INVESTIGATIONS IN THE SYSTEMS PbS-Sb$_2$S$_3$-As$_2$S$_3$ and PbS-Bi$_2$S$_3$-As$_2$S$_3$

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ABSTRACT

Phases and phase relations in the systems PbS-Sb$_2$S$_3$-As$_2$S$_3$ and PbS-Bi$_2$S$_3$-As$_2$S$_3$ were studied at 400°C. using sealed glass capsule techniques. In the system PbS-Sb$_2$S$_3$-As$_2$S$_3$, three ternary phases, madocite, guettardite, and veenite, are stable. Veenite was also found to form a complete solid solution series with dufrenoysite. Jordanite extends its stability region into the ternary system, taking up 58 mole per cent Sb$_2$S$_3$ in its structure, and zinckenite has a solid solution range with a maximum of 30 mole per cent As$_2$S$_3$.

Two new phases, designated as Phase A and Phase B, were found in the system PbS-Bi$_2$S$_3$-As$_2$S$_3$. Phase A has a composition range between 27PbS.7(As$_{0.75}$Bi$_{0.25}$)$_2$S$_3$ and 27PbS.7(As$_{0.65}$Bi$_{0.35}$)$_2$S$_3$ and is in equilibrium with galena, jordanite, dufrenoysite, phase B, lillianite and bismuthinite. Phase B has a composition of 2PbS.(As$_{0.60}$Bi$_{0.40}$)$_2$S$_3$ and shows no solid solution range.

INTRODUCTION

Lead sulphosalt minerals, although they rarely form large ore bodies, are widespread in hydrothermal ores, and generally were deposited late in the paragenetic sequence. Recently, Jambor (1967a, 1967b, 1968) published an extensive study of the Madoc deposit, Ontario, Canada, and described a number of new lead sulphosalt minerals of antimony and arsenic. It was the purpose of this investigation to synthesize these minerals and to study their chemical compositions and phase relations in the systems PbS-Sb$_2$S$_3$-As$_2$S$_3$ and PbS-Bi$_2$S$_3$-As$_2$S$_3$.

EXPERIMENTAL PROCEDURES

Reagent grade metallic elements and sulphur were used for preparing starting compositions. Before each set of sample preparations, the metallic arsenic was fire-polished in the reducing portion of a gas flame, so that any oxide film present was sublimed. The reactants in desired proportions were thoroughly mixed by grinding very lightly in the dry state, and were then sealed in evacuated glass capsules, using a technique described in detail by Kullerud & Yoder (1959).

Heat treatment was in two stages: at 200°C for twenty-four hours to melt the sulphur slowly, and then at selected temperatures for sufficient periods of time for equilibration. Samples were reground after a week at the reaction temperature and then re-sealed under vacuum. The regrinding ensures that components are thoroughly mixed and are in complete contact with each other. In some cases pellets of the samples were made for experimentation. Temperatures were measured with chromel-alumel thermocouples and read with a Leeds and Northrup potentiometer. The readings were estimated to be accurate within ±5°C.

The samples were air-quenched to room temperature on completion of heat treatment. Phases were identified by using both x-ray diffraction and ore microscopy. Nickel filtered Cu$K\alpha$ radiation was used thoughout the study. In the measurement of d-spacings, the (110) line of metallic tungsten at $2\theta = 40.26°$ ($a_0 = 2.1648$Å, Swanson & Tatge 1953) was used as an internal standard.

THE SYSTEM *PbS-Sb$_2$S$_3$-As$_2$S$_3$*

Previous studies

Although several investigations were made in the binary systems PbS-As$_2$S$_3$ and PbS-Sb$_2$S$_3$, there are no reports of equilibrium studies in this system, except four experimental runs made by Roland (1968) to synthesize geocronite.

Rösch & Hellner (1959) carried out experimental syntheses of lead sulpharsenides by heating mixtures of galena and orpiment hydrothermally in the temperature range between 150° and 600°C. They reported the synthesis of six phases: sartorite, baumhauerite, rathite I and II, dufrenoysite, and jordanite.

