

INVESTIGATIONS IN THE SYSTEMS $\text{Ag}_2\text{S} - \text{Cu}_2\text{S} - \text{Bi}_2\text{S}_3$ AND $\text{Ag}_2\text{S} - \text{Cu}_2\text{S} - \text{Sb}_2\text{S}_3$

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ABSTRACT

Phases and phase relations in the systems $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}-\text{Bi}_2\text{S}_3$ and $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ were studied in the temperature range between 454°C and 300°C using sealed glass capsule techniques. AgBi_3S_4 forms a complete series of solid solution with CuBi_3S_4 , whereas AgBi_2S_3 has an extensive range of solid solution in the system $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}-\text{Bi}_2\text{S}_3$. Copper-silver sulphides identified at room temperature are stromeyerite, jalpaite, and mckinstryite.

Liquid forms extensively at 453°C and 398°C in the system $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$. Phase assemblages containing no liquid were found only at $\text{Ag}_2\text{S}-$ and Cu_2S -rich corners. The system becomes completely solidified below 354°C. Three ternary phases were found: polybasite with a composition of $9(\text{Ag}_{1.88}\text{Cu}_{0.11})\text{S}\cdot\text{Sb}_2\text{S}_3$ is stable only in the presence of copper, antimonepearcite has a range of solid solution from $9(\text{Ag}_{1.87}\text{Cu}_{0.33})\text{S}\cdot\text{Sb}_2\text{S}_3$ to $9(\text{Ag}_{1.51}\text{Cu}_{0.49})\text{S}\cdot\text{Sb}_2\text{S}_3$, and a new phase is stable along the join Ag_3SbS_3 -“ Cu_3SbS_3 ” with composition varying between $(\text{Ag}_{0.47}\text{Cu}_{0.53})_3\text{SbS}_3$ and $(\text{Ag}_{0.86}\text{Cu}_{0.44})_3\text{SbS}_3$.

INTRODUCTION

More than twenty silver- and copper-sulpho-salt minerals are known to have compositions within the systems $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}-\text{Bi}_2\text{S}_3$ and $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$. In addition to the well-known end members, phases such as miagryrite, matildite, chalcostibite, polybasite, and stromeyerite, all with variable compositions, also commonly occur in hypogene deposits. The mode of occurrence has attracted the attention of many geologists in their attempts to establish the stabilities of these minerals and to use them as indicators of depositional environments. It was the purpose of this investigation to study the compositional variation of these minerals in the systems $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}-\text{Bi}_2\text{S}_3$ and $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$.

EXPERIMENTAL PROCEDURES

Reactants were prepared from finely powdered sulphur (Fisher's U.S.P.), bismuth (Baker's reagent), antimony (Fisher's purified), copper (Baker's purified), and silver sulphide (A. D. Mackay's C.P.). Each run, totalling ap-

proximately one gram, was mixed in the desired proportion and sealed in evacuated glass capsules, using a technique described in detail by Kullerud & Yoder (1959). To minimize excessive heating during sealing, the charged end of the capsule was immersed in cold water. The samples were heated in muffle furnaces, and temperatures were measured using calibrated chromel-alumel thermocouples. The accuracy of measurement is estimated to be within $\pm 1^\circ\text{C}$.

Preliminary experimental work had indicated that the rate of reaction in the mixtures was not too sluggish, and equilibrium phase assemblages could be obtained after a period of two months at 300°C with one intermediate grinding. Longer periods of treatment up to three months with two intermediate grindings were found to give the same results. To check on the equilibrium, a number of samples were pre-heated to their melting temperature (around 700°C), quenched, ground, and annealed in the desired temperature range. In addition, some samples prepared from synthetic sulphides (Ag_2S , Cu_2S , Sb_2S_3 and Bi_2S_3) instead of the elements were also treated. In all cases, phase assemblages obtained showed no differences in their x-ray powder diffraction patterns.

