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THE JAMESONITE - BENAVIDESITE SERIES

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ABSTRACT

Phase relations in the systems PbS–FeS–Sb_2S_3 and PbS–MnS–Sb_2S_3, on the plane $Pb_4Sb_6S_{13}$–FeS–MnS and along the join $Pb_4FeSb_6S_{14}$–$Pb_4MnSb_6S_{14}$, were studied using the conventional sealed-capsule technique. $Pb_4FeSb_6S_{14}$ (jamesonite) and $Pb_4MnSb_6S_{14}$ (benavidesite) form a complete series of solid solutions, with melting temperature varying from 583 ± 3 to 592 ± 3°C, respectively. On the plane, solid solutions in equilibrium with pyrrhotite have compositions covering almost the entire series, whereas solid solutions that coexist with alabandite are limited to the Mn-rich end. Compositions ranging from Fe-rich to Mn-rich in the solid-solution series were found at Dachang, China; there, jamesonite is the most abundant sulfosalt. It formed as acicular or capillary crystals in cavities, as a result of late-stage processes.

Keywords: jamesonite, benavidesite, solid-solution series, natural examples, synthesis experiments, Dachang deposit, China.

SOMMAIRE

Les équilibres des phases des systèmes PbS–FeS–Sb_2S_3 et PbS–MnS–Sb_2S_3, dans le plan $Pb_4Sb_6S_{13}$–FeS–MnS et pour la série entre les pôles $Pb_4FeSb_6S_{14}$ et $Pb_4MnSb_6S_{14}$, ont fait l'objet d'une étude conventionnelle au moyen de capsules scellées. $Pb_4FeSb_6S_{14}$ (jamesonite) et $Pb_4MnSb_6S_{14}$ (bénavidésite) forment une solution solide complète, le long de laquelle le point de fusion va de 583 ± 3 à 592 ± 3°C. Dans le plan, les compositions de la solution solide en équilibre avec la pyrrhotine s'étendent sur presque toute la série, tandis que celles qui coexistent avec l'alabandite se trouvent tout près du pôle manganésifère. On trouve des membres de la solution solide riches en fer et riches en manganèse à Dachang, en Chine, dans des assemblages où la jamesonite est le sulfosel prédominant. Ces minéraux se présentent en cristaux aciculaires et capillaires et sont le résultat de processus tardifs.

(Traduit par la Rédaction)

Mots-clés: jamesonite, bénavidésite, solution solide, exemples naturels, expériences de synthèse, gîte Dachang, Chine.

INTRODUCTION

Jamesonite, $Pb_4FeSb_6S_{14}$, one of the relatively common sulfosalt minerals, occurs in close association with pyrrhotite, pyrite, and other iron-bearing sulfides in hydrothermal deposits. In general, the chemical composition of jamesonite does not vary much (Chang & Knowles 1977). Metallic elements that are normally present in geological environments where sulfosalts form do not substitute extensively for the constituents of jamesonite because of structural restrictions. The Fe atom has a distinct structural position, co-ordinated by six sulfur atoms in a distorted octahedron in association with PbS_7 and PbS_8 (Niizeki & Buerger 1957). As a result, silver and copper are present only in small amounts. On the other hand, metallic elements that are suitable for the jamesonite structure are not abundant in the environments of sulfosalt formation. Jamesonite rarely contains nickel or cobalt, although a jamesonite-type phase has been synthesized in the systems PbS–NiS–Sb_2S_3 and PbS–CoS–Sb_2S_3 (Chang, unpubl. data).

With the identification of benavidesite from Uchucchacua, Peru and Sätra, Sweden (Oudin *et al.* 1982), manganese appears to represent the element that bridges the gap between these two groups of metallic elements. Benavidesite has an ideal composition $Pb_4(Mn,Fe)Sb_6S_{14}$, with a Mn:Fe ratio varying from 73:27 to 62:38. The purpose of this investigation is to study the jamesonite–benavidesite series in the system PbS–FeS–MnS–Sb_2S_3, and its natural occurrence in the Dachang ore field, China.

