Canadian Mineralogist
Vol. 15, pp. 374-379 (1977)

PHASE RELATIONS IN THE SYSTEMS $PbS–Fe_{1-x}S–Sb_2S_3$ AND $PbS–Fe_{1-x}S–Bi_2S_3$

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ABSTRACT

Phase relations in the systems $PbS–Fe_{1-x}S–Sb_2S_3$ and $PbS–Fe_{1-x}S–Bi_2S_3$ were studied in the temperature range 400 to 500°C, with melting points determined to 750°C, using sealed, evacuated glass capsules. In the system $PbS–Fe_{1-x}S–Sb_2S_3$, jamesonite was synthesized from its reported composition ($Pb_8Fe_2Sb_{12}S_{28}$) and has a range of solid solution elongated toward Sb_2S_3 at 500°C. Jamesonite forms equilibrium assemblages with zinkenite, robinsonite, $Pb_2Sb_2S_5$, boulangerite, berthierite, pyrrhotite, and stibnite, but not with galena.

The introduction of iron into lead sulfbismuthides produced no ternary phases in the system $PbS–Fe_{1-x}S–Bi_2S_3$. Lead sulfbismuthides stable in the temperature range of this study are galenobismutite, lillianite, and heyrovskyite. Each forms binary and ternary equilibrium assemblages with pyrrhotite.

SOMMAIRE

Les relations de phases des systèmes $PbS–Fe_{1-x}S–Sb_2S_3$ et $PbS-Fe_{1-x}S-Bi_2S_3$ sont étudiées de 400 à 500°C, avec points de fusion déterminés jusqu'à 750°C, à l'aide de capsules de verre scellées sous vide. Dans le système $PbS–Fe_{1-x}S–Sb_2S_3$, la jamesonite a été synthétisée à partir de sa composition ($Pb_8Fe_2Sb_{12}S_{28}$). Son domaine de solution solide s'allonge vers Sb_2S_3 à 500°C. La jamesonite forme des assemblages en équilibre avec la zinkénite, la robinsonite, $Pb_2Sb_2S_5$, la boulangérite, la berthiérite, la pyrrhotite et la stibine, mais non avec la galène.

L'introduction de fer dans les sulfobismuthures de plomb n'a pas produit de phase ternaire dans le système $PbS–Fe_{1-x}S–Bi_2S_3$. Les sulfobismuthures de plomb stables dans le domaine de température des expériences sont la galénobismuthine, la lillianite et l'heyrovskyite. Chacun de ces minéraux forme des assemblages binaires et ternaires en équilibre avec la pyrrhotite.

(Traduit par la Rédaction)

INTRODUCTION

Iron is commonly present in lead sulfosalt minerals. In some minerals, it takes well-defined structural positions, and thus is essential for the formation of such sulfosalts. The best known example is jamesonite, a ferrous lead sulfantimonide (Palache *et al.* 1944). Structural determinations made by Niizeki & Buerger (1957) showed that Fe atoms in jamesonite occupy distinct structural positions. They are coordinated by six sulfur atoms in distorted octahedra unlike the PbS_7 and PbS_8 polyhedra. Iron and lead atoms both serve to link Sb_6S_{14} groups. Equilibrium studies in the system $PbS–Sb_2S_3$ (Craig *et al.* 1973; Garvin 1973) show that there is no iron-free jamesonite. Iron is present in many analyses of lead sulfbismuthide minerals, but jamesonite-like phases seem to be rare. For example, iron was included by Nuffield (1948) in the formula of kobellite, but subsequent microprobe analyses by Harris *et al.* (1968) showed that this element is not essential. However, an exception is sakharovite, which is the bismuth analogue of jamesonite and has Bi:Sb close to 1:1 (*Amer. Mineral.* 45, p. 1134).

The purpose of this investigation was to study the effect of iron on the formation of lead sulfantimonides and sulfbismuthides with special reference to jamesonite.