The quenched samples were examined by x-ray powder diffraction and reflected light microscopy. Nickel-filtered, Cu-radiation was used throughout the study. Recrystallized MgO with $d_{(200)} = 2.106\text{\AA}$ was employed as an internal standard. Cell dimensions were calculated using a least-squares program.

A vapour phase, although omitted in the following discussion, was always present in the assemblages.

THE SYSTEM $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}-\text{Bi}_2\text{S}_3$

Previous studies

No study on this system has been found, but many investigations have been done in the related binary systems.

Phase relations in the system $\text{Ag}_2\text{S}-\text{Bi}_2\text{S}_3$ were

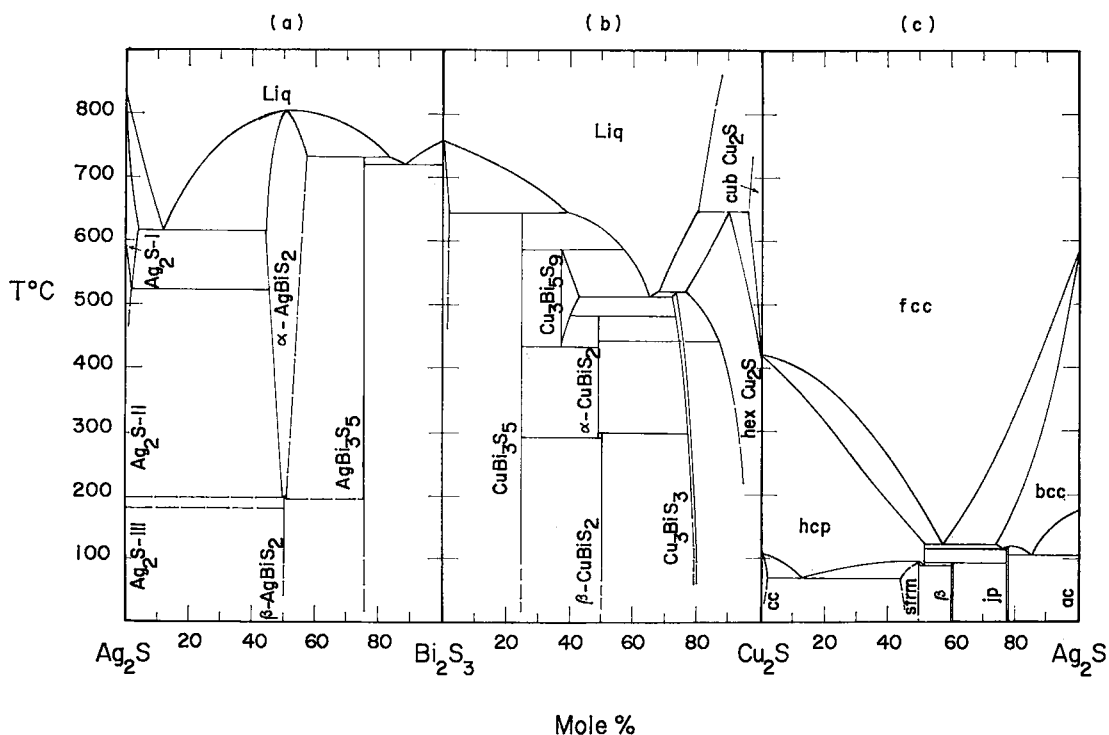


FIG. 1. Phase relations in related binary systems: (a) the system $\text{Ag}_2\text{S}-\text{Bi}_2\text{S}_3$ after Van Hook (1960), (b) the system $\text{Cu}_2\text{S}-\text{Bi}_2\text{S}_3$ after Buhlmann (1971), and (c) the system $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}$ after Skinner (1966).

first studied by Gaudin & McGlashan (1938) and Schenck *et al.* (1939), and later investigated in detail by Van Hook (1960) and Craig (1967). Van Hook's diagram (Fig. 1a) illustrates the presence of Ag_2S , AgBiS_2 , AgBi_3S_5 , and Bi_2S_3 in the system.

