

## Study of the minerals on the $\text{PbS-Sb}_2\text{S}_3$ join

### Part 1: Phase relation above 400°C

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#### Abstract

The phase equilibrium studies of the  $\text{PbS-Sb}_2\text{S}_3$  join were carried out by the evacuated glass tube method and DTA at temperatures above 400°C. In addition to the end-members of stibnite and galena, three minerals, zinkenite, robinsonite and boulangerite, and five synthetic phases D, E, F, H and I were found on this join, and their chemical compositions, thermal stabilities and crystallographic properties were determined.

Stibnite melts congruently at 546°C. Zinkenite has a composition of  $9\text{PbS} \cdot 11\text{Sb}_2\text{S}_3$  and melts incongruently to robinsonite and liquid at 546°C. A eutectic reaction between stibnite and zinkenite occurs at 516°C. Robinsonite having  $4\text{PbS} \cdot 3\text{Sb}_2\text{S}_3$  composition melts incongruently to phase D and liquid at 582°C. Phase D having a composition of  $5\text{PbS} \cdot 3\text{Sb}_2\text{S}_3$  is stable on the  $\text{PbS-Sb}_2\text{S}_3$  join at temperatures from 510° to 590°C, at which it melts incongruently to phase E and liquid. Phase E with an ideal composition of  $7\text{PbS} \cdot 4\text{Sb}_2\text{S}_3$  is stable at temperatures from 584° to 603°C and melts incongruently to boulangerite and liquid at 603°C. Phase F with a composition of  $2\text{PbS} \cdot \text{Sb}_2\text{S}_3$  is stable from 490° to 584°, at which it decomposes to phase E and boulangerite. Boulangerite with a composition of  $5\text{PbS} \cdot 2\text{Sb}_2\text{S}_3$  melts incongruently to phase H and liquid at 640°C. Phase H having a composition of  $3\text{PbS} \cdot \text{Sb}_2\text{S}_3$  is stable only at a temperature range from 625° to 647°, and incongruently melts to galena and liquid at 647°C. Phase I has a composition of  $16\text{PbS} \cdot 5\text{Sb}_2\text{S}_3$ , stable from 610° to 636°C, at which it decomposes to phase H and galena.

#### Introduction

Many species of lead-antimony sulfosalt minerals have been reported. They are generally classified into two types; one is acicular group minerals such as zinkenite, robinsonite, boulangerite having acicular crystal form (Robinson, 1948), and the other is pligionite group minerals with an ideal formula of  $\text{Pb}_{9-2X}\text{Sb}_8\text{S}_{21-2X}$ , semseyite ( $X=0$ ), pligionite ( $X=1$ ), heteromorphite ( $X=2$ ) and fuloppite ( $X=3$ ) having prismatic form.

Although many studies on the mineral synthesis and phase relations for this binary join have been performed, stable phases and their chemical compositions differ from each other as seen in Table 1. The sulfosalt minerals synthesized by previous dry experiments were only the

TABLE 1. Reported synthetic phases on the PbS-Sb<sub>2</sub>S<sub>3</sub> join.

	Robinson (1948)	Jambor (1967)	Kitakaze (1968)	Salanci & Moh (1970)	Garvin (1973)	Craig et al. (1973)	Salanci & Klein (1979)	Salanci (1979)	Present study
<b>Synthetic minerals</b>									
Fulopit	-	-	-	-	-	-	-	-	-
Zinkenite	1:1	6:7	9:11	6:7	6:7	1:1	7:9	7:9	9:11
Plagionite	-	-	-	-	-	-	-	-	-
Robinsonite	7:6	7:6	9:7	11:9	7:6	6:5	9:7	9:7	4:3
Heteromorphite	-	-	-	-	-	-	-	-	-
Semseyite	-	-	-	-	-	-	-	-	-
Boulangerite	5:2	5:2	5:2	5:2	5:2	5:2	5:2	5:2	5:2
<b>Synthetic phases</b>									
Phase AN	-	6:5	-	-	-	-	-	-	-
Phase D,Va	-	-	D(8:5)	-	-	-	-	Va(5:4)	D(5:3)
Phase E, II, IVa	-	-	E(5:3)	-	-	II(3:2)	IVa(2:1)	-	E(7:4)
Phase F, IV, V	-	-	F(2:1)	IV(2:1)	2:1	-	IV(2:1)	V(2:1)	F(2:1)
Phase K-1	12:5	-	-	-	-	-	-	-	-
Phase H, III	-	-	H(3:1)	-	-	-	III(17:6)	III(17:6)	H(3:1)
Phase I, II	-	-	I(10:3)	II(13:4)	-	I(3:1)	II(13:4)	II(13:4)	I(16:5)