Roland (1968) studied the composition and stability of jordanite in the system Pb-As-S, and found that jordanite is stable between 250°C and 549°C. Above the upper limit, jordanite melts to galena, liquid, and a sulphur-rich vapor phase. Below 250°C, it inverts to gratonite which is considered to be a low-temperature dimorphic form. Roland also found that confining pressures of up to 2 kbars do not measurably change the upper stability limit.

Kutoglu (1969) proposed a phase diagram for the system PbS-As$_2$S$_3$, which is reproduced in
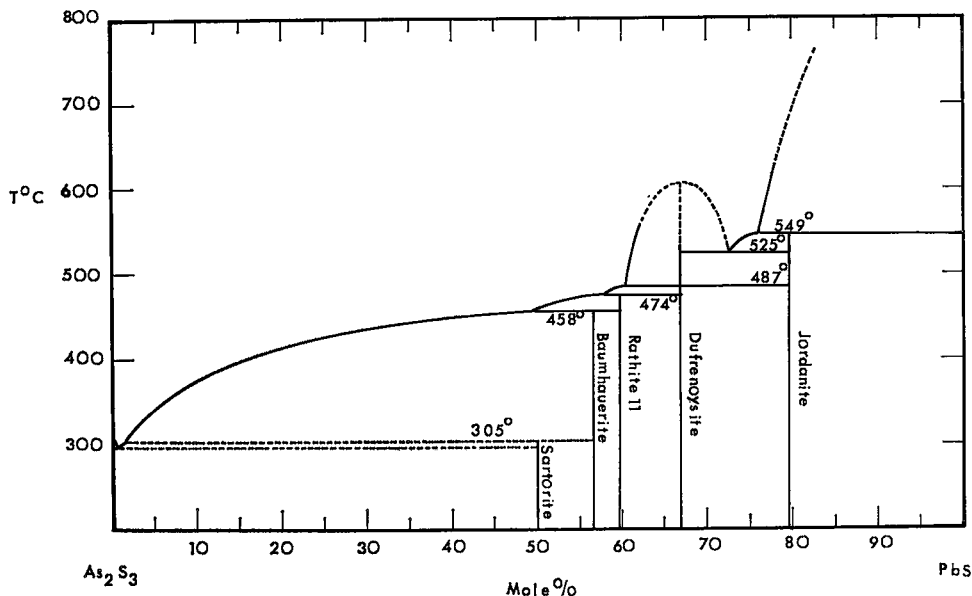
Fig. 1. Phase relations in the system PbS-As$_2$S$_3$ (after Kutoglu 1968).

Figure 1. He found five phases: sartorite, baumhauerite, rathite II, dufrenoysite, and jordanite, with melting points, respectively, at 305°, 458° ± 5°, 474 ± 4°, ~ 630°, and 549 ± 5°C.

A recent study was made of the system PbS-Sb$_2$S$_3$ by Craig, Chang, & Lees (1973), and they also summarized all published information pertinent to this system. Their diagram is shown in Figure 2. There are five phases: Phase I (3PbS.Sb$_2$S$_3$) stable between 642° and 605°C, boulangerite (5PbS.2Sb$_2$S$_3$) stable below 638°C, Phase II (3PbS.2Sb$_2$S$_3$) stable below 603°C robinsonite (PbS.5Sb$_2$S$_3$) stable between 582°C and 318°C, and zinckenite (PbS.Sb$_2$S$_3$) stable below 545°C. Each phase melts incongruently to the next more PbS-rich phase and a Sb$_2$S$_3$-enriched liquid.

Present work

Experimental work was performed at both 300°C and 400°C, but only runs made at 400°C for a period of nine weeks were used in the description of phase relations in the system. Reactions at 300°C were very sluggish and equilibrium could not be attained even after samples were treated for a period of six months. The major features of the phase relations are presented in Figure 3. A vapor phase was always present with the solid assemblages.