THE $Pb_4FeSb_6S_{14}$–$Pb_4MnSb_6S_{14}$ SERIES IN THE SYSTEM PbS–FeS–MnS–Sb_2S_3

Experimental procedure

Starting compositions were prepared from reagent-grade lead, antimony, iron, manganese and sulfur; all have 99.99% purity or better. Synthesis and heat treatment were made in muffle furnaces using the conventional technique of sealed, evacuated glass capsules (Kullerud & Yoder 1959). Generally, the duration of treatment ranged from 120 days at 400°C to 45 days at 500°C, to 5 days at and above 600°C. X-ray powder diffraction, reflected-light microscopy, and electron-microprobe analysis were used for

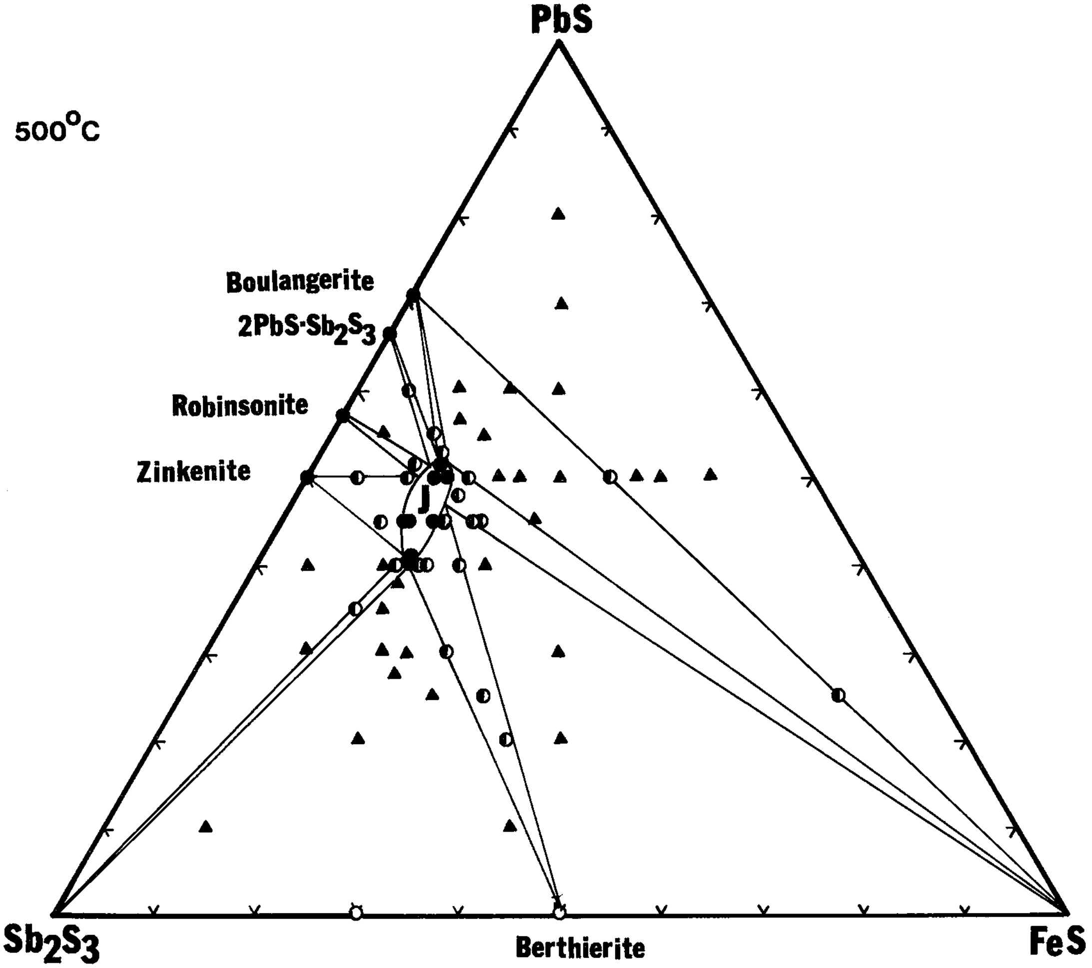

FIG. 1. Phase relations in the system PbS–FeS–Sb_2S_3 at 500°C. In this and the following figure, the solid triangles, half-filled circles and filled circles represent, respectively, three-phase, two-phase and one-phase assemblages. Jamesonite solid-solution is denoted by "J".

characterization of phases. Cell dimensions (± 0.02 Å) were computed using a least-squares refinement program.