A large number of investigations has been made on the system $\text{Cu}_2\text{S}-\text{Bi}_2\text{S}_3$ (Gaudin & Dicke 1939; Schenck *et al.* 1939; Ross 1954; Vogel 1956; Godovikov & Ptitsyn 1969; Buhlmann 1971; and Godovikov *et al.* 1972), but no two investigators have shown the same phase assemblages for this system. Phases which have been reported are (in $\text{Cu}_2\text{S}/\text{Bi}_2\text{S}_3$): 5:1, 3:1, 3:2, 1:1, 3:4, 3:5, 1:2, 1:3, and the end members. Phase relations proposed by Buhlmann are shown in Figure 1b.

Djurle (1958) reported three phases, $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$ (α , jalpaite), $\text{Ag}_{1.2}\text{Cu}_{0.8}\text{S}$ (β , mckinstryite, Skinner *et al.* 1966), and $\text{Ag}_{0.93}\text{Cu}_{1.07}\text{S}$ (γ , stromeyerite), in the system $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}$. Each has three modifications. All high-temperature forms, including the end members Ag_2S and Cu_2S , have the *f.c.c.* structure. A detailed study on the system was made by Skinner (1966). His results are in good agreement with Djurle's, and his phase diagram is

shown in Figure 1c. Skinner states that all phase changes in this system are non-quenchable. On the basis of differential thermal analysis, Krestovnikov *et al.* (1958) reported a minimum on the liquidus at $640 \pm 3^\circ\text{C}$ and 43–45 mole % Cu_2S in the system $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}$. This is in agreement with Skinner's (1966) conclusion.

Present work

The system $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}-\text{Bi}_2\text{S}_3$ was studied in the temperature range between 454° and 300°C , and its phase relations at $454^\circ \pm 3^\circ\text{C}$ are shown in Figure 2. AgBiS_2 exists in its α -form (NaCl-type) and has an extensive range of solid solution with a maximum of 28 mole % Cu_2S in the ternary system. The cell dimension varies from 5.655\AA for AgBiS_2 to 5.669\AA for $\text{Cu}_{0.75}\text{Ag}_{2.25}\text{Bi}_1\text{S}_{4.5}$, which illustrates the increase in dimension with increasing amount of ($\text{Ag}_2\text{S} + \text{Cu}_2\text{S}$) in the solid solution, and to 5.645\AA for $\text{Cu}_{0.40}\text{Ag}_{1.60}\text{Bi}_1\text{S}_4$, which illustrates the decrease in dimension with increasing amount of Cu_2S . The solid solution limits along the binary join $\text{Ag}_2\text{S}-\text{Bi}_2\text{S}_3$ correspond with those of Van Hook (1960) and Craig (1967).