EXPERIMENTAL PROCEDURE

Starting compositions were prepared from reagent-grade elemental lead, antimony, bismuth, iron, and sulfur; all have 99.99% or better purity as specified by suppliers' analyses. Synthesis and heat treatment were made in muffle furnaces using the conventional sealed, evacuated glass capsule technique (Kullerud & Yoder 1959). Generally, 50 days were used for equilibration at 500°C and 90 days at temperatures below 500°C. X-ray powder diffraction and reflected-light microscopy were used for phase identification, and compositions of selected samples were determined by electron probe analysis. For measuring *d*-values, the (110) reflection of tungsten at $2\theta=40.26°$ was used as an internal standard, and cell dimensions ±0.02Å were computed by a least-squares refinement program (Chao, Carleton University, Ottawa).

THE SYSTEM $PbS–Fe_{1-x}S–Sb_2S_3$

Phase relations involving galena, stibnite, and pyrrhotite in the system lead-antimony-iron-sulfur at 500°C are projected, as shown in Figure 1, onto a $PbS–Fe_{1-x}S–Sb_2S_3$ plane. One run was made along the join $PbS–Fe_{1-x}S$, and an assemblage of galena and pyrrhotite was obtained, corresponding with Brett & Kullerud's result (1967). Along the join $Fe_{1-x}S–Sb_2S_3$, berthierite was prepared with a composition of $Fe_{0.98}Sb_2S_4$ as determined by probe analysis. This phase was synthesized by Barton (1971). A comparison of X-ray powder-diffraction data obtained in the present study with Barton's shows good correlation, except for several reflections of weak to medium intensities. The following diffraction lines were observed by Barton but were not registered in the present study: 330(9), 141(17), 060(4), 241(8), 331(19), 160(7), 411(23), and 520(17). The cell dimensions calculated are a 11.46, b 14.10, c 3.74Å, in moderately good agreement with a 11.46, b 14.15, c 3.77Å obtained by Buerger & Hahn (1955).

Phases and phase relations along the join $PbS–Sb_2S_3$ established in the present study correspond well with previous investigations of Garvin

TABLE 1. MICROPROBE ANALYSIS OF SYNTHESIZED JAMESONITE*

Sample No.	Probe Data Pb	Sb	Fe	S	Total	Suggested Formula
0	40.15	35.39	2.71	21.75	100.00	$Pb_{8.00}Fe_{2.00}Sb_{12.00}S_{28}$
27	40.02	35.47	2.65	21.56	99.70	$Pb_{8.04}Fe_{1.96}Sb_{12.13}S_{28}$
26	41.69	34.40	2.99	21.11	100.19	$Pb_{8.56}Fe_{2.28}Sb_{12.02}S_{28}$
25	41.80	34.00	2.60	21.50	99.90	$Pb_{8.42}Fe_{1.94}Sb_{11.66}S_{28}$
9	40.99	33.42	3.83	21.75	99.99	$Pb_{8.16}Fe_{2.83}Sb_{11.33}S_{28}$

Sample 0 - jamesonite, theoretical composition
Samples 27 and 26 - jamesonite single phase
Sample 25 - jamesonite in association with boulangerite and pyrrhotite
Sample 9 - jamesonite in association with berthierite and pyrrhotite

* Standards used were pyrite, galena, stibnite and bismuthinite. The compositions of these standards were checked against elemental Fe, Pb, Sb and Bi. The ZAF program was used for correction.

TABLE 2. CELL DIMENSIONS OF JAMESONITE

		a(Å)	b(Å)	c(Å)	β
Berry (1940a)		15.71*	19.05*	4.04*	91°48'
Niizeki & Buerger (1957)		15.57	18.98	4.03	91°48'
Present study	(1)	15.75	19.17	3.98	91°22'
	(2)	15.78	18.92	4.02	92°44'
	(3)	16.27	18.73	3.99	92°46'

*Converted to Å by the conventional factor, 1.00202

(1) jamesonite, $Pb_{8.04}Fe_{1.96}Sb_{12.13}S_{28}$, synthesized from the reported composition.
(2) jamesonite, $Pb_{7.00}Fe_{2.33}Sb_{12.44}S_{28}$, solid solution.
(3) jamesonite, $Pb_{5.74}Fe_{2.15}Sb_{12.92}S_{28}$, solid solution.