Jordanite was synthesized with a composition of 27PbS.7As$_2$S$_3$ (79.41 mole % PbS and 20.58 mole % As$_2$S$_3$). Compositions of 80.00 mole %

PbS and 20.00 mole % As$_2$S$_3$, and, 78.00 mole % PbS and 22.00 mole % As$_2$S$_3$ produced two-phase assemblages consisting of, respectively, jordanite + galena and jordanite + dufrenoysite. This suggests that the range of solid solution of jordanite in the binary system PbS-As$_2$S$_3$ is very limited. In the ternary system, jordanite can take a maxi-

TABLE 1. LATTICE PARAMETERS OF SULPHOSALTS AND SOLID SOLUTIONS

|	a(Å)	b(Å)	c(Å)	β	Reference
Jordanite	8.86	31.93	8.48	117° 26'	Palache *et al.* 1938
Jordanite	8.90*	31.71	8.42	118° 18'	Peacock & Berry 1940
Jordanite	8.96†	31.92	8.45	117° 10'	Nowacki *et al.* 1961
Jordanite	8.92	31.88	8.457	117° 43'	Jambor 1968
Jordanite	8.931	31.934	8.453	118° 37'	This study
--with 25 mole % Sb$_2$S$_3$	9.030	32.056	8.525	119° 03'	This study
--with 50 mole % Sb$_2$S$_3$	9.116	32.147	8.622	119° 51'	This study
Dufrenoysite	8.41	25.85	7.88	90° 30'	Berry & Thompson 1961
Dufrenoysite	8.37	25.74	7.90	90° 21'	Marumo & Nowacki 1967
Dufrenoysite	8.380	25.735	7.881	90°	This study
--with 9 mole % Sb$_2$S$_3$	8.426	25.781	7.928	90°	This study
--with 21 mole % Sb$_2$S$_3$	8.441	25.965	7.952	90°	This study
--with 45 mole % Sb$_2$S$_3$	8.470	26.170	7.979	90°	This study
Veenite	8.44	26.2	7.9	90°	Jambor 1967a
Zinckenite	44.15		8.62		Vaux & Bannister 1938
Zinckenite	44.4		8.65		Jambor 1968
Zinckenite	44.361		8.640		This study
--with 24 mole % As$_2$S$_3$	44.131		8.636		This study
--with 25 mole % As$_2$S$_3$	44.1		8.61		Jambor 1968
--with 30 mole % As$_2$S$_3$	44.064		8.626		This study

* a, b, c all ±0.03
† a ± 0.04, b ± 0.01, c ± 0.03
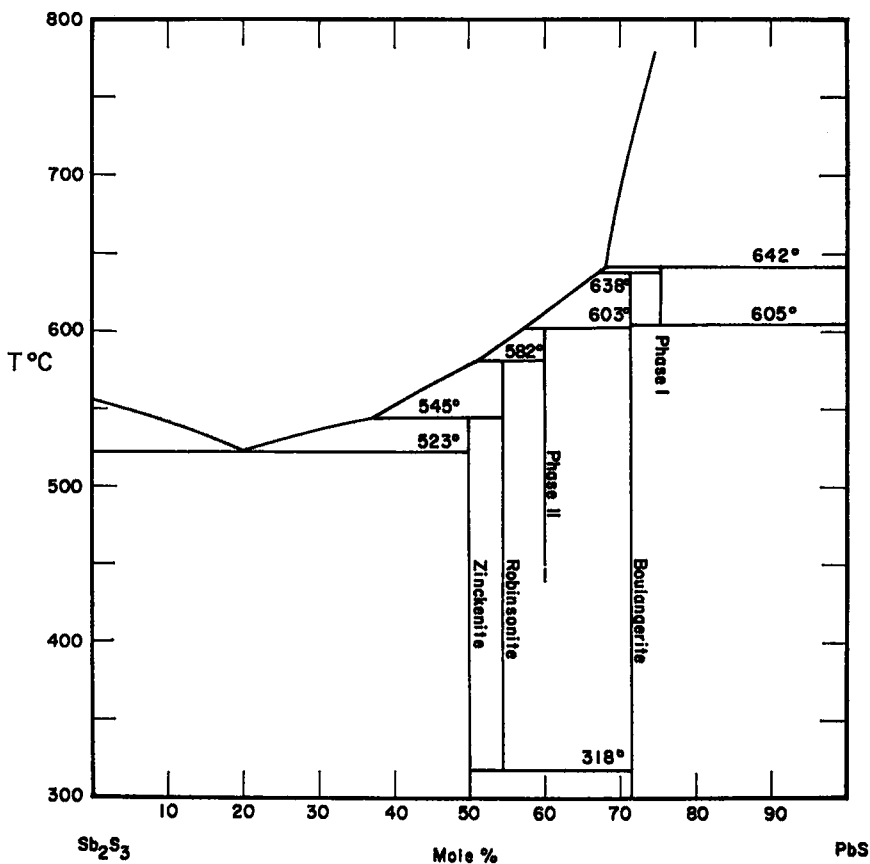
FIG. 2. Phase relations in the system PbS-Sb$_2$S$_3$ (after Craig *et al.* 1973).