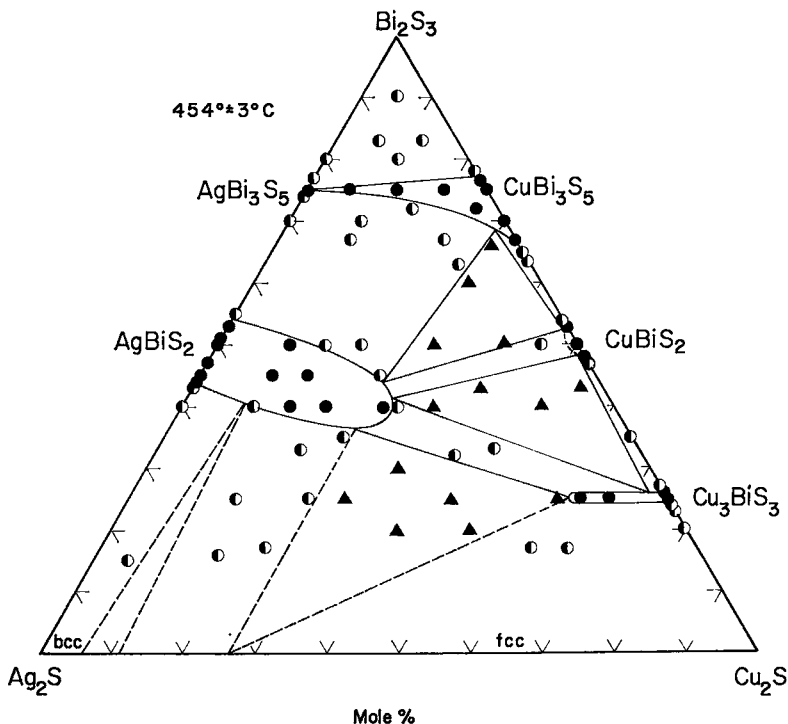


FIG. 2. Phase relations in the system $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}-\text{Bi}_2\text{S}_3$ at 454°C . In the diagram, solid circle represents one-phase, half-filled circle represents two-phase, and solid triangle represents three-phase assemblages. *bcc* and *fcc* are body-centered cubic and face-centered cubic.

A complete solid solution series exists between CuBi_3S_5 and AgBi_3S_5 . At 454°C , the series has a wedge shape in the ternary system because of solid solution in CuBi_3S_5 along the join $\text{Cu}_2\text{S}-\text{Bi}_2\text{S}_3$, and the absence of solid solution in AgBi_3S_5 along the join $\text{Ag}_2\text{S}-\text{Bi}_2\text{S}_3$. At 300°C , the range of solid solution of CuBi_3S_5 along the join $\text{Cu}_2\text{S}-\text{Bi}_2\text{S}_3$ diminishes, and the complete series with AgBi_3S_5 , although stable in the ternary system, is strictly limited to the join $\text{CuBi}_3\text{S}_5-\text{AgBi}_3\text{S}_5$.

Cu_3BiS_3 has a solid solution range up to a composition of $(\text{Cu}_{0.8}\text{Ag}_{0.2})_3\text{BiS}_3$ in the ternary system at 454°C , and the range reduces to $(\text{Cu}_{0.84}\text{Ag}_{0.16})_3\text{BiS}_3$ at 300° . Cu_3BiS_3 has also a small range of solid solution, containing 1 mole % excess Cu_2S and Bi_2S_3 along the join $\text{Cu}_2\text{S}-\text{Bi}_2\text{S}_3$, and it is not sensitive to temperature change in the range between 454° and 300°C .

CuBiS_2 (cuprobismuthite) is stable in the temperature range, and has a solid solution ranging from 52 to 47 mole % Cu_2S and 51 to 48 mole % Cu_2S along the join $\text{Cu}_2\text{S}-\text{Bi}_2\text{S}_3$, respectively, at 454° and 300°C .

Because all the high-temperature silver-cop-

per sulphides are nonquenchable, the stable phase assemblages observed at room temperature in the present study need to be extrapolated to high temperatures using available information. The phases found along the join $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}$ are Ag_2S , $\text{Ag}_{1.5}\text{Cu}_{0.5}\text{S}$, $\text{Ag}_{1.2}\text{Cu}_{0.8}\text{S}$, AgCuS , and Cu_2S , which agree well with Skinner's results (1966). Thus the changes of phase assemblages from 454°C to room temperature may be described in general as shown in Table 1.

TABLE 1. CHANGES IN PHASE ASSEMBLAGES IN THE SYSTEM $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}-\text{Bi}_2\text{S}_3$ FROM 454°C TO ROOM TEMPERATURE

454°C	room temperature
$\text{Cu}_3\text{BiS}_3+\text{AgCuS}$ (<i>f.o.o.</i>)	$\text{Cu}_3\text{BiS}_3+\text{AgCuS}$
$\text{Cu}_3\text{BiS}_3+\text{Ag}_{1.2}\text{Cu}_{0.8}\text{S}$ (<i>f.o.o.</i>) ($0 < x < 1$)	$\text{Cu}_3\text{BiS}_3+\text{Cu}_2\text{S}+\text{AgCuS}$
$\text{Cu}_3\text{BiS}_3+\text{Ag}_{1.2}\text{Cu}_{0.8}\text{S}$ (<i>f.o.o.</i>) ($1.2 < x < 1.55$)	$\text{Cu}_3\text{BiS}_3+\text{Ag}_{1.2}\text{Cu}_{0.8}\text{S}+\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$
$\alpha\text{-AgBiS}_2+\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$ (<i>f.o.o.</i>)	$\alpha\text{-AgBiS}_2+\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$
$\alpha\text{-AgBiS}_2+\text{Cu}_3\text{BiS}_3+\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$ (<i>f.o.o.</i>)	$\alpha\text{-AgBiS}_2+\text{Cu}_3\text{BiS}_3+\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$