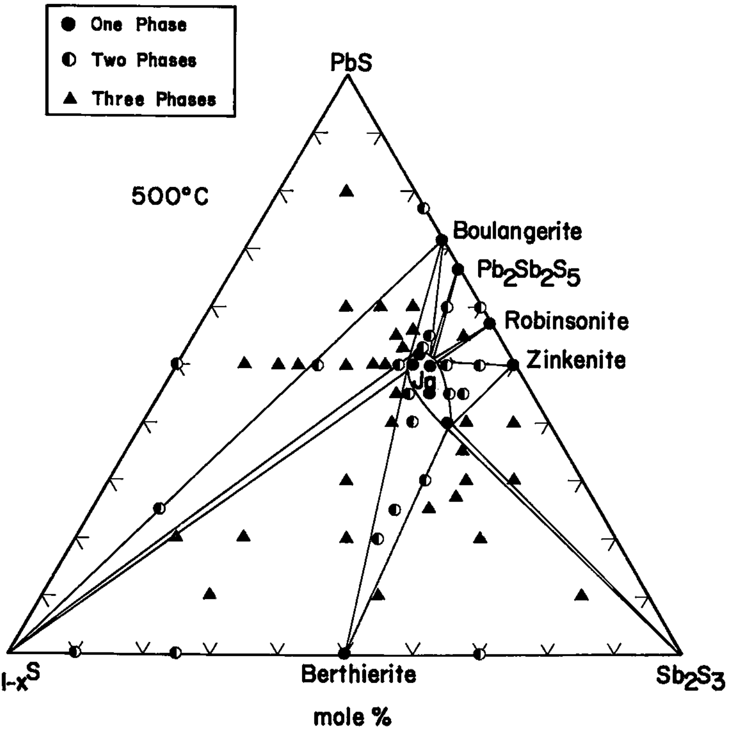

FIG. 1. Phase relations in the system $PbS–Fe_{1-x}S–Sb_2S_3$ at 500°C. Jamesonite is represented by "Ja". The zinkenite was synthesized from the composition of 50 mole % PbS and 50 mole % Sb_2S_3.

TABLE 3. $d_{(102)}$ OF PYRRHOTITE IN THE SYSTEM $PbS\text{-}Fe_{1-x}S\text{-}Sb_2S_3$

Sample No.	Phase Assemblage	$2\theta_{(102)}$	$d_{(102)}$	N_{FeS}
1	pyrrhotite+ berthierite	43.64	2.0723	0.957
2	pyrrhotite+ berthierite	43.64	2.0723	0.957
8	pyrrhotite+ jamesonite s.s	43.66	2.0714	0.956
9	pyrrhotite+ berthierite+ jamesonite s.s	43.60	2.0741	0.961
13	pyrrhotite+ boulangerite	43.64	2.0723	0.957
21	pyrrhotite+ boulangerite	43.64	2.0723	0.957
22	pyrrhotite+ boulangerite+ galena	43.66	2.0714	0.956
33	pyrrhotite+ boulangerite+ galena	43.66	2.0714	0.956

TABLE 4. $d_{(102)}$ OF PYRRHOTITE IN THE SYSTEM $PbS\text{-}Fe_{1-x}S\text{-}Bi_2S_3$

Sample No.	Phase Assemblage	$2\theta_{(102)}$	$d_{(102)}$	N_{FeS}
1	pyrrhotite+ bismuthinite	43.72	2.0687	0.951
2	pyrrhotite+ bismuthinite	43.70	2.0696	0.952
3	pyrrhotite+ galenobismutite	43.76	2.0669	0.947
7	pyrrhotite+ galenobismutite	43.76	2.0669	0.947
8	pyrrhotite+ bismuthinite+ galenobismutite	43.74	2.0678	0.949
9	pyrrhotite+ bismuthinite+ galenobismutite	43.74	2.0678	0.949
15	pyrrhotite+ galena	43.76	2.0669	0.947
19	pyrrhotite+ galenobismutite+ lillianite	43.76	2.0669	0.947
28	pyrrhotite+ galena+ heyrovskyite	43.72	2.0687	0.951

(1973), Craig *et al.* (1973), and Hoda & Chang (1975). Robinsonite prepared in this study was analyzed by J. L. Jambor and was found to have a composition similar to that suggested recently by Jambor & Plant (1975). Boulangerite, Garvin's phase IV, and zinkenite were synthesized from $Pb_5Sb_{14}S_{11}$, $Pb_2Sb_2S_5$, and $PbSb_2S_4$, respectively.