To check for equilibrium, a different procedure of synthesis was used in selected experiments. The charges were heated to complete melting, quenched, and annealed at the desired temperatures for the same length of time as their counterparts prepared by the direct union of the elements. There is no difference in the phase assemblages produced by these two procedures.

Jamesonite in the system PbS–FeS–Sb_2S_3

The formation of jamesonite in the system was studied by Chang & Knowles (1977). At 500°C, jamesonite has a range of solid solution elongated toward Sb_2S_3, and forms equilibrium assemblages with all phases on the related joins except galena. The extent of solid solution is very sensitive to temperature change. At 400°C, it is limited to within 1 or 2 mole% around the ideal composition. In this study, additional compositions were prepared and treated at 500°C. From the results obtained, several minor modifications were made to the phase relations in the system (Fig. 1): (1) the width of the field of jamesonite solid-solution along the 45 mole% PbS line was reduced; (2) the composition of jamesonite solid-solution in equilibrium with berthierite and pyrrhotite is $Pb_{3.7}Fe_{1.2}Sb_6S_{14}$, and (3) the region occupied by the assemblage of robinsonite + jamesonite solid-solution is slightly enlarged.

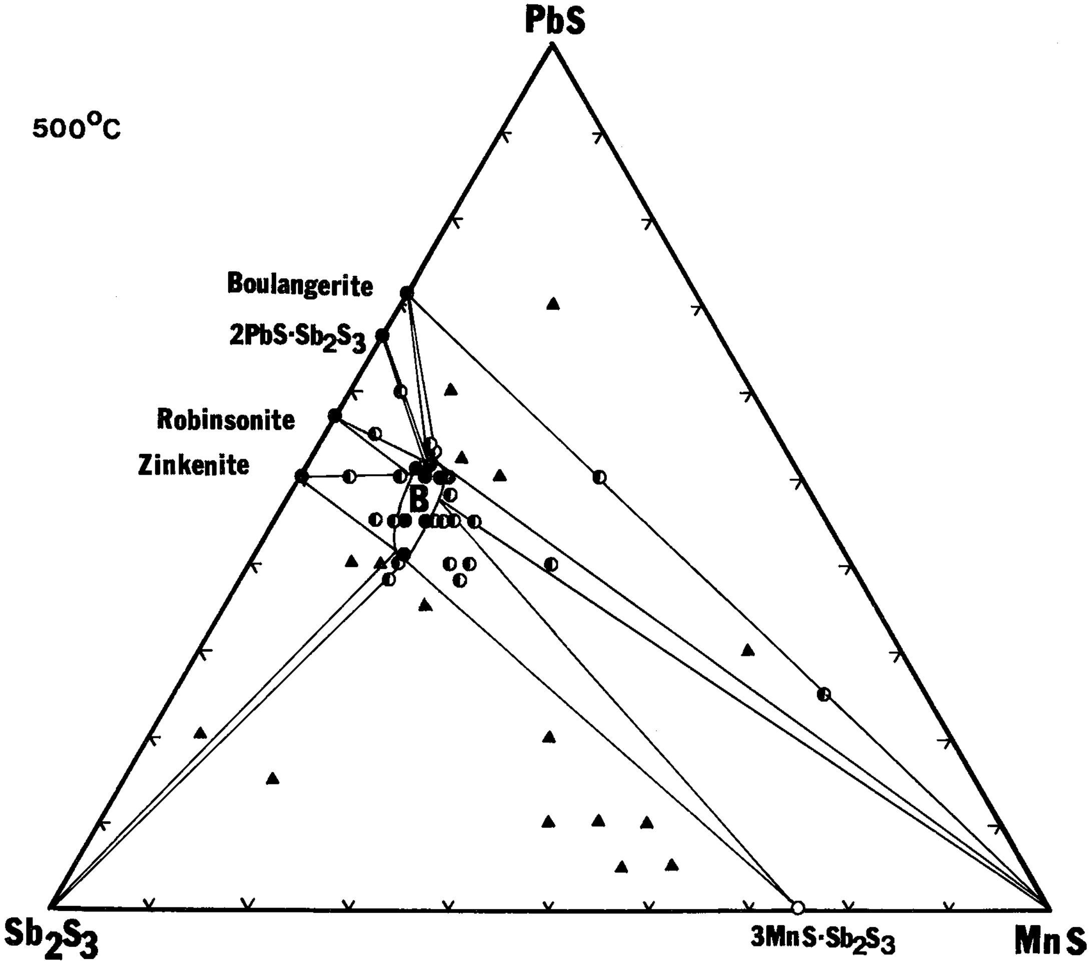

FIG. 2. Phase relations in the system PbS–MnS–Sb_2S_3 at 500°C. "B" represents the $Pb_4MnSb_6S_{14}$ solid-solution.

