American Mineralogist, Volume 62, pages 346–350, 1977

Phase relations in the system $PbS–Cu_2S–Bi_2S_3$ and the stability of galenobismutite

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Abstract

Phase relations in the system were studied between 500°C and 375°C using sealed, evacuated glass-capsule techniques. Complete solid solution exists between aikinite ($PbCuBiS_3$) and bismuthinite (Bi_2S_3) with lattice parameters varying linearly with composition. Aikinite also has a range of solid solution elongated along the lillianite–wittichenite join. The $CuBi_3S_5$ solid solution is extensive at 500°C, but diminishes rapidly with decreasing temperature. A new phase of composition 23.8 mole percent PbS, 64.8 mole percent Cu_2S, and 11.4 mole percent Bi_2S_3 is stable below 495° ± 3°C.

Experimental data obtained in this study suggest that galenobismutite ($PbBi_2S_4$) has a lower stability limit between 375° and 390°C.

Introduction

Phase relations in the system $PbS–Cu_2S–Bi_2S_3$ (Fig. 1) have not been investigated previously, except along the aikinite ($PbCuBiS_3$)–bismuthinite (Bi_2S_3) join where Springer (1971) reported complete solid solution above 300°C. Mineral phases in the series and their structural relationships below 300°C were discussed by Welin (1966), Moore (1967), Ohmasa and Nowacki (1970), Mumme *et al.* (1976), and Harris and Chen (1976).

Among the constituent binaries, several studies of the $Cu_2S–Bi_2S_3$ join have been made (recent ones are: Sugaki and Shima, 1971; Buhlmann, 1971; Godovidov *et al.*, 1972), but there is no agreement as to the stability of phases. Phases reported include (as $Cu_2S:Bi_2S_3$ ratio): 5:1, 3:1, 3:2, 1:1, 3:4, 3:5, 1:2, and 1:3.

The state of knowledge of stability relations along the $PbS–Bi_2S_3$ join is similar to that of the $Cu_2S–Bi_2S_3$ join. Phases reported include (as $PbS:Bi_2S_3$ ratio): 6:1, 3:1, 8:3, 5:2, 2:1, 3:2, 1:1, 1:2, and 1:3. Recently in this laboratory, galenobismutite ($PbBi_2S_4$) was determined to have a lower stability limit at about 400°C (Hoda and Chang, 1975). This is at variance with previous studies (Craig, 1967; Otto and Strunz, 1968; Salanci and Moh, 1969), hence further investigation was made in this study.

Craig and Kullerud (1968) investigated the system Cu–Pb–S between 1130° and 200°C and reported a new phase, $Cu_{14}Pb_2S_{9-x}$ ($0 < x < 0.15$), very close to the $PbS–Cu_2S$ join. Their diagram shows the absence of any phase intermediate between PbS and Cu_2S.

Experimental procedure

Reactants were prepared from finely powdered sulfur (Fisher, U.S.P.), bismuth (Baker analyzed reagent), copper (Mc/B reagent), and lead (Mc/B reagent). All have 99.99 percent or better purity. Experimental work was conducted using the sealed, evacuated glass capsules described by Kullerud and Yoder (1959), and experimental details have been reported elsewhere (Hoda and Chang, 1975). Lattice parameters were calculated to ±0.02Å using a least squares refinement program obtained from Dr. G. Chao, Carleton University, Ottawa, Canada. The (110) reflection of tungsten at 40.26° (a = 2.1648Å, Swanson and Tatge, 1953) was used as an internal standard.

Results and discussion

Phase relations in the system at 500°C are shown in Figure 2. A narrow liquid field exists, trending parallel with the $Cu_2S–PbCuBiS_3$ join, midway between 10 and 30 mole percent PbS and 55 and 80 mole percent Cu_2S. Complete solidification occurs at 492° ± 3°C.