mum of 58 mole per cent Sb$_2$S$_3$ into its structure, and the solid solution forms equilibrium assemblages with galena, dufrenoysite and madocite. In nature, Sb-bearing jordanite is known as geocronite. Jambor (1968) found that these two minerals have very similar x-ray diffraction patterns. A comparison of x-ray powder diffraction data from the synthesized jordanite and jordanite solid solution, and a natural geocronite from the Smithsonian Institute (No. 106120) confirms Jambor's conclusion. The lattice parameters of synthetic jordanite and its solid solution in the ternary system were calculated using the reflections (0.10.0), (021), (240), and (142). The results are listed in Table 1 along with previously-reported values. An increase in magnitude of the lattice parameters with increasing amounts of Sb$_2$S$_3$ in solid solution is shown.

As with jordanite, the stability region of dufrenoysite extends into the ternary system with an extensive solid solution. It is found that dufrenoysite with a composition of 2PbS . As$_2$S$_3$ can have 45 mole per cent of its As$_2$S$_3$ replaced

by Sb$_2$S$_3$. The Sb-rich end member of this solid solution series is equivalent to veenite found by Jambor (1967a) in the sulphosalt deposit at Madoc, Ontario. Lattice parameters of the dufrenoysite solid solution series were calculated using the reflections (022), (400), and (080). These results, and previously-reported values, are listed in Table 1.

Two other lead sulpharsenides, baumhauerite and rathite, were synthesized from compositions of 60.0 mole per cent PbS and 58.1 mole per cent PbS, respectively. Neither of the x-ray powder diffraction patterns of these phases is very sharp, and attempts to promote crystallinity of these phases by prolonged treatment at 400°C failed. Jambor (1968) also reported poor x-ray powder diffraction results for these two phases, which he obtained in his synthesis. Rathite produced in this study was identified as rathite II using Graeser's data (Graeser 1965).

Sartorite melts below 400°C in the binary system PbS-As$_2$S$_3$. With the substitution of antimony for arsenic, however, it becomes stabilized,