At room temperature, jalpaite shows a range of solid solution from $(\text{Ag}_{1.55}\text{Cu}_{0.45})\text{S}$ to $(\text{Ag}_{1.50}\text{Cu}_{0.50})\text{S}$, whereas the composition of stromeyerite, $\text{Ag}_{1-x}\text{Cu}_{1+x}\text{S}$ with x between 0 and 0.1 as proposed by Skinner (1966), was con-

firmed. The β -phase, $\text{Ag}_{1.2}\text{Cu}_{0.8}\text{S}$, synthesized in this study has characteristic x -ray powder diffraction data as follows (in $d, \text{\AA}/(I/I_0)$), 3.51(4), 3.06(4), 2.86(5), 2.61(10), 2.56(4), 2.41(5), 2.31(4), 2.07(5), and 1.95(5), which correspond well with the x -ray powder data of mckinstyrite (Skinner *et al.* 1966). The close similarity in both x -ray powder data and optical properties of this phase with those of stromeyerite suggests that this phase may be overlooked or misidentified in silver-copper sulphide ores.

The ranges of solid solutions in both *f.c.c.* and *b.c.c.* phases along the join $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}$ were directly taken from Skinner's data (Skinner 1966).

THE SYSTEM $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$

Previous studies

Jensen (1947) presented a phase diagram for the system $\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3$ (Fig. 3) showing that four phases, Ag_2S , Ag_3SbS_3 , AgSbS_2 , and Sb_2S_3 , and three eutectics were present in the system. Barstad (1959), Cambi & Elli (1965a),

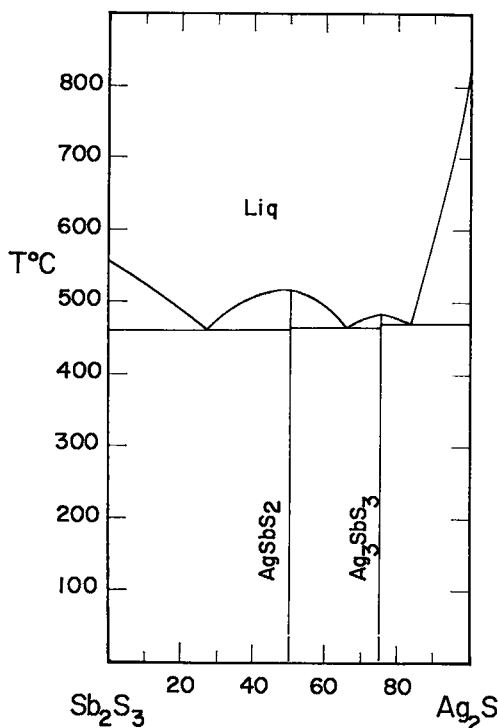


FIG. 3. Phase relations in the system $\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3$ after Jensen (1947).

and Keighin & Honea (1969) reported results consistent with Jensen's.

Gaudin & Dicke (1939) prepared two phases in the system $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$, namely, Cu_3SbS_3 and CuSbS_2 . Ross (1954) proposed four more phases in addition to those found by Gaudin & Dicke. They can be represented by 5:1, 4:5, 3:4, and 2:3 in terms of $\text{Cu}_2\text{S}/\text{Sb}_2\text{S}_3$ ratio. Cambi & Elli (1965b) presented a phase diagram of the system having melting points of Cu_2S , Cu_3SbS_3 , CuSbS_2 , and Sb_2S_3 at, respectively, 1130° , 610° , 552.6° and 548.1°C , and three eutectics at 583.2° and 83.28 mole % Cu_2S , 541.8°C and 58.73 mole % Cu_2S , and 496.0°C and 20.12 mole % Cu_2S .