Numbers are mole ratio of PbS and Sb<sub>2</sub>S<sub>3</sub>.

acicular group minerals as zinkenite, robinsonite and boulangerite. Synthetic phases which do not correspond to any natural minerals were also found, but their species or chemical compositions do not always agree among reports, and the identities of these synthetic phases have not been established to date.

Thus, we reexamined the phase relations on the PbS-Sb<sub>2</sub>S<sub>3</sub> binary join and carried out the mineral syntheses and determined the phase relations above 400°C by the dry experiments and determined also cell parameters of some synthetic phases. The results of the studies are reported.

## Experimental techniques and procedures

The reagents used in the synthetic experiments were lead and antimony metals of 99.999% and sulfur of 99.99% in purity. Using these elements, lead and antimony sulfides were synthesized previously by the same method as Sugaki and Shima (1965a), Scott (1974), or Kullerud (1971) reported. Then, they were used as the starting materials for the phase equilibrium study which was conducted in horizontal or vertical electric furnaces controlled within  $\pm 2^\circ\text{C}$ . The synthetic products were identified by the ore microscopy, X-ray powder and single crystal diffractometry. The optical properties and the X-ray powder patterns of these phases are very similar to each other. Therefore, the identification was mainly performed by referring to some diffraction peaks characteristic of each phase.

The crystallographic data of some synthetic phases were obtained using Weissenberg and

precession cameras. Their cell parameters were calculated by the least squares method from X-ray powder data. The differential thermal analysis (DTA) in the evacuated glass tube was useful to determine the temperatures of incongruent melting reaction of the phases. The same apparatus and method were employed as Sugaki and Shima (1965b). Temperatures obtained by DTA were corrected by measurements of melting points for some standard pure metals such as Bi, Sb, Al and Ag. The accuracy of the temperature was within  $\pm 2^\circ\text{C}$ .

### Previous studies

Mineral syntheses on the  $\text{PbS-Sb}_2\text{S}_3$  join were performed by Jaeger and Van Klooster (1912), Iitsuka (1920) and others. They synthesized some phases by direct fusion of mixtures of PbS and  $\text{Sb}_2\text{S}_3$  in air, but the phases were identified only by the ore microscope. Since lead-antimony sulfosalts have very similar optical properties to each other, phase identification by that is very difficult. Therefore, their identification is questionable.

Robinson (1948) synthesized some lead-antimony sulfosalts as seen in Table 1 by direct fusion of PbS and  $\text{Sb}_2\text{S}_3$  in evacuated silica glass tube. Jambor (1968) also performed the mineral syntheses along this join by dry reaction and obtained some minerals as shown in Table 1.

The phase equilibrium experiments within evacuated silica glass tube method and by differential thermal analysis were performed by Kitakaze (1968), Salanci and Moh (1970), Garvin (1973), Craig *et al.* (1973), Salanci (1979) and Salanci and Klein (1979). Their data are also compiled in Table 1. Identification of synthetic phases and their chemical compositions do not agree among the reports except boulangerite. Especially, the chemical compositions for zinkenite, robinsonite, and some synthetic phases are different in the works as seen in the table.

### Experimental result and discussion

Experimental results of phase equilibrium are summarized in Fig. 1 as the phase diagram of the  $\text{PbS-Sb}_2\text{S}_3$  join above  $400^\circ\text{C}$ . This diagram was obtained from the experiments of about 250 runs of durations from 2 to 40 days and at temperatures from  $400^\circ$  to  $800^\circ\text{C}$ . In addition to the end-members of stibnite and galena, three sulfosalt minerals, zinkenite, robinsonite and boulangerite, and five synthetic phases designated as D, E, F, H and I which were first reported by Kitakaze (1968) are found on this join.