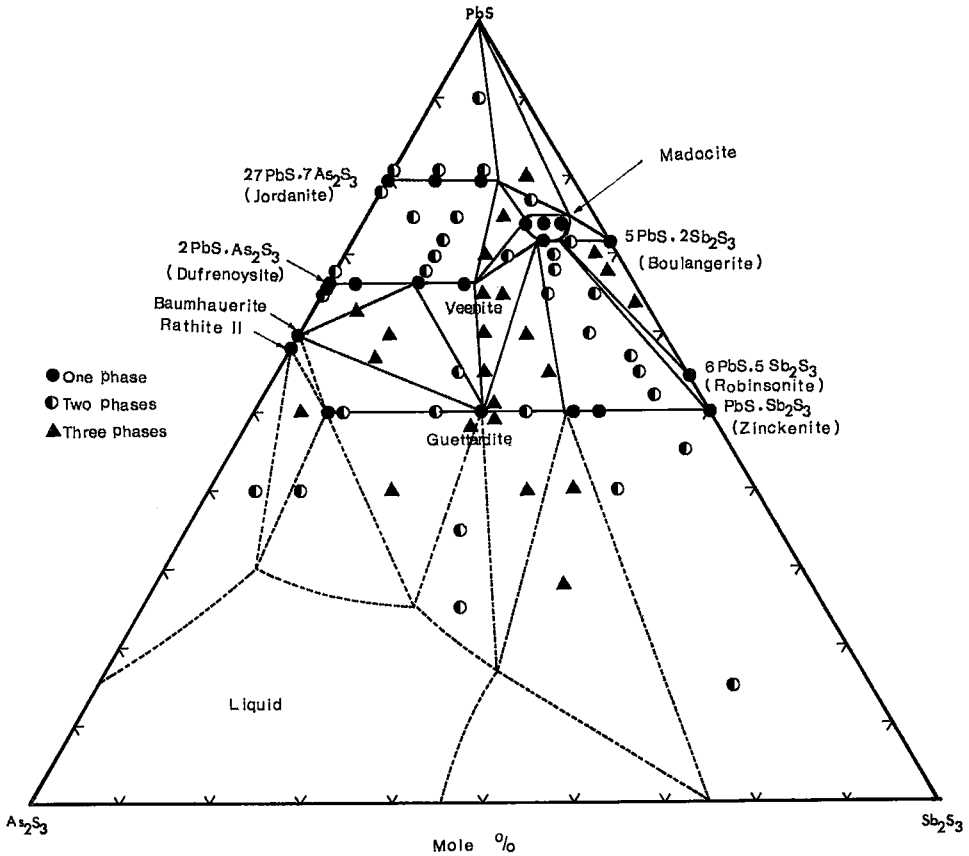FIG. 3. Phase relations in the system $PbS-Sb_2S_3-As_2S_3$ at 400°C.

thus existing in the ternary system with an approximate composition of $PbS.(As_{0.84}Sb_{0.16})_2S_3$.

Three lead sulphantimonides were observed to form at 400°C. Boulangerite and robinsonite show very limited association with other phases in the system. With As_2S_3 content over 5 mole per cent, both boulangerite and robinsonite disappear from the system. Zinckenite has a range of solid solution in the ternary system from $PbS.Sb_2S_3$ to $PbS.(Sb_{0.70}As_{0.30})_2S_3$, and forms equilibrium assemblages with liquid, stibnite, robinsonite, madocite, and guettardite. Lattice parameters of the zinckenite solid solution series obtained in this study and those reported by Vaux & Bannister (1938) and Jambor (1968) are listed in Table 1. A decrease in dimensions with increased amounts of As_2S_3 was observed.

Two ternary phases, madocite and guettardite (Jambor 1967a, 1967b), were observed to form in the system. Madocite is stable in the composition range between $3PbS.(As,Sb)_2S_3$ and $5PbS.2(As,Sb)_2S_3$ with As/Sb ratio varying, respectively, from 0.30/0.70 to 0.12/0.88 and from 0.30/0.70 to 0.17/0.83. Madocite forms equili-

brium assemblages with all major solid phases at 400°C. Guettardite was synthesized with a composition of $PbS.(As_{0.50}Sb_{0.50})_2S_3$, in close agreement with the composition reported by Jambor (1967b).

Compositions in the As_2S_3-rich region produced either liquid or liquid + solid assemblages at 400°C. On the basis of microscopic examination of polished sections, tentative liquid-solid relationships as shown in Figure 3 were determined.