The complete solid solution along the aikinite–bismuthinite join established by Springer (1971) was confirmed. In addition, aikinite shows a range of solid solution elongated along the lillian-

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ite–wittichenite join between 42 and 55 mole percent PbS. Members of the aikinite–bismuthinite series such as gladite, hammarite, krupkaite, and lindstromite were not identified at 500°C. The calculated lattice parameters are listed in Table 1. These show linear relations with composition in this series.

$CuBi_3S_5$ has a range of solid solution between 60 and 77 mole percent Bi_2S_3 in the binary system Cu_2S–Bi_2S_3, and can take a maximum of 26 mole percent PbS into solid solution in the ternary system, observations consistent with those of Godovikov *et al.* (1972) and Chen and Chang (1974). In contrast, Buhlmann (1971) reported two phases, $CuBi_3S_5$ (75 mole percent Bi_2S_3) and $Cu_3Bi_5S_9$ (a narrow range of solid solution between 59 and 63 mole percent Bi_2S_3). Interestingly, these two phases mark the limits of the solid solution found in the present study; thus, it is likely that Buhlmann mistook the end members to be separate phases. Due to lack of X-ray data for the

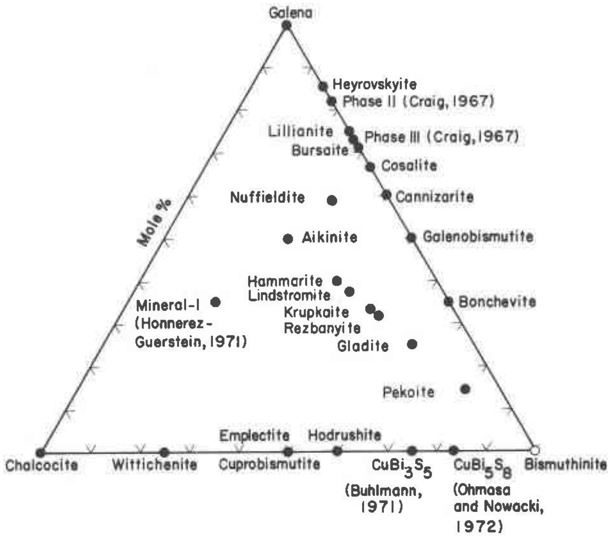

Fig. 1. Phases reported in the system PbS–Cu_2S–Bi_2S_3.