Cambi & Elli (1965b) observed a phase change in Cu_3SbS_3 with transformation temperatures ranging from 500° to 530°C in the solid solution $3\text{Cu}_2\text{S}\cdot\text{Sb}_2\text{S}_3-4\text{Cu}_2\text{S}\cdot\text{Sb}_2\text{S}_3$. Both high (β)- and low (α)-temperature forms are cubic with $a = 10.44\text{\AA}$ and $a = 10.31\text{\AA}$, respectively. Godovikov & Il'yasheva (1970) reported that an orthorhombic, wittichenite-equivalent phase exists in Cu_3SbS_3 at 480°C . This phase melts at 618°C , and on cooling it yields an assemblage of α - and β -phase, the two cubic phases reported by Cambi & Elli.

Skinner *et al.* (1972) proposed that "phase B" represents the phase of composition Cu_3SbS_3 above 359°C , below which phase B decomposes to chalcostibite + tetrahedrite + antimony. This decomposition is complicated by a metastable phase transformation of phase B to phase B' at $122^\circ\pm 3^\circ\text{C}$. Skinner *et al.* also showed that tetrahedrite has no stability field along the join $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ and dissociates into two tetrahedrite phases below $125^\circ\pm 5^\circ\text{C}$.

Tatsuka & Morimoto (1973) also studied the composition variation and polymorphism of Cu_3SbS_3 and tetrahedrite. Their results show Cu_3SbS_3 , prepared either by slow cooling from melt or by annealing the cooled melt at 300°C , produced tetrahedrite + antimony. No phase B was obtained. The tetrahedrite has a superstructure with $a = 20.848\text{\AA}$, twice that of normal tetrahedrite. This superstructure disappears at 350°C , and above 361°C the assemblage tetrahedrite + antimony changes to phase B.

In the ternary system $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$, Cambi *et al.* (1966) reported a Cu-bearing polybasite and a metastable stephanite along the join $3.5\text{Cu}_2\text{S}\cdot\text{Sb}_2\text{S}_3-\text{Ag}_2\text{S}$. Hall (1967) observed the formation of polybasite and antimonpearceite at 200°C with compositions, respectively, represented by $x = 0.07 - 0.16$ and $x = 0.16 - 0.39$ in the general formula of $8(\text{Ag}_{1-x}\text{Cu}_x)_2\text{S}\cdot\text{Sb}_2\text{S}_3$.

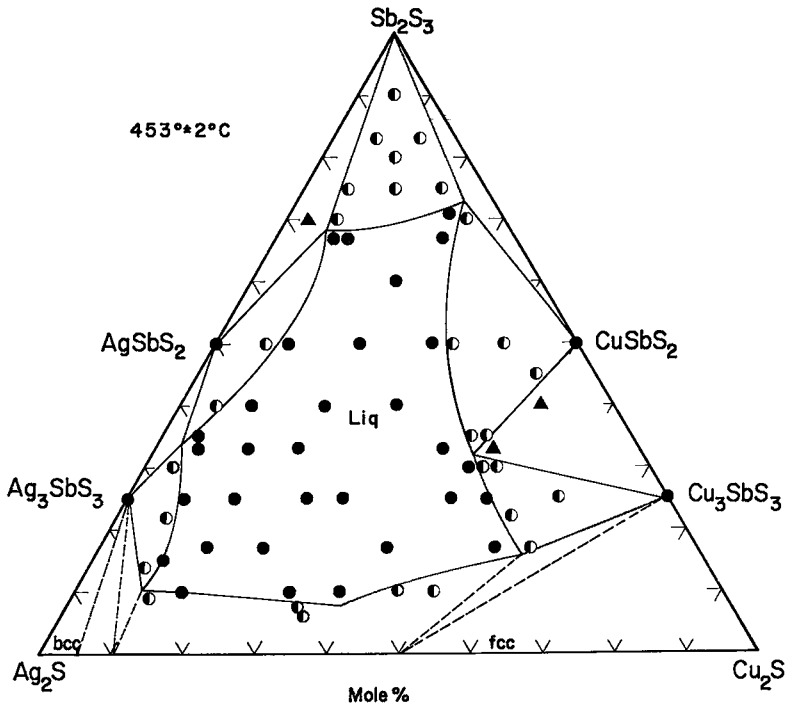


FIG. 4. Phase relations in the system $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ at 453°C .