The temperatures for eutectic and incongruent melting reactions and liquidus shown in Fig. 1 were mainly determined by DTA. Zinkenite, robinsonite, boulangerite and the phases D, E and H melt incongruently to more PbS-rich solid phases and more  $\text{Sb}_2\text{S}_3$ -rich liquids.

Stibnite melts congruently at  $546 \pm 3^\circ\text{C}$ . Although Salanci and Moh (1970), Salanci (1979) and Salanci and Klein (1979) reported that solubility of PbS in stibnite is 1.5 mole % at  $521^\circ\text{C}$ , the differences of d-values in X-ray powder data between pure stibnite and stibnite

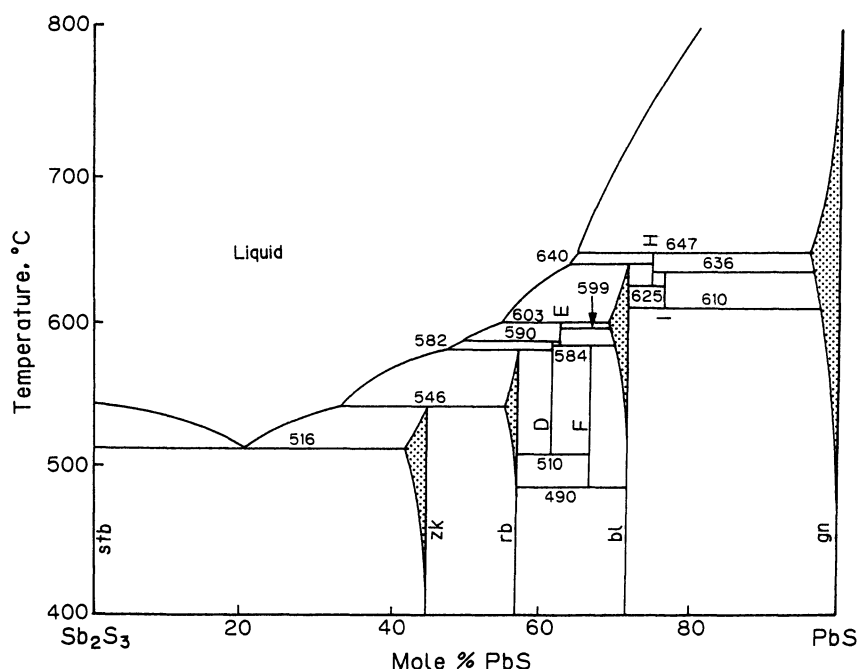


FIG. 1. Phase relations on the PbS-Sb<sub>2</sub>S<sub>3</sub> join.

stb: stibnite, rb: robinsonite, bl: boulangerite, gn: galena, D, E, F, H, I: synthetic phase D (5PbS•3Sb<sub>2</sub>S<sub>3</sub>), phase E (7PbS•4Sb<sub>2</sub>S<sub>3</sub>), phase F (2PbS•Sb<sub>2</sub>S<sub>3</sub>), phase H (3PbS•Sb<sub>2</sub>S<sub>3</sub>) and phase I (16PbS•5Sb<sub>2</sub>S<sub>3</sub>).

containing galena component could not detect at 520°C. Therefore, distinct solid solution could not be confirmed (less than 0.1 mole % PbS). The eutectic reaction between stibnite and zinkenite occurred at  $516 \pm 3^\circ\text{C}$  in composition of 20 mole % PbS.