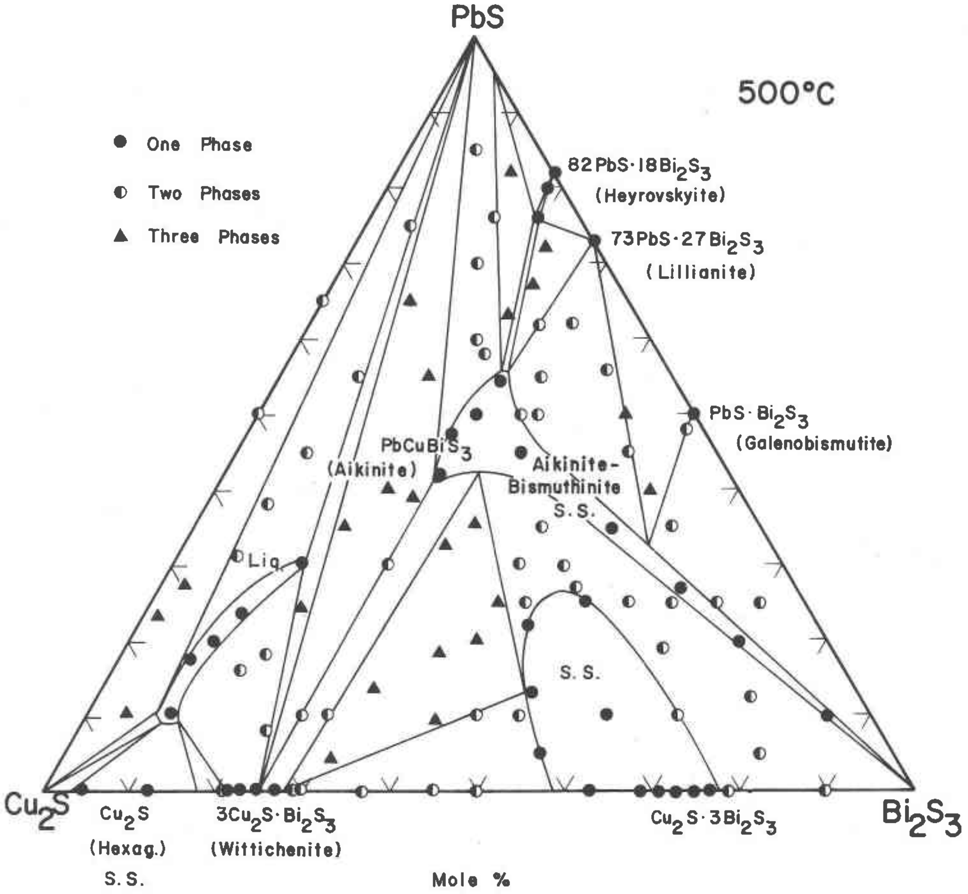

Fig. 2. Phase relations in the stystem PbS–Cu_2S–Bi_2S_3 at 500°C.

Table 1. Lattice parameters and compositions of mineral phases synthesized in the system $PbS-Cu_2S-Bi_2S_3$

Name	Composition mole%			Cryst. System	a	b in Å	c
	PbS	Cu_2S	Bi_2S_3				
Wittichenite	-	75.0	25.0	orthorhombic	7.60	10.39	6.70
Cuprobismutite	-	50.0	50.0	orthorhombic	17.53	3.90	15.37
$CuBi_3S_5$	-	25.0	75.0	orthorhombic	13.21	4.06	17.03
$CuBi_3S_5$ s.s.	-	37.0	63.0	orthorhombic	13.23	4.02	16.59
$CuBi_3S_5$ s.s.	5.0	40.0	55.0	orthorhombic	13.24	4.00	16.71
$CuBi_3S_5$ s.s.	10.0	30.0	60.0	orthorhombic	13.29	4.03	16.67
$CuBi_3S_5$ s.s.	22.0	33.0	45.0	orthorhombic	13.34	4.00	17.05
Aikinite	50.0	25.0	25.0	orthorhombic	11.34	11.60	4.02
Aikinite-bismuthinite s.s.	36.0	18.0	46.0	orthorhombic	11.28	11.54	4.02
Aikinite-bismuthinite s.s.	26.8	13.2	60.0	orthorhombic	11.24	11.43	4.01
Aikinite-bismuthinite s.s.	20.0	10.0	70.0	orthorhombic	11.22	11.42	4.01
Aikinite-bismuthinite s.s.	10.0	5.0	85.0	orthorhombic	11.19	11.35	4.00
Bismuthinite	-	-	100.0	orthorhombic	11.17	11.30	3.99

phase $Cu_3Bi_5S_9$, no verification could be made. Lattice parameters of $CuBi_3S_5$ and its solid solution were calculated on the basis of a pavonite structure (Table 1), because a complete solid solution was found between $CuBi_3S_5$ and $AgBi_3S_5$ (pavonite) by Chen and Chang (1974). Melting occurs at intermediate compositions between $CuBi_3B_5$ and aikinite at 595° ± 3°C before a complete solid solution series can form.

Wittichenite (Cu_3BiS_3), reported by almost all previous workers, was found to have a range of solid solution between 73 and 78 mole percent Cu_2S along the $Cu_2S-Bi_2S_3$ join. Lattice parameters of synthetic wittichenite (Table 1) agree well with those previously reported (Nuffield, 1947, $a = 7.66$, $b = 10.31$, and $c = 6.69$Å).

Heyrovskyite shows a small range of solid solution toward aikinite and accepts as much as 5 molepercent Cu_2S.