Benavidesite in the system PbS–MnS–Sb_2S_3

As shown in Figure 2, phase relations in the system PbS–MnS–Sb_2S_3 at 500°C are very similar to those in the system containing FeS. End-member benavidesite, $Pb_4MnSb_6S_{14}$, is a jamesonite-type phase, and the two display similar solid-solution relationships. Its relations with other phases in the system are also similar to those of jamesonite in the system PbS–FeS–Sb_2S_3 except that a 3:1 phase ($Mn_3Sb_2S_6$) takes the place of the 1:1 phase ($FeSb_2S_4$). At 400°C, $Pb_4MnSb_6S_{14}$ has a much reduced range of solid solution.

The jamesonite – benavidesite series

A complete solid-solution series extends between $Pb_4FeSb_6S_{14}$ and $Pb_4MnSb_6S_{14}$ (Fig. 3), with cell dimensions varying within a very narrow range: *a* 15.75, *b* 19.17, *c* 3.99 Å, *β* 91°22′ for jamesonite and *a* 15.74, *b* 19.14, *c* 4.04 Å, *β* 91°20′ for the Mn end-member. $Pb_4(Mn_{0.70}Fe_{0.30})Sb_6S_{14}$, a composition of benavidesite reported by Oudin *et al.* (1982), has *a* 15.74, *b* 19.14, *c* 4.03 Å, *β* 91°30′. Melting relations in the series were determined by examining polished sections of quenched samples using reflected-light microscopy. $Pb_4FeSb_6S_{14}$ becomes sintered at 550°C and melts congruently at 583 ± 3°C, whereas $Pb_4MnSb_6S_{14}$ melts at 592 ± 3°C without apparent sintering. The two-phase region cannot be well defined because of the narrow separation between liquidus and solidus. This feature is obviously due to the small difference in melting points of the end members.

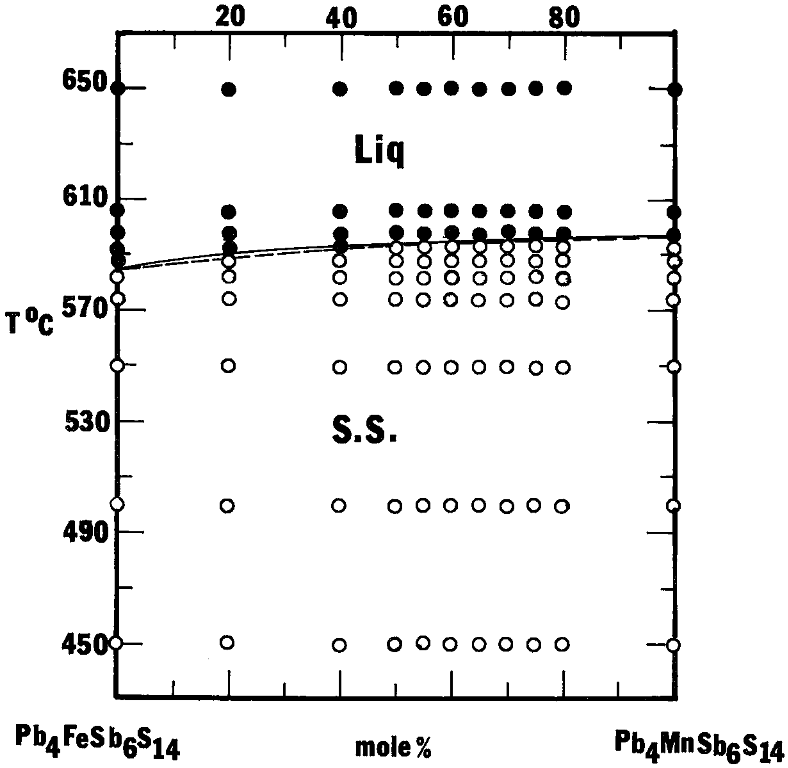

FIG. 3. Phase relations along the join $Pb_4FeSb_6S_{14}$–$Pb_4MnSb_6S_{14}$. In this figure, open circles and filled circles represent solid phase and liquid phase, respectively.