Four minerals with compositions in this system reported by Jambor (1967b) from Madoc have not been synthesized in the present study. They are playfairite, $16PbS.9(Sb,As)_2S_3$ with Sb:As = 8:1, sterryite, $12PbS.(Sb,As)_2S_3$ with Sb:As = 12:5, sorbyite, $17PbS.11(Sb,As)_2S_3$ with Sb:As = 3:1, and twinnite, $PbS.(Sb,As)_2S_3$ with Sb:As = 3:2.

THE SYSTEM $PbS-Bi_2S_3-As_2S_3$

Previous studies

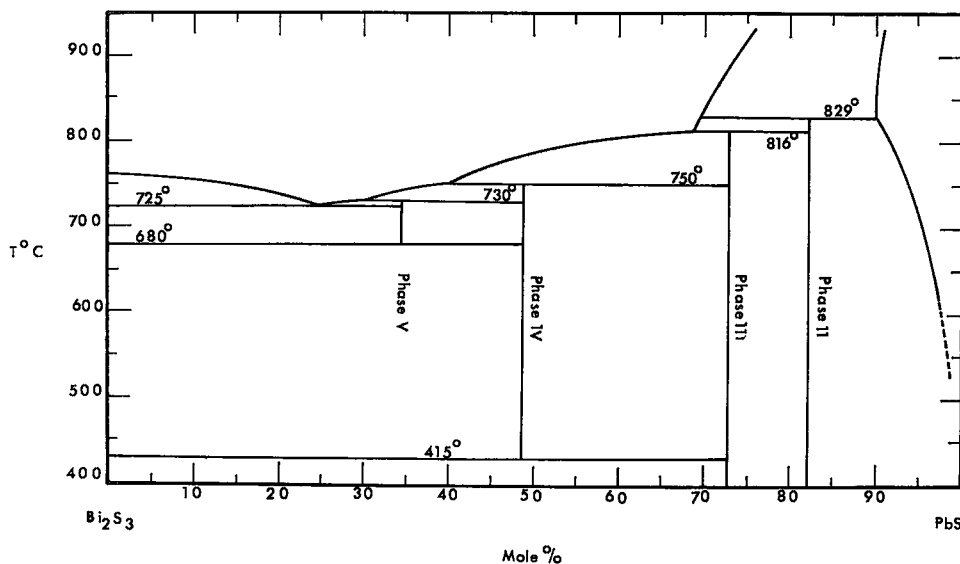As with the preceding system, no studies have been reported for this system, although the related

FIG. 4. Phase relations in the system PbS-Bi₂S₃ (after Van Hook 1960, Craig 1967, and modified after Hoda & Chang 1972).

binary system PbS-Bi₂S₃ has been investigated extensively. Schenck *et al.* (1939) reported the synthesis of beegerite (6PbS . Bi₂S₃) and lillianite (3PbS . Bi₂S₃), and Graham (1950) prepared cosalite (2PbS . Bi₂S₃), galenobismutite (PbS . Bi₂S₃), cannizzarite (6PbS . 5Bi₂S₃), and weibullite (4PbS . 3Bi₂S₃) in the system. The first equilibrium study was by Van Hook (1960). He obtained three phases and designated them as Phase II, III, and IV with approximate 5:1, 8:3, and 1:1 PbS:Bi₂S₃ ratios. Craig (1967) confirmed Van Hook's findings and added a new phase, V, stable above 680°C, with the composition 65PbS . 35Bi₂S₃. Further confirmation of the formation of phases II through V was made by Salanci & Moh (1969). These phases, respectively, correspond with heyrovskyite, lillianite, and galenobismutite. No natural equivalent to phase V is known. Phase relations established by Van Hook and Craig are illustrated in Figure 4.

In a recent study, Hoda & Chang (1972) demonstrated that there is a lower stability limit for galenobismutite at 415°C, below which it decomposes to lillianite and bismuthinite.