Phase relations at 400°C are shown in Figure 3. The instability of galenobismutite was reexamined in a series of samples heated between 420° and 360°C. Mixtures of Pb, Bi, and S, and synthetic galenobismutite prepared at 500°C, were used as starting materials (Table 2). Galenobismutite synthesized at 500°C remained unchanged down to 390°C, but showed some signs of decomposition to bismuthinite and lillianite at 375°C, as judged by X-ray powder diffraction data. Galenobismutite was synthesized from mixtures of Pb, Bi, and S at 390°C and above, but at lower temperatures these mixtures reacted to give lillianite and bismuthinite. Doubling the duration of runs described in Table 2 at 375°C did not complete the decomposition of galenobismutite. Experimental data suggest that galenobismutite has a lower stability limit between 375°C and 390°C. This is lower than previously reported (Hoda and Chang, 1975). It appears that runs of eight weeks were not sufficient to produce equilibrium assemblages containing galenobismutite at 400°C.

The compositional range of the $CuBi_3S_5$ solid solution is extremely sensitive to temperature change, as can be seen from a comparison of the 500° and 400°C isothermal sections. It narrows down to a range between 73 and 77 mole percent Bi_2S_3 along the $Cu_2S-Bi_2S_3$ join, and is limited between 0 and 17 mole percent PbS and 23 and 27 mole percent Cu_2S in the ternary system. Chen and Chang (1974) reported that at 300°C $CuBi_3S_5$ is stoichiometric. Considering the rapid reduction of its solid solution range with decreasing temperature, a lower stability limit of $CuBi_3S_5$ is indicated. Perhaps phase relationships at temperatures below 300°C become extremely complicated with the appearance of new phases such as hodrushite and emplectite.

Cuprobismutite ($CuBiS_2$), which has an upper limit of stability at 482°C (Buhlmann, 1972), shows a small range of solid solution along the $Cu_2S-Bi_2S_3$ join with a maximum of 2 mole percent excess Bi_2S_3 or Cu_2S. Cuprobismutite synthesized in this study has X-ray powder diffraction data similar to those given