As shown in Figure 4, the jamesonite – benavidesite series is stable in the plane $Pb_4Sb_3S_{13}$ (robinsonite) – FeS – MnS at 500°C. Solid solutions in equilibrium with pyrrhotite have compositions covering almost the entire series, whereas solid solutions in equilibrium with alabandite are limited in their compositions to the Mn-rich end of the series. At 400°C, the ranges of the two-phase region vary in accordance with the decrease of mutual solubilities between FeS and MnS, but the composition of the jamesonite – benavidesite series that defines the three-phase region remains unchanged, as verified by electron-microprobe analysis.

THE JAMESONITE – BENAVIDESITE SERIES FROM DACHANG ORE FIELD, CHINA

Geological occurrence

The Dachang district, located in northwestern Guangxi, China, is a polymetallic ore field dominated by cassiterite–sulfide deposits, and contains abundant sulfosalt minerals. These sulfosalts are widely distributed in the ore field and occur in almost all types of deposits (Li & Zhang 1980). Of the sulfosalt minerals, jamesonite is by far the most abundant and most widespread.

At Dachang, jamesonite has seven distinct modes of occurrence: (1) massive with ferroan sphalerite and pyrite, (2) granular and columnar in pyrite, (3) in cavities, acicular or capillary, in association with calcite and pyrite, (4) in plumose and sheaf-like forms, (5) in veins with ferroan sphalerite, arsenopyrite, pyrite and pyrrhotite, (6) disseminated in calcite, and (7) in thin plates, some radiating, on joint planes. Among these, only the acicular or capillary jamesonite that occurs in cavities contains significant Mn.

Most of the sulfosalt minerals at Dachang, including jamesonite, are products of late-stage mineralization. Solid solutions of the jamesonite – benavidesite series are among the latest minerals to crystallize. Their restricted occurrence in cavities of orebodies as acicular or capillary crystals indicates that the ore-forming solution underwent a late enrichment in Mn.