Zinkenite has an ideal composition of 9PbS•11Sb<sub>2</sub>S<sub>3</sub> (45 mole % PbS). Narrow solid solution ranges of 1.0 at 530°C, 2.7 at 512°C and 2.0 mole % PbS at 500°C in more Sb<sub>2</sub>S<sub>3</sub>-rich region than the ideal compositions are given from the d-spacings vs. composition curve. Although the composition of zinkenite was determined to be PbS•Sb<sub>2</sub>S<sub>3</sub> (50 mole % PbS) by Craig *et al.* (1973), the present run products with bulk composition of 50 mole % PbS are a mixture of zinkenite and robinsonite at a temperature range from 400° to 530°C. The chemical compositions of 6PbS•7Sb<sub>2</sub>S<sub>3</sub> (46.15 mole % PbS, Jambor, 1967; Salanci and Moh, 1970; Garvin, 1973) and 7PbS•9Sb<sub>2</sub>S<sub>3</sub> (43.75 mole % PbS, Salanci and Klein, 1979; Salanci, 1979) were also derived as the ideal formula as seen in Table 1, but the calculated densities from these compositions or the cell volumes do not agree with the observed values by Sugaki *et al.* (1969,

1973). The present study has confirmed the chemical composition of zinkenite determined by Kitakaze (1968),  $9\text{PbS} \cdot 11\text{Sb}_2\text{S}_3$ . Zinkenite melts incongruently to robinsonite and liquid at  $546^\circ \pm 3^\circ\text{C}$ .

The ideal composition of robinsonite has been determined as  $4\text{PbS} \cdot 3\text{Sb}_2\text{S}_3$  (57.14 mole % PbS) from the synthetic experiment and a crystallographic consideration. It is concordant with the results of Sugaki *et al.* (1973) and Jambor and Plant (1975), although various formulae of robinsonite such as  $7\text{PbS} \cdot 6\text{Sb}_2\text{S}_3$  (53.85 mole %, Robinson, 1948; Berry *et al.*, 1956; Jambor 1967; Garvin, 1973),  $11\text{PbS} \cdot 9\text{Sb}_2\text{S}_3$  (55.00 mole %, Salanci and Moh, 1970), and  $9\text{PbS} \cdot 7\text{Sb}_2\text{S}_3$  (56.25 mole % PbS, Kitakaze, 1968) have been proposed. Robinsonite has a very narrow solid solution from 56.25 to 57.14 mole % PbS at  $540^\circ\text{C}$ . It melts incongruently to phase D and liquid at  $582^\circ \pm 3^\circ\text{C}$ .

Phase D, first found by Kitakaze (1968), has a composition of  $62.5 \pm 0.5$  mole % PbS, not analogous to any known minerals. It incongruently melts to phase E and liquid at  $590^\circ \pm 3^\circ\text{C}$ . No evidence of solid solution has been observed. The ideal formula for this phase is shown as  $5\text{PbS} \cdot 3\text{Sb}_2\text{S}_3$  (62.50 mole %). Phase D was found in the runs at  $520^\circ\text{C}$  along the PbS-Sb<sub>2</sub>S<sub>3</sub> join, decomposed into robinsonite and phase F at  $500^\circ\text{C}$ . Thus, it is stable above  $510^\circ \pm 10^\circ\text{C}$ . But, within the Pb-Sb-S ternary system, it is stable at  $490^\circ \pm 10^\circ\text{C}$  having a more metal-rich composition than the composition on the PbS-Sb<sub>2</sub>S<sub>3</sub> join (Sugaki *et al.*, 1974). This phase corresponds to  $5\text{PbS} \cdot 3\text{Sb}_2\text{S}_3$  phase by Wang (1976), because the X-ray powder data are in good agreement with each other. It is monoclinic, space group A2/m with cell parameters of  $a=21.98$ ,  $b=35.12$ ,  $c=4.02\text{\AA}$  and  $\beta=126.25^\circ$ , which were determined by Wang (1976).