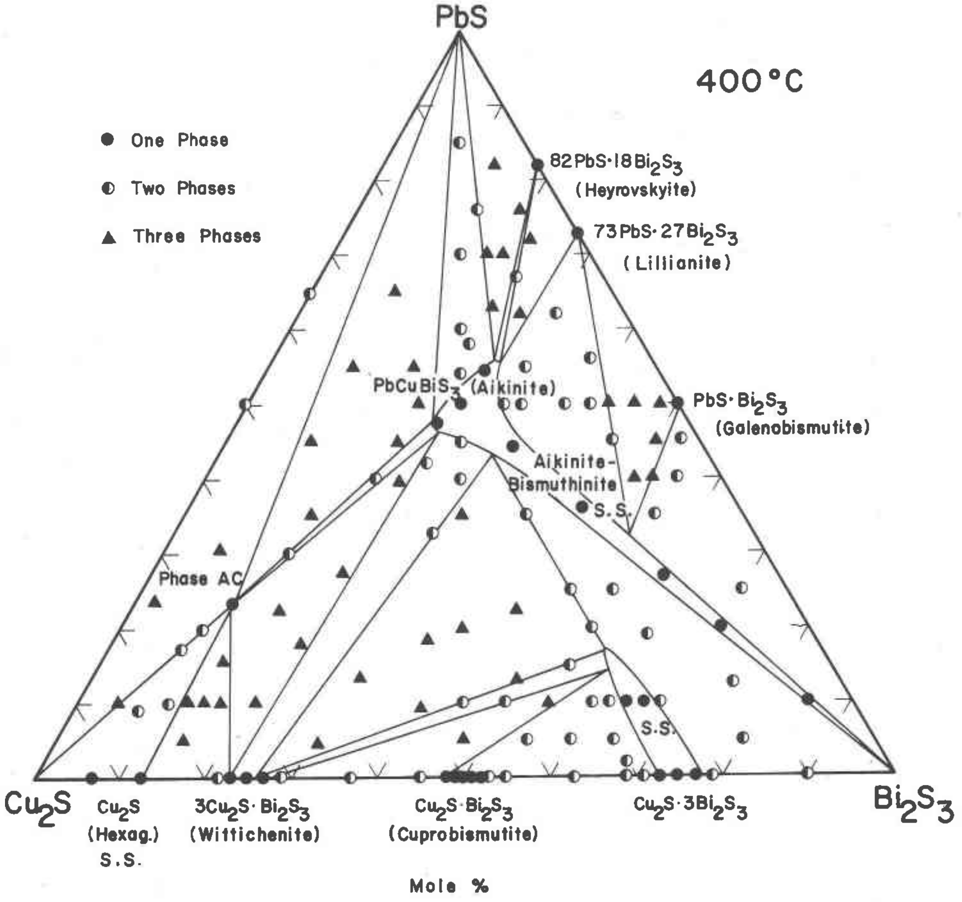

Fig. 3. Phase relations in the system $PbS–Cu_2S–Bi_2S_3$ at 400°C.

Table 2. Selected results of experimental runs made on the stability of galenobismutite. Starting materials used were: (a) mixture of Pb, Bi, and S in the ratio of 1:2:4 ($PbBi_2S_4$) and (b) galenobismutite synthesized at 500°C.

Starting Material	Temperature, °C.	Time, days	Products, Phases
(a)	420°±2°	180	galenobismutite
(b)	420°±2°	180	galenobismutite
(a)	400°±3°	180	galenobismutite
(b)	400°±3°	180	galenobismutite
(a)	390°±3°	180	galenobismutite
(b)	390°±3°	180	galenobismutite
(a)	375°±2°	180	lillianite + bismuthinite
(b)	375°±2°	180	galenobismutite + lillianite + bismuthinite
(a)	375°±3°	360	lillianite + bismuthinite
(b)	375°±3°	360	galenobismutite + lillianite + bismuthinite

by Nuffield (1952), but calculated lattice parameters (Table 1) show an orthorhombic symmetry rather than monoclinic. Attempts to synthesize cuprobismutite at the composition of $3Cu_2S \cdot 4Bi_2S_3$ reported by Ramdohr (1969) were not successful.

Wittichenite solid solutions do not appear very sensitive to temperature change, as least within the present range of investigation. Their range is reduced only by one mole percent between 500° and 400°C.

The most striking change at 400°C is the appearance of a new phase, designated as AC (between aikinite and chalcocite), of a composition of 23.8 mole percent PbS, 64.8 mole percent Cu_2S, and 11.4 mole percent Bi_2S_3 (or about $Pb_{2.4}Bi_{2.3}Cu_{12.9}S_{12.3}$). It may exist with wittichenite, chalcocite, aikinite, or galena. Phase AC melts congruently at 495° ± 3°C. X-ray powder diffraction data for phase AC are as follows: [*d*, Å (I/I_0)] 3.78(10), 3.54(4), 3.27(5), 3.15(5), 3.08(6), 2.93(7), 2.80(8), 2.77(3), 2.60(3), 2.55(2), 2.40(4), 2.31(3), 2.04(5), 1.997(6), 1.916(3), 1.888(2), 1.726(3), 1.665(3). Honnorez-Guerstein (1971) described tiny inclusions of Cu–Bi sulfosalts in galena from La-Leona mine, Argentina. One of the phases described, Mineral I (Fig. 1), represents a naturally occurring member of this aikinite–chalcocite join. Because of the minute size of the grains, X-ray diffraction data could not be obtained by Honnorez-Guerstein.

Acknowledgments

The authors wish to thank their colleague, James E. Bever, for reading the manuscript.

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Manuscript received, January 7, 1976; accepted for publication, August 3, 1976.