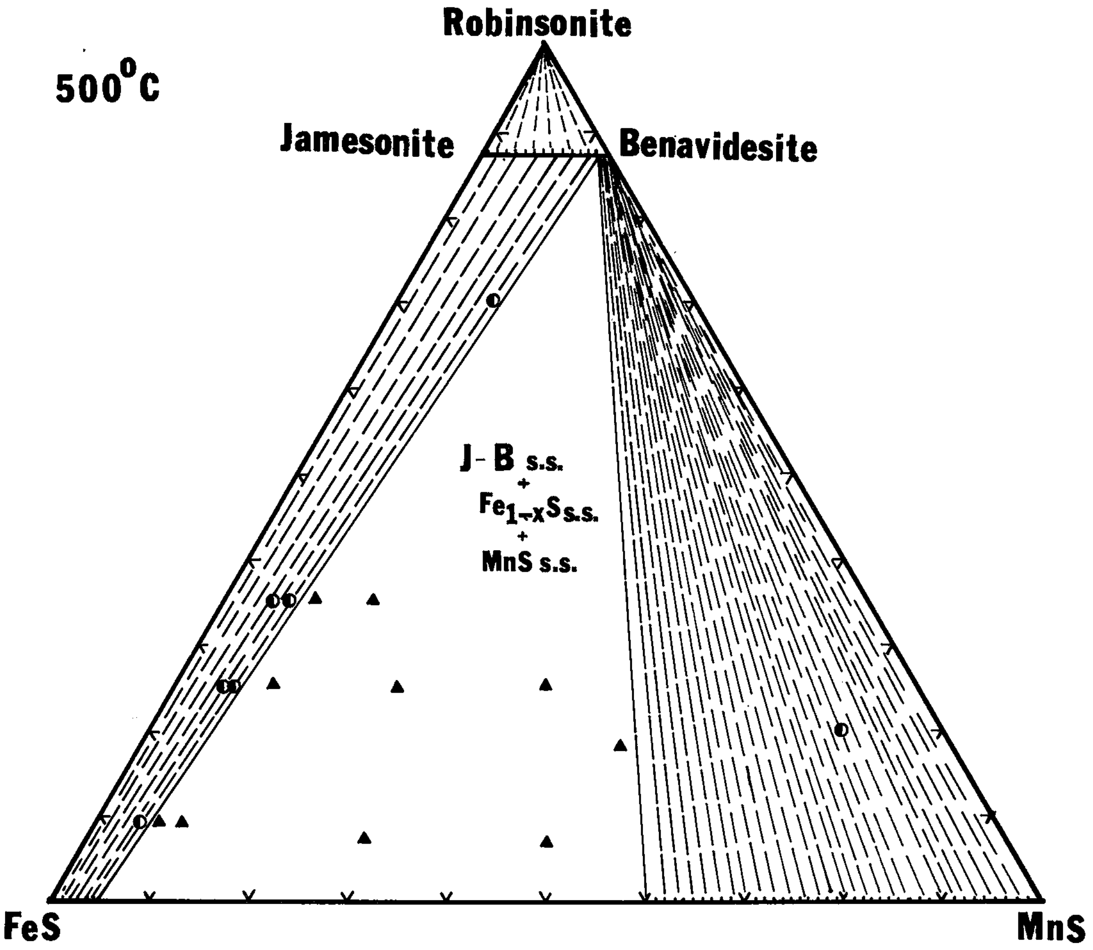

FIG. 4. Phase relations in the plane $Pb_4Sb_6S_{13}$ (robinsonite) - FeS - MnS at 500°C. In this figure, solid triangles and half-filled circles represent, respectively, three-phase and two-phase assemblages.

Chemical composition

Electron-microprobe results of jamesonite and benavidesite from all major ore assemblages of the Dachang deposit are presented in Table 1. An average of the first 12 compositions listed gives (wt. %) Pb 40.44, Fe 2.66, Sb 34.03, S 21.84, Mn 0.10, Zn 0.02, Cu 0.10, Mg 0.01, Sn 0.26, As 0.16, Bi 0.34 (0.17 without sample 84002), In 0.02 and Ag 0.05, for a total of 99.98. The theoretical chemical composition of jamesonite is Pb 40.15, Fe 2.71, Sb 35.59 and S 21.75%. Bi, Mn and Sn are present in all grains of jamesonite analyzed.

Among the eight samples of jamesonite with significant amount of Mn, one (W1028) has a Mn:Fe ratio comparable to benavidesite as proposed by Oudin *et al.* (1982). Samples W274, 85823 and 85896 represent iron-rich members of the series, whereas sample 84828 is a Mn-rich member. The remaining three samples have a Mn:Fe ratio close to one.

Physical properties

Members of the jamesonite - benavidesite series at Dachang occur as acicular or capillary, closely packed crystals measuring on average 0.4 mm long and 0.02 mm wide, and with the maximum dimensions of 0.8 × 0.03 mm. They are lead-grey in color, with a metallic lustre and a dark greyish streak. Attempts to determine their density failed, but the hardness is estimated to be 2 - 2.5 on the Mohs scale.

Under reflected light, the jamesonite - benavidesite minerals are white with a pale greenish tint and