Jamesonite was synthesized from its reported composition, $Pb_8Fe_2Sb_{12}S_{28}$ (Berry 1940a), and has a range of solid solution elongated toward Sb_2S_3 at 500°C. Jamesonite forms equilibrium assemblages with all phases on the related joins except galena. Chemical compositions of jamesonite synthesized from the reported composition, and jamesonite solid solutions occurring in assemblages with pyrrhotite, were determined by probe analyses of selected samples and are listed in Table 1. The results, based on 28 sulfur atoms for comparison with theoretical values, show that jamesonite in equilibrium with nonstoichiometric pyrrhotite has compositions close to the ideal formula. Cell dimensions of jamesonite solid solutions are listed in Table 2. Parajamesonite, which may be an orthorhombic dimorph of jamesonite but is not well-established, was not found in this study.

Pyrrhotite, as shown in Figure 1, exists in equilibrium with galena, boulangerite, jamesonite, and berthierite in binary and ternary assemblages. In X-ray powder patterns obtained at room temperature, all pyrrhotite showed the NiAs structure (1*C* type). Solid solution in pyrrhotite of both Pb (Brett & Kullerud 1967), and Sb (Barton 1971), are known to be very limited. The $d_{(102)}$ values of pyrrhotite from various assemblages were used to determine its composition using the data of Toulmin & Barton (1964), and are listed in Table 3. The results indicate that compositions of pyrrhotite range from 0.956 to 0.961 in terms of mol fraction of FeS. The corresponding log $f(S_2)$ values, calculated from Toulmin & Barton's equation, are −13.64 and −13.96 atm.

Phase relations at 450°C differ little from those at 500°C, except for the reduction in size of jamesonite solid solution. At this temperature, the most Sb_2S_3-rich jamesonite has a composition of 40 mol Sb_2S_3, as compared with jamesonite with a maximum of 46 mole % Sb_2S_3 at 500°C. At 400°C, jamesonite solid solution is further reduced, and is limited within 1 or 2 mole % around the formula composition. This composition has a congruent melting point at 545±5°C.

In the temperature range of this study, determination of phase relations in the Sb_2S_3-rich portion was made with difficulty because of the sluggish rate of reaction. Prolonged periods of treatment, in some cases to 210 days, were used.

The system $PbS\text{–}Fe_{1-x}S\text{–}Bi_2S_3$

Phase relations of galena, bismuthinite, and pyrrhotite in the system lead-bismuth-iron-sulfur at 500°C are projected, as shown in Figure 2, onto a $PbS\text{–}Fe_{1-x}S\text{–}Bi_2S_3$ plane. No ferrous lead sulfbismuthide was found. Phases synthesized from compositions of $82PbS{\bullet}18Bi_2S_3$, $73PbS{\bullet}27Bi_2S_3$, and $50Pbs{\bullet}50Bi_2S_3$ have X-ray powder-diffraction data corresponding to, respectively, heyrovskyite (Klominsky *et al.* 1971), lillianite (Klyakhiv & Dimitriyeva 1968), and galenobismutite (Berry 1940b). Each forms equilibrium assemblages with pyrrhotite. $FeBi_4S_7$ synthesized by Craig *et al.* (1971) was not observed at 500°C, which confirms their statement that $FeBi_4S_7$ is a high-temperature phase and has a narrow range of stability. The $d_{(102)}$ values of pyrrhotite in various assemblages are tabulated in Table 4. The composition of pyrrhotite varies