Present work

Phase relations in the system at $453 \pm 2^\circ\text{C}$ are shown in Figure 4. Liquid forms extensively, occupying the central portion and co-existing with solid phases in all phase assemblages except those at the Ag_2S - and Cu_2S -rich corners. This isotherm intersects the extension of several binary eutectics, and the invariant points correspond well with known eutectics in the binaries: " $6\text{Cu}_2\text{S} \cdot 26\text{Ag}_2\text{S} \cdot 68\text{Sb}_2\text{S}_3$ ", " $3\text{Cu}_2\text{S} \cdot 64\text{Ag}_2\text{S} \cdot 33\text{Sb}_2\text{S}_3$ ", and " $9\text{Cu}_2\text{S} \cdot 80\text{Ag}_2\text{S} \cdot 11\text{Sb}_2\text{S}_3$ "* to the eutectics at 28, 66, and 83 mole per cent Ag_2S , respectively, in the system $\text{Ag}_2\text{S}-\text{Sb}_2\text{S}_3$ (Jensen 1947, Fig. 3); and " $23\text{Cu}_2\text{S} \cdot 4\text{Ag}_2\text{S} \cdot 73\text{Sb}_2\text{S}_3$ " and " $60\text{Cu}_2\text{S} \cdot 24\text{Ag}_2\text{S} \cdot 16\text{Sb}_2\text{S}_3$ " to the eutectics at 20 and 83 mole per cent Cu_2S , respectively, in the system $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ (Cambi & Elli 1965b). The point at " $38\text{Cu}_2\text{S} \cdot 54\text{Ag}_2\text{S} \cdot 8\text{Sb}_2\text{S}_3$ " represents the intersection of this isotherm with the minimum point on the liquidus of the system $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}$ (Krestonikov *et al.* 1968).

Phase relations in the system at 398°C are primarily the same as those at 453°C , except that the liquid field diminishes in size and occupies only the central portion of the system.

Liquid solidified completely in the system below $345 \pm 5^\circ\text{C}$, and phase relations among

solid phases at $300 \pm 1^\circ\text{C}$ are shown in Figure 5. Three ternary phases are present. Polybasite with a composition of $9(\text{Ag}_{1.80}\text{Cu}_{0.11})\text{S} \cdot \text{Sb}_2\text{S}_3$ is stable only in the presence of copper. Antimonpearceite exists in the system with a range of solid solution from $9(\text{Ag}_{1.67}\text{Cu}_{0.33})\text{S} \cdot \text{Sb}_2\text{S}_3$ to $9(\text{Ag}_{1.51}\text{Cu}_{0.49})\text{S} \cdot \text{Sb}_2\text{S}_3$. A new phase, $3(\text{Ag}_{1-x}\text{Cu}_x)_2\text{S} \cdot \text{Sb}_2\text{S}_3$, was found to be stable below 345°C along the join $\text{Ag}_3\text{SbS}_3 - \text{Cu}_3\text{SbS}_3$ with " x " varying between 0.53 and 0.44. X-ray powder diffraction data for this phase are listed in Table 2. Under reflected light microscopic examination, this phase is grayish white, weakly anisotropic, and shows strong red internal reflection. A natural mineral of this composition has not been reported.