Phase E has a composition of  $63.5 \pm 0.25$  mole % PbS, which is identically described as  $7\text{PbS} \cdot 4\text{Sb}_2\text{S}_3$  (63.64 mole %). This phase corresponds to  $5\text{PbS} \cdot 3\text{Sb}_2\text{S}_3$  phase (62.50 mole %) by Kitakaze (1968), phase II ( $3\text{PbS} \cdot 2\text{Sb}_2\text{S}_3$ , 60 mole %) by Craig *et al.* (1973),  $2\text{PbS} \cdot \text{Sb}_2\text{S}_3$  (66.67 mole % PbS) phase by Wang (1973), and phase VIa ( $2\text{PbS} \cdot \text{Sb}_2\text{S}_3$ ) by Salanci and Klein (1979), because they have almost the same X-ray powder patterns. Phase E is stable only in the temperature region from  $586^\circ \pm 3^\circ\text{C}$ , below which it decomposes to phase D and phase F, to  $603^\circ \pm 3^\circ\text{C}$ , at which it melts incongruently to boulangerite and liquid. Cell parameters of phase E determined by X-ray single crystal methods are as follows: orthorhombic, space group Pbnm,  $a=11.31$ ,  $b=19.78$ ,  $c=4.04\text{\AA}$  and  $Z=1$ . These data are very close to those ( $a=19.80$ ,  $b=11.40$ ,  $c=4.04\text{\AA}$ ,  $Z=4$ ) of  $2\text{PbS} \cdot \text{Sb}_2\text{S}_3$  phase reported by Wang (1973), although the exchange between a and b is necessary.

Phase F with a composition of  $66.5 \pm 0.25$  mole % PbS, which is described as an ideal composition of  $2\text{PbS} \cdot \text{Sb}_2\text{S}_3$  (66.67 mole % PbS), does not correspond to any minerals. It is stable at temperatures from  $490 \pm 5^\circ\text{C}$  to  $584^\circ \pm 3^\circ\text{C}$ . But below  $490 \pm 5^\circ\text{C}$  it has more sulfur-rich compositions than PbS-Sb<sub>2</sub>S<sub>3</sub> join (Sugaki *et al.*, 1974), and disappears on the binary join. This phase corresponds to  $2\text{PbS} \cdot \text{Sb}_2\text{S}_3$  phase by Kitakaze (1968), Salanci and Moh (1970), Garvin (1973), and Salanci (1979). Crystallographic data obtained by the single crystal method are as follows: monoclinic, space group C2/m,  $a=50.30$ ,  $b=4.01$ ,  $c=20.78\text{\AA}$ ,  $\beta=114.50^\circ$  and  $Z=17$ .

These data are close to those obtained by Wang (1976), although he adopted A-centered monoclinic cell ( $a=20.81$ ,  $b=50.52$ ,  $c=4.03$ ,  $\beta=114.08^\circ$ ).

Boulangerite with an ideal composition of  $5\text{PbS}\cdot 2\text{Sb}_2\text{S}_3$  melts incongruently to phase H and liquid at  $640\pm 3^\circ\text{C}$ . The solid solution range of the mineral is richer in Sb<sub>2</sub>S<sub>3</sub> by 2.7 at  $598^\circ\text{C}$ , 1.5 at  $580^\circ\text{C}$  and 1.0 mole % PbS at  $570^\circ\text{C}$  than that of ideal compositions. The ranges were determined using d-spacings vs. compositions curve.

Phase H with a composition of  $3\text{PbS}\cdot \text{Sb}_2\text{S}_3$  (75.00 mole % PbS) is stable at temperatures from  $625\pm 4^\circ\text{C}$  to  $647\pm 3^\circ\text{C}$ , at which it melts incongruently to galena and liquid. It corresponds to  $3\text{PbS}\cdot \text{Sb}_2\text{S}_3$  phase by Kitakaze (1968), Cu-free meneghinite by Wang (1977), and phase III ( $17\text{PbS}\cdot 6\text{Sb}_2\text{S}_3$ , 73.91 mole % PbS) by Salanci and Klein (1979) and Salanci (1979). Cell parameters of phase H determined by the single crystal method are orthorhombic, space group Pbnm,  $a=11.40$ ,  $b=23.68$ ,  $c=4.09\text{\AA}$  and  $Z=4$ . These data are in good agreement with those of phase H ( $3\text{PbS}\cdot \text{Sb}_2\text{S}_3$ ) by Sugaki *et al.* (1969) and Cu-free meneghinite ( $\text{Pb}_{3+x}\text{Sb}_2\text{S}_3$ ) by Wang (1977).