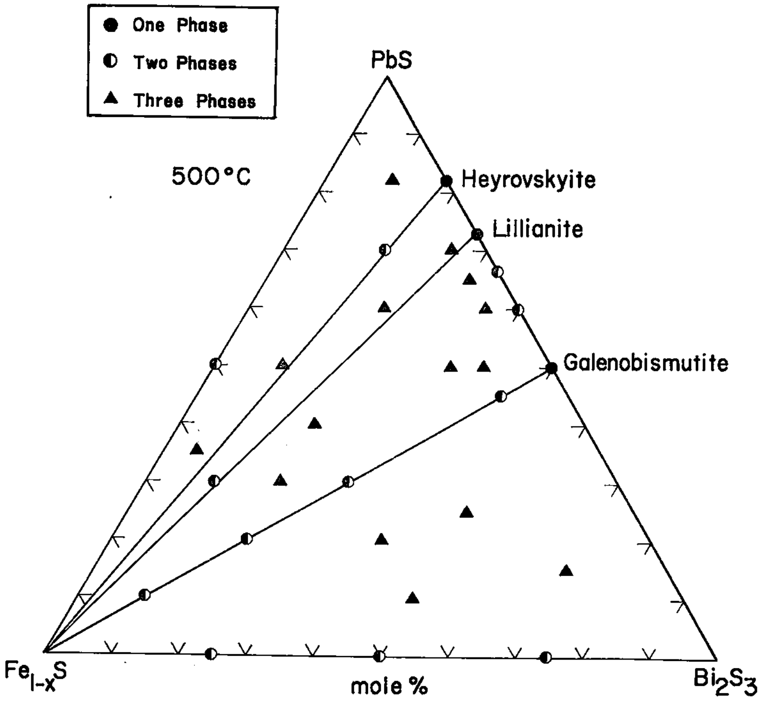

FIG. 2. Phase relations in the system PbS–$Fe_{1-x}S$–Bi_2S_3 at 500°C. The lillianite was synthesized from the composition 73 mole % PbS and 27 mole % Bi_2S_3. (Ed. note: the starting compositions for zinkenite in Figure 1 and lillianite in Figure 2 do not conform with their generally accepted formulae of $Pb_3Bi_2S_6$ for lillianite and $Pb_6Sb_{14}S_{27}$ for zinkenite).

within a narrow range from 0.947 to 0.952 in terms of mol fraction and FeS with corresponding log $f(S_2)$ values from −13.38 to −13.06 atm.

Runs made at 450°C and 400°C produced phase relations no different from those shown at 500°C. Cosalite, giessenite, bonchevite, and other reported lead sulfbismuthides (see Chang & Bever 1973) were not found.

GEOLOGICAL CONSIDERATIONS

Jamesonite was synthesized in the system PbS–$Fe_{1-x}S$–Sb_2S_3 and showed a solid-solution range between 400° and 500°C. The presence of iron is essential for its formation.

Equilibrium assemblages of jamesonite established in the present study correspond well with those in its natural occurrences. Reported mineral assemblages containing jamesonite are: jamesonite+stibnite+zinkenite (Palache *et al.* 1944), jamesonite+berthierite+stibnite (Palache *et al.* 1944; Roger 1969), jamesonite+pyrrhotite +boulangerite (Turneaure 1960; Kapustin 1971), jamesonite+boulangerite (Hak 1966; Gross *et al.* 1967), and jamesonite+pyrrhotite (Gasper 1967). Among them, the most common ones are jamesonite+boulangerite+pyrrhotite and jamesonite+berthierite+pyrrhotite. The constant association of jamesonite with iron-bearing sulfides is a direct consequence of the abundance of iron in the ore-forming solutions.

Jamesonite-galena association with or without boulangerite has also been reported in nature (Arkhangel'skaya 1963; Ramdohr 1969; Kupcik *et al.* 1969). This association suggests that, outside the temperature range of this study, the join galena-jamesonite becomes a stable one in the system. Because jamesonite melts at a temperature slightly higher than 500°C (545°C), it seems more likely that this association represents a low-temperature assemblage, stable below 400°C. There is, however, always a possibility that the presence of other elements may alter the conditions of formation.

Known chemical analyses of jamesonite are plotted in Figure 3 to compare with the synthetic solid-solution range. All but five fall in the solid-solution region around the composition of ideal jamesonite. Natural Bi- and Zn-bearing jamesonites have been reported (Arkhangel'skaya 1963; Godovikov & Kochetkova 1972; Bororaev & Mozgova 1975).