Phase relations in the region near Cu_3SbS_3 are complicated as shown by Skinner *et al.* (1972) and Tatsuka & Morimoto (1973). The three reported phases, α , β , (Cambi & Elli 1965b; Skinner *et al.* 1972) and B (Godovikov & Il'yasheva 1970; Skinner *et al.* 1972) were all observed in quenched samples in the present study. Samples of composition Cu_3SbS_3 quenched from 453°C and 398°C produced β - and B-

*Represent compositions in mole per cent in the ternary system.

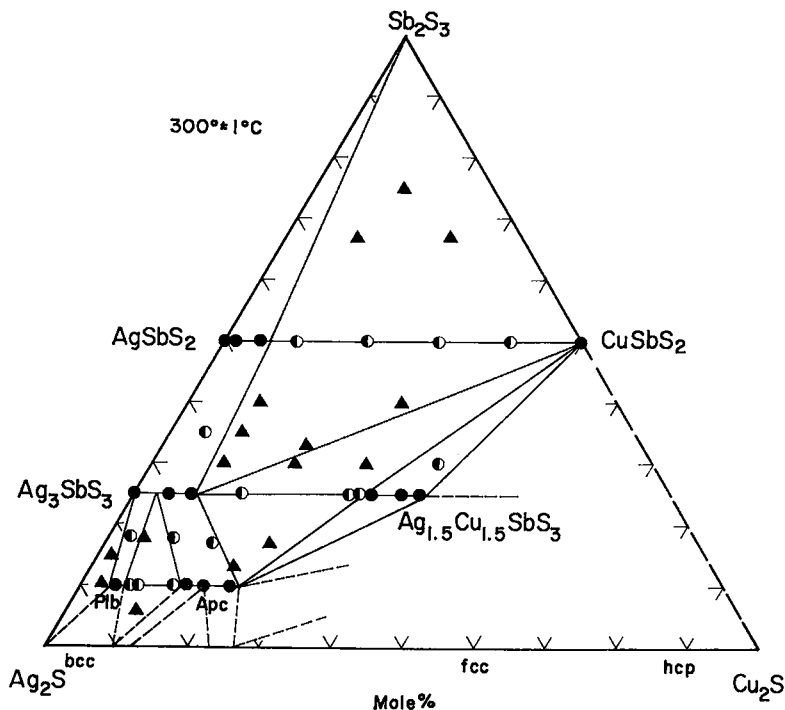


FIG. 5. Phase relations in the system $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ at 300°C . Plb and Apc represent, respectively, polybasite and antimonpearceite. Phase relations in the Cu_2S -rich portion are not established.

phase. B-phase is predominant over β -phase at 453°C , whereas β -phase is predominant at 398°C . Quenched from 300°C , composition Cu_3SbS_3 gave rise to an assemblage of co-existing α - and β -phase. A small amount of metallic antimony is present in all phase assem-

blages. The α - and β -phase are the dissociated products of tetrahedrite solid solution as correlated with Skinner *et al's* results. The one having the larger cell $a_0 = 10.424 \pm 0.001 \text{ \AA}$ is designated as β -phase and the other as α -phase with $a_0 = 10.323 \pm 0.001 \text{ \AA}$ in accordance with Cambi & Elli's usage. In *x*-ray powder diffraction patterns, the superstructure of tetrahedrite as shown by Tatsuka & Morimoto cannot be recognized.

The system $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ at 300°C , as shown, is no longer a ternary system, and phase relations in the Cu_2S -rich portion can only be established by studying the larger system $\text{Ag}-\text{Cu}-\text{Sb}-\text{S}$.

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TABLE 2. X-RAY POWDER DIFFRACTION DATA OF $\text{Ag}_{1.5}\text{Cu}_{1.5}\text{SbS}_3$

d (Å)	I	d (Å)	I
5.246	1	2.234	1
3.997	6	2.119	2
3.283	1	2.059	1
3.213	6	2.020	2
3.114	2	1.945	4
3.072	2	1.853	1
3.002	1	1.828	1
2.915	10	1.797	2
2.738	4	1.748	3
2.632	2	1.710	2
2.549	3	1.705	1
2.461	2	1.662	1
2.419	2	1.583	2
2.351	1	1.556	1
2.283	2		

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