Present study

As in the system PbS-Sb₂S₃-As₂S₃ equilibrium could not be achieved at 300°C after a period of six months. Only runs made at 400°C were used to construct phase relations in the system, as shown in Figure 5.

Two new ternary phases were found in the system PbS-Bi₂S₃-As₂S₃, and are designated as

"Phase A" and "Phase B". Phase A is stable in the composition range between 27PbS . 7(As₀.₇₅Bi₀.₂₅)₂S₃ and 27PbS . 7(As₀.₆₅Bi₀.₃₅)₂S₃, and forms equilibrium assemblages with all major solid phases in the system at 400°C. Phase B has a composition of 2PbS . (As₀.₆₀Bi₀.₄₀)₂S₃, and is in equilibrium with phase A, dufrenoysite, and (Bi,As)₂S₃ solid solution. The composition of phase A is shown to be closely related to that of jordanite, whereas phase B has the same PbS/(As,Bi)₂S₃ ratio as that of the dufrenoysite-veenite series. X-ray powder diffraction data of phase A and phase B, as listed in Table 2, also show some similarities to those of jordanite and veenite, respectively. Thus, possible extensive solid solutions may develop, at some higher temperatures, between phase A and jordanite and between phase B and dufrenoysite. The lack of such solid solutions in this system at 400°C as compared with those observed in the preceding system is apparently due to the larger difference in ionic size between bismuth and arsenic than that between antimony and arsenic.

Sartorite is also stabilized by substitution of bismuth for arsenic in the system. The stabilized phase has an approximate composition of PbS . (As₀.₈₆Bi₀.₁₄)₂S₃.

In this system, melting was also observed in the As₂S₃-rich portion. A tentative solid-liquid relationship is shown by dashed lines in Figure 5 based on microscopic examination of polished sections.
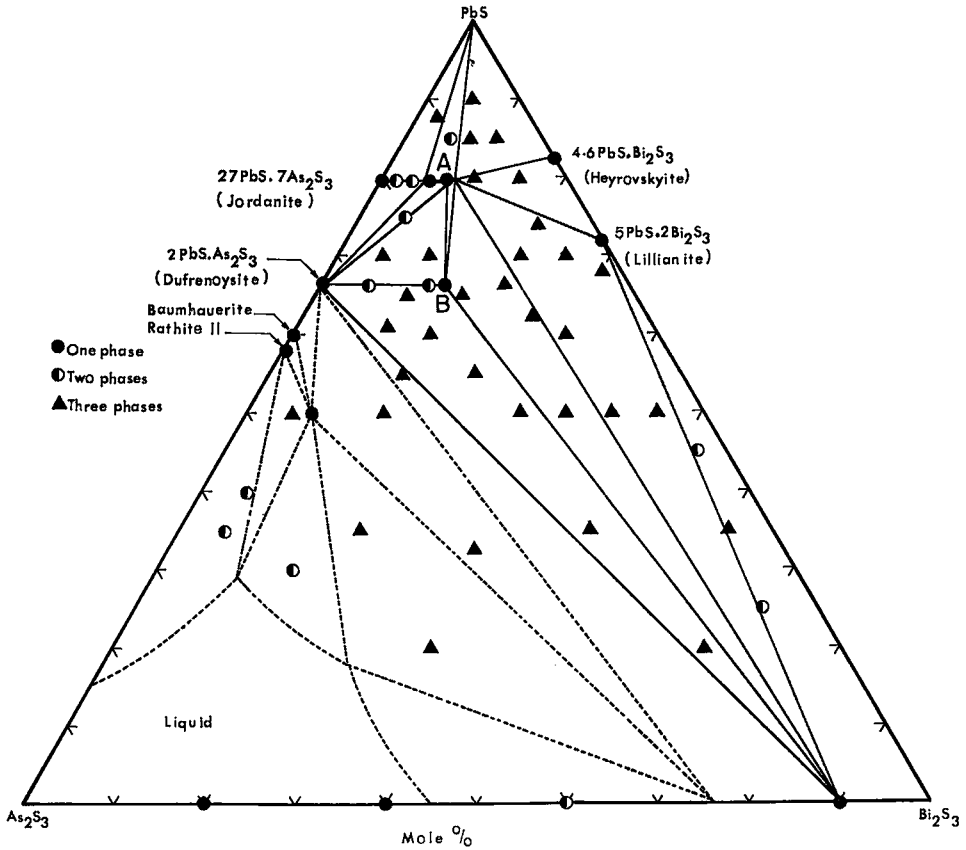
FIG. 5. Phase relations in the system PbS-Bi$_2$S$_3$-As$_2$S$_3$ at 400°C.