TABLE 1. CHEMICAL COMPOSITIONS OF JAMESONITE - BENAVIDESITE SERIES FROM DACHANG, CHINA

Sample	Composition, wt.%													Formula Ratios				
Number	Pb	Sb	As	Bi	Fe	Mn	Zn	Cu	Mg	In	Sn	Ag	S	Total	Pb	Fe	Mn	Sb	S
W277 (4)*	39.32	34.17	0.69	0.64	2.68	0.30	0.030	0.080			0.23	0.000	21.84	99.98	3.90	0.99	-	5.77	14
83626 (2)	41.03	33.71	0.043	0.11	2.50	0.14	0.005	0.11	0.012	0.066	0.21	0.003	22.08	100.02	4.03	0.91	-	5.63	14
W007 (3)	41.46	33.46	0.056	0.080	2.78	0.15	0.000	0.035	0.016	0.024	0.25	0.013	21.70	100.02	4.14	1.03	-	5.68	14
W244 (3)	41.15	33.59	0.019	0.093	2.89	0.096	0.012	0.011	0.010	0.061	0.25	0.000	21.87	100.05	4.08	1.06	-	5.66	14
W1400 (1)	40.11	34.65	0.000	0.12	2.55	0.087	0.000	0.000	0.000	0.000	0.36	0.017	22.00	99.89	3.95	0.93	-	5.81	14
82087 (1)	40.18	33.92	0.84	0.45	2.48	0.12	0.040	0.000			0.36	0.000	21.74	99.53	4.12	0.94	-	5.92	14
W1142 (4)	41.56	33.45	0.000	0.007	2.91	0.010	0.000	0.12	0.009	0.109	0.17	0.013	22.00	100.36	4.09	1.06	-	5.61	14
W1600 (3)	39.37	34.55	0.037	0.34	2.34	0.063	0.006	0.37	0.009	0.004	0.25	0.32	22.11	99.77	3.86	0.85	-	5.76	14
84097 (4)	40.17	34.98	0.073	0.014	2.72	0.023	0.034	0.19	0.012	0.012	0.24	0.19	21.41	100.07	4.06	1.02	-	6.02	14
84092 (3)	40.46	33.98	0.057	0.050	2.74	0.058	0.022	0.16	0.007	0.000	0.22	0.000	22.15	99.90	3.96	0.99	-	5.66	14
84093 (4)	39.98	35.51	0.011	0.012	2.64	0.12	0.044	0.16	0.008	0.000	0.20	0.042	21.32	100.05	4.06	1.00	-	6.14	14
84002 (4)	40.55	32.37	0.053	2.23	2.69	0.089	0.008	0.007	0.005	0.000	0.21	0.021	21.89	100.12	4.01	0.99	0.22 (Bi)	5.45	14
W274 (3)	41.59	33.01	0.20	0.11	2.18	0.43	0.011	0.054	0.009	0.045	0.58	0.008	21.89	100.12	4.12	0.80	0.16	5.56	14
85823 (4)	41.37	34.26	0.17	0.042	1.71	0.78	0.042	0.13	0.012	0.032	0.27	0.013	21.51	100.34	4.17	0.64	0.30	5.87	14
85896 (1)	40.16	34.41	0.24	0.000	1.64	0.94	0.13	0.13	0.004	0.030	0.26	0.000	22.01	99.95	3.95	0.60	0.35	5.76	14
W275 (4)	39.39	33.91	0.057	0.69	1.43	1.25	0.12	0.43	0.001	0.005	0.26	0.049	22.19	99.78	3.85	0.51	0.46	5.63	14
W1044 (3)	39.74	34.92	0.13	0.079	1.32	1.30	0.065	0.16	0.020	0.018	0.31	0.027	22.05	100.14	3.90	0.48	0.48	5.84	14
W1194 (2)	39.71	34.64	0.55	0.050	1.19	1.17	0.080	0.040			0.29	0.040	21.63	99.39	3.98	0.44	0.44	5.90	14
W1028 (4)	38.74	34.58	0.19	0.36	0.83	1.91	0.050	0.018	0.014	0.014	0.35	0.000	22.49	99.55	3.79	0.30	0.69	5.75	14
84828 (2)	38.55	35.06	0.74	0.23	0.51	1.92	0.13	0.057		0.019	0.21	0.002	22.66	99.69	3.69	0.18	0.69	5.70	14

* Number of grains analyzed by electron microprobe. Analytical conditions: mixed metal and sulfide standards, 20 kV, 0.03 mA, ZAF correction.

strongly anisotropic, with polarization colors ranging from greyish green through greyish brown to dark blue. There are no internal reflections. The extinction angles observed are from 30° to 32°, and there is a distinct cleavage parallel to the long axis. No twins were recognized.

SUMMARY AND CONCLUSION

$Pb_4FeSb_6S_{14}$ and $Pb_4MnSb_6S_{14}$ form a complete series of solid solutions in the system PbS–FeS–MnS–Sb_2S_3, with melting temperature varying continuously from 583 ± 3°C (Fe) to 592 ± 3°C (Mn). Compositions of this solid-solution series ranging from Fe-rich to Mn-rich were found in the Dachang ore field, in which jamesonite is the most abundant sulfosalt mineral. They formed as acicular or capillary crystals in cavities, representing products of late-stage processes.

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