Phase I has a composition of  $76.5\pm 0.5$  mole % PbS. It decomposes to phase H and galena at  $636\pm 3^\circ\text{C}$ , and below  $610\pm 5^\circ\text{C}$ , further to boulangerite and galena. It has an ideal composition of  $16\text{PbS}\cdot 5\text{Sb}_2\text{S}_3$  (76.19 mole % PbS), and corresponds to phase I ( $10\text{PbS}\cdot 3\text{Sb}_2\text{S}_3$ , 76.92 mole % PbS) by Kitakaze (1968), phase I ( $3\text{PbS}\cdot \text{Sb}_2\text{S}_3$ , 75.00 mole % PbS) by Craig *et al.* (1973) and phase II ( $13\text{PbS}\cdot 4\text{Sb}_2\text{S}_3$ , 76.40 mole % PbS) by Salanci (1979). X-ray powder data for these phases are in good accordance with each other. Cell parameters determined by precession and Weissenberg cameras are as follows: orthorhombic, space group Pbnm,  $a=14.24$ ,  $b=25.50$ ,  $c=4.04\text{\AA}$ ,  $Z=1$ .

Galena has a limited solid solution of 1.5 mole % Sb<sub>2</sub>S<sub>3</sub> at  $636^\circ\text{C}$  and melts congruently at  $1133\pm 3^\circ\text{C}$ .

All phases appeared in this study belong to the acicular group mineral. Although the plagionite group minerals can not be synthesized by dry method as described by Robinson (1948), they were successfully synthesized in hydrothermal conditions at  $300^\circ\text{C}$  (Robinson, 1948), and can not be found in the runs at  $350^\circ\text{C}$  (Kitakaze *et al.*, in preparation). Therefore, it is assumed that the plagionite group minerals are stable at temperatures below  $350^\circ\text{C}$ . Their stability fields are under investigation.

Precise X-ray powder data, cell parameters and hydrothermal experimental results of synthetic lead antimony sulfosalts will be described in another paper.

## Summary

The phase relations on the PbS-Sb<sub>2</sub>S<sub>3</sub> join were determined by the experiments using the evacuated glass tube method above  $400^\circ\text{C}$ . The phases of stibnite, zinkenite, robinsonite, boulangerite and five synthetic phases designated as phase D, E, F, H and I belonging to the acicular group minerals were synthesized. The natural analogues of the latter five synthetic

phases are not been known. The chemical compositions and thermal stabilities for the phases synthesized are as follows;

Stibnite melts congruently at 546°C and does not constitute a solid solution with PbS.

Zinkenite has an ideal composition of  $9\text{PbS} \cdot 11\text{Sb}_2\text{S}_3$  and is stable below 546°C, at which it incongruently melts to robinsonite and liquid.

Robinsonite having an ideal composition of  $4\text{PbS} \cdot 3\text{Sb}_2\text{S}_3$ , stable below 582°C, at which it incongruently melts to phase D and liquid.

Phase D with an ideal composition of  $5\text{PbS} \cdot 3\text{Sb}_2\text{S}_3$  is not known as natural mineral, stable from 510° to 590°C.

Phase E having an ideal formula of  $7\text{PbS} \cdot 4\text{Sb}_2\text{S}_3$  is not known as mineral, stable from 584° to 603°C, at which it incongruently melts to boulangerite and liquid.

Phase F with the composition of  $2\text{PbS} \cdot \text{Sb}_2\text{S}_3$  is also not known as mineral, stable from 490° to 584°C.

Boulangerite has an ideal composition of  $5\text{PbS} \cdot 2\text{Sb}_2\text{S}_3$ , stable below 640°C at which it incongruently melts to phase H and liquid.

Phase H with an ideal composition of  $3\text{PbS} \cdot \text{Sb}_2\text{S}_3$  corresponds to synthetic Cu-free meneghinite, stable from 625° to 647°C.

Phase I having the composition of  $16\text{PbS} \cdot 5\text{Sb}_2\text{S}_3$  is not known as natural mineral, stable from 610° to 636°C.

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