TABLE 2.   X-RAY POWDER DIFFRACTION DATA FOR
PHASE A AND PHASE B

	PHASE A				PHASE B		
d$\overset{o}{A}$	I/I$_o$	d$\overset{o}{A}$	I/I$_o$	d$\overset{o}{A}$	I/I$_o$	d$\overset{o}{A}$	I/I$_o$
3.633	55	1.8180	55	3.934	10	2.136	8
3.550	23	1.7780	23	3.850	10	2.071	25
3.477	70	1.7430	8	3.738	25	2.027	6
3.388	13	1.7307	12	3.633	13	2.012	10
3.277	100	1.6808	6	3.548	50	1.9020	25
3.068	100	1.6372	10	3.493	13	1.8806	8
2.978	17	1.6130	4	3.293	100	1.8625	10
2.858	70	1.5325	6	3.121	15	1.8597	40
2.740	13	1.4796	10	3.079	13	1.7712	10
2.623	13	1.4260	12	3.016	75	1.7529	13
2.517	10	1.4154	12	2.940	13	1.7460	10
2.414	6	1.3973	12	2.894	15	1.7098	5
2.356	4	1.3786	12	2.849	10	1.6709	5
2.309	4	1.3627	8	2.780	10	1.6474	8
2.190	70	1.3576	8	2.741	30	1.6234	6
2.155	23	1.3308	8	2.652	8	1.5505	6
2.103	8	1.3099	15	2.611	8	1.4357	10
2.014	30	1.3068	12	2.585	8	1.4041	8
1.8879	23	1.2552	10	2.269	15	1.3822	8
1.8697	15			2.196	40	1.3195	13

SUMMARY AND CONCLUSIONS

Known lead sulphosalts synthesized in the present study were: rathite II, baumhauerite, dufrenoysite and jordanite in the system PbS-As$_2$S$_3$; zinckenite, robinsonite and boulangerite in the system PbS-Sb$_2$S$_3$; heyrovskyite and lillianite in the system PbS-Bi$_2$S$_3$; and geocronite, madocite, veenite and guettardite in the system PbS-Sb$_2$S$_3$-As$_2$S$_3$.

Three extensive solid solution series exist in the system PbS-Sb$_2$S$_3$-As$_2$S$_3$: the jordanite-geocronite series between 27PbS.7As$_2$S$_3$ and 27PbS.7(As$_{0.45}$Sb$_{0.55}$)$_2$S$_3$, the dufrenoysite-veenite series between 2PbS.As$_2$S$_3$ and 2PbS.(As$_{0.55}$Sb$_{0.45}$)$_2$S$_3$, and the zinckenite series between PbS.Sb$_2$S$_3$ and PbS.(Sb$_{0.70}$As$_{0.30}$)$_2$S$_3$.

Two new ternary phases were synthesized in the system PbS-Bi$_2$S$_3$-As$_2$S$_3$, and are designated as "Phase A" and "Phase B". Phase A has compositions ranging from 27PbS.7(As$_{0.75}$Bi$_{0.25}$)$_2$S$_3$ to 27PbS.7(As$_{0.65}$Bi$_{0.35}$)$_2$S$_3$, whereas phase B with a composition of 2PbS.(As$_{0.60}$Bi$_{0.40}$)$_2$S$_3$ shows no solid solution range.

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