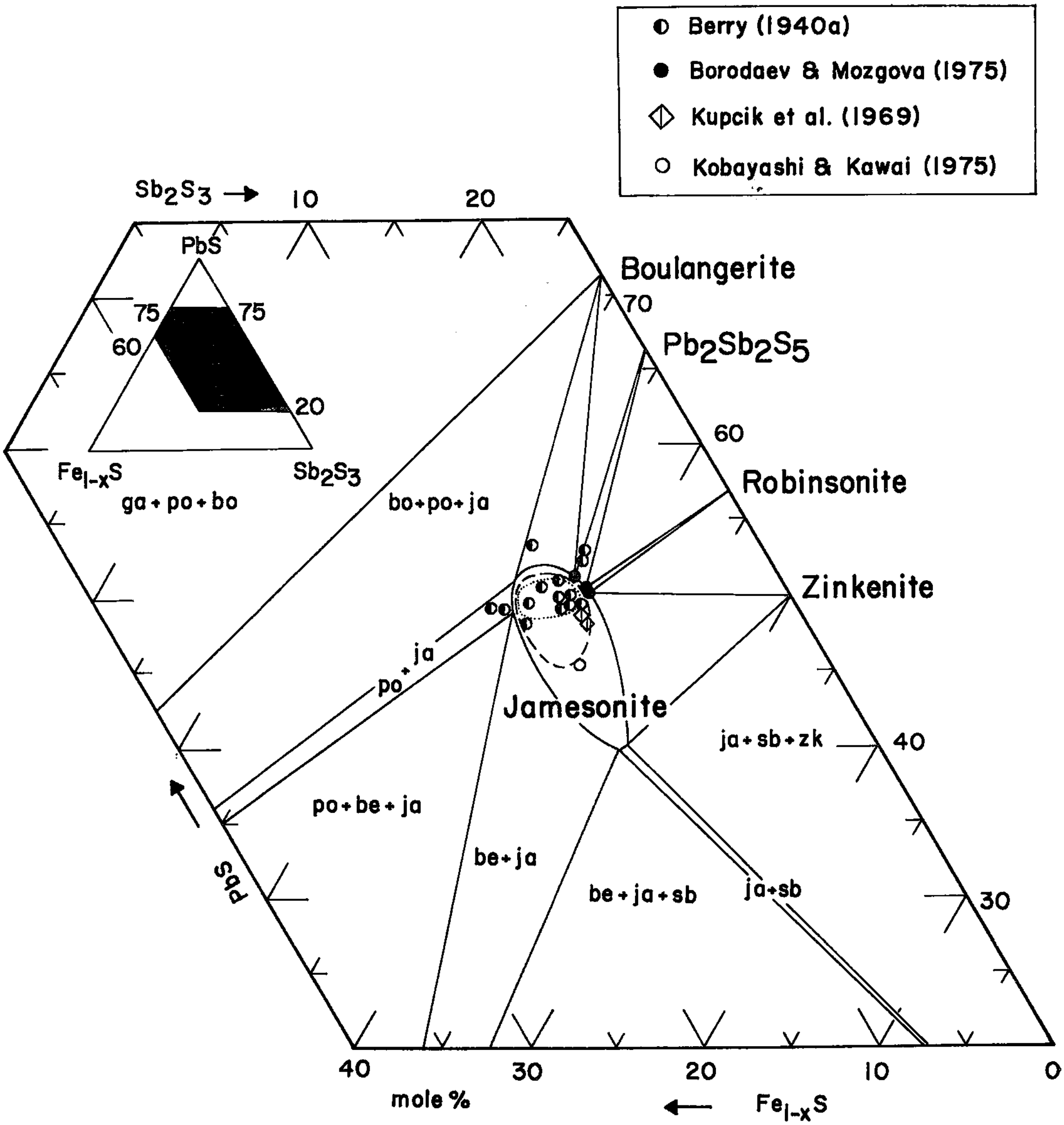

FIG. 3. Ranges of solid solution of jamesonite established in the present study (solid lines: range at 500°C; dashed lines: at 450°C; dotted lines: at 400°C) compared with compositions of natural jamesonite. Abbreviations are: be berthierite; bo boulangerite; ga galena; ja jamesonite; po pyrrhotite; sb stibnite; zk zinkenite.

ACKNOWLEDGMENTS

We are indebted to Drs. J. E. Bever, B. F. Leonard, and R. W. Potter III for reviewing the manuscript, to Dr. J. L. Jambor for analyzing robinsonite, and to Dr. D. S. Walia for assisting with the experimental work. We also thank Dr. Leonard for kindly sending us four Russian papers pertinent to the chemical composition of jamesonite.

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Manuscript received September 1976, emended April 1977.