<i>Sb</i> , α <i>AgSbS₂</i> , ϵ
C	47.5	21.5	31.0	α <i>AgSbS₂</i> , ϵ , <i>Ag₃SbS₃</i>
L	76.5	16.5	7.0	ϵ , <i>Ag₃SbS₃</i> , ζ
D	69.3	7.7	23.0	<i>Ag₃SbS₃</i> , ζ , <i>Ag₂S</i>
E	79.0	5.3	15.7	ζ , <i>Ag₂S</i>
H	87.7	7.4	4.9	ζ , <i>Ag₂S</i> , <i>Ag</i>

α Ag_2S . The diffraction lines of Ag_2S in the alloys D, E, and H were identified by a comparison with those of pure Ag_2S . Due to the transformation to β Ag_2S on cooling, the lattice constant of α Ag_2S has not been obtained.

Ag-Phase. The lattice constant of the silver-phase in alloy H was found to be $a = 4.112$ Å compared with the value $a = 4.121$ Å given as the upper limit for the α phase in the system Ag—Sb.

The following conclusions can be drawn:

There is no indication of more than very limited homogeneity ranges of the phases Sb_2S_3 , Sb, $AgSbS_2$, and Ag_3SbS_3 as deviations from the lattice dimensions of the pure stoichiometric phases have not been observed.

No significant solubility of sulfur in α Ag, ζ and ε seems to occur as the three-phase samples have lattice constants which do not differ from the lattice constants at the phase boundaries in the corresponding binary system Ag—Sb.

As sample D contains ζ -phase with lattice constants nearly equal to the lattice constants at the Sb-rich end of the ζ -phase in the system Ag—Sb, the tie lines from nearly the whole phase area must be directed towards the Ag_2S phase. The tie lines from the α Ag phase area are also directed towards the Ag_2S phase.

Sample C contains ε -phase with lattice constants nearly equal to the lattice constants at the Sb-rich end of the ε -phase in the system Ag—Sb. The tie lines from nearly the whole ε -phase area are thus directed towards the Ag_3SbS_3 phase.

There is no indication of a phase with the approximate composition

$31 Ag \cdot 2Ag_2S \cdot Sb_2S_3$ as reported in the paper by Schenk *et al.*¹

The experimental data given by Schenck *et al.*¹ are not in obvious conflict with the phase diagram in Fig. 1 although they have been interpreted differently. It must be recalled, however, that some of the reported steps of the H_2S/H_2 vs. composition plots are not very distinct and, therefore, do not permit a definite construction of the phase fields.

REACTION BETWEEN PELLETS OF DIFFERENT COMPOSITION

The pellet combinations Sb— $AgSbS_2$, Ag_3Sb — $AgSbS_2$, Ag_3Sb — Ag_3SbS_3 and Ag_3Sb — Ag_2S gave no indication of a reaction after heating 170 h at 400°C. Except for the combination Ag_3Sb — Ag_2S , the phases involved are connected by tie lines in the Fig. 1 and thus coexist at 400°C.

After 170 h at 400°, the pellets of the combinations Sb— Ag_3SbS_3 and Sb— Ag_2S were easily separated, but a thin reaction layer could be observed at the contact surfaces. The pellet combination Ag_3Sb — Sb_2S_3 showed a more pronounced reaction; the pellets stuck together. Reactions between the phases Ag and Ag_3SbS_3 , Ag and $AgSbS_2$, and Ag and Sb_2S_3 take place very rapidly. After 100 h virtually only the reaction products could be observed on staining polished cross sections according to Gaudin and McGlashan¹⁶.

In all the pellet combinations where a reaction was observed, the two initial phases do not coexist according to the phase diagram in Fig. 1.

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