Phase relation of some sulfide systems-(6) Especially Pb-Sb-S ternary system

Arashi KITAKAZE (Museum of Sugaki Ore Collection)

Miyuki NAKAMURA and

Ryuichi KOMATSU (Graduate School of Science and Technology)

Abstract:

Phase relation studies for ternary Pb-Sb-S system have been performed by author and some students at Yamaguchi and Tohoku Universities. Their results are mainly reported as some phase diagrams. This paper is described the new phase diagram including some additional data.

Phase relations of the PbS-Sb_2S_3 pseudo system from 700 to 270°C carried by evacuated silica glass tube and hydrothermal synthetic methods were obtained as seen in Fig. 3.

Also, the phase relations for Pb-Sb-S ternary systems determined at 600, 500, 400, 370, 300 and 270° C using dry and hydrothermal methods.

From these experiments, synthetic phases such as I ($Pb_{16}Sb_{10}S_{31}$), H ($Pb_3Sb_4S_6$), F ($Pb_2Sb_2S_5$), E ($Pb_7Sb_8S_{19}$), D ($Pb_5Sb_6S_{14}$), and acicular group minerals such as boulangerite ($Pb_5Sb_4S_{11}$), robinsonite ($Pb_4Sb_6S_{13}$) and zinkenite ($Pb_9Sb_{22}S_{42}$), and prismatic semseyite group minerals ($Pb_{9-2x}Sb_8S_{21-2x}$) as semseyite (x=0), heteromorphite (x=2), plagionite (x=3) and fuloppite (x=4) were obtained.

***Key Words**: PbS-Sb_2S_3 join, Pb-Sb-S ternary system, lead-antimony sulfosalt minerals*

1. Introduction

Many minerals and synthetic phase are reported in PbS-Sb_2S_3 pseudo-binary system. These phases are separated to acicular grope minerals such as Cu-free meneghinite, boulangerite, robinsonite and zinkenite and polyhedral group minerals such as semseyite, heteromorphite, plagionite and fuloppite.

The phase relations of the PbS-Sb_2S_3 pseudo-binary system have been studied by many authors[1)-13)] using the evacuated silica glass-tube method (dry method) above 400°C, and many synthetic phases of acicular group minerals were reported. The crystallographic data of these minerals and synthetic phase were determined by Kitakaze *et al.*[14)], Kitakaze *et al.*[15)] and Wang[16)].

Hydrothermal synthetic study has been only done below 400°C by Robinson[1)] until 1970, but we have been performed above 350°C by the thermal gradient transporting method under hydrothermal condition for the PbS-Sb_2S_3 pseudo-binary system, and reported by Kitakaze *et al.*[17)], and Sugaki *et al.*[18)].

Pb-Sb-S ternary system by Yamamoto *at al.*[12], Nakamura.[18]. However, the reaction rates below 400°C are very sluggish. Therefore, it is necessary very long-time experiments to obtain the equilibrium state. Then, mineral synthesis was done using hydrothermal method below 350°C by as same as Kitakaze *et al.*[17] and Sugaki *et al.*[18]. From their data, phase diagrams below 300°C were obtained. This report is mainly described of studies by our laboratories at Yamaguchi and Tohoku Universities.

Crystallographic and chemical formula of the synthetic phases and minerals appeared in this study are shown in Table 1.

Table 1. Mineral name and synthetic phases of chemical formula and cell parameters appeared in this study

Mineral name & phases	Abb.	Chemical formula	Crystal system	Space group	Z	Cell parameters			
						a	b	c	β
Galena	gn	PbS	Cub	Fm3m	4	5.936(1)	—	—	
Phase I	I	$Pb_{16}Sb_{10}S_{31}$	Orth	Pbnm	1	14.240(12)	25.500(18)	4.040(1)	
Phase H (Cu-free meneghinite)	H	$Pb_3Sb_2S_6$	Orth	Pbnm	4	11.425(6)	24.072(11)	4.102(3)	
Boulamgerite	blg	$Pb_5Sb_4S_{11}$	Orth	Pbnm	6	21.235(16)	23.464(16)	4.032(6)	
Semseyite	sms	$Pb_9Sb_8S_{21}$	Mon	C2/c	4	13.642(7)	11.941(7)	24.54(2)	106.42(4)
Phase F	F	$Pb_2Sb_2S_5$	Mon	C2/m	17	20.780(12)	50.300(20)	4.010(5)	114.50(19)
Phase E	E	$Pb_7Sb_8S_{19}$	Orth	Pbnm	1	11.310(5)	19.780(12)	4.040(3)	
Heteromorphite	htr	$Pb_7Sb_8S_{19}$	Mon	C2/c	4	13.638(8)	11.960(7)	21.290(9)	90.76(5)
Phase D	D	$Pb_5Sb_6S_{14}$	Mon	A2/m	4	21.980(9)	35.120(10)	4.020(3)	126.25(11)
Robinsonite	rbs	$Pb_4Sb_6S_{13}$	Mon	I2/m	4	23.661(12)	3.977(2)	24.433(12)	93.79(4)
Plagionite	plg	$Pb_5Sb_8S_{17}$	Mon	C2/c	4	13.468(6)	11.831(4)	19.897(10)	106.47(5)
Zinkenite	znk	$Pb_9Sb_{22}S_{42}$	Hex	P63	4	22.120(4)	—	4.325(2)	
Fuloppite	flp	$Pb_3Sb_8S_{15}$	Mon	C2/c	4	13.420(7)	11.717(6)	16.909(7)	94.78(5)
Stibnite	stb	Sb_2S_3	Orth	Pbnm	4	11.229(2)	11.310(2)	3.893(1)	

2. Experimental Procedures

2.1 Evacuated silica glass tube method

Synthetic experiments for PbS-Sb_2S_3 pseudo-binary system were mainly carried out by the evacuated silica-glass tube method which is about as same as described by Kitakaze[3], Kitakaze *et al.*[11], Sugaki *et al.*[14], Kitakaze *et al.*[15] and Nakamura[19] using previously synthetic lead and antimony sulfide by reaction between metals (over 99.999% in purity) and crystalline sulfur (99.99%). Their sulfides were grinding under acetone in agate mortar, and they were heated at temperatures from 600 to 350°C from 6 to 200 days. From these experiments, aggregate of acicular crystals is obtained as seen in Fig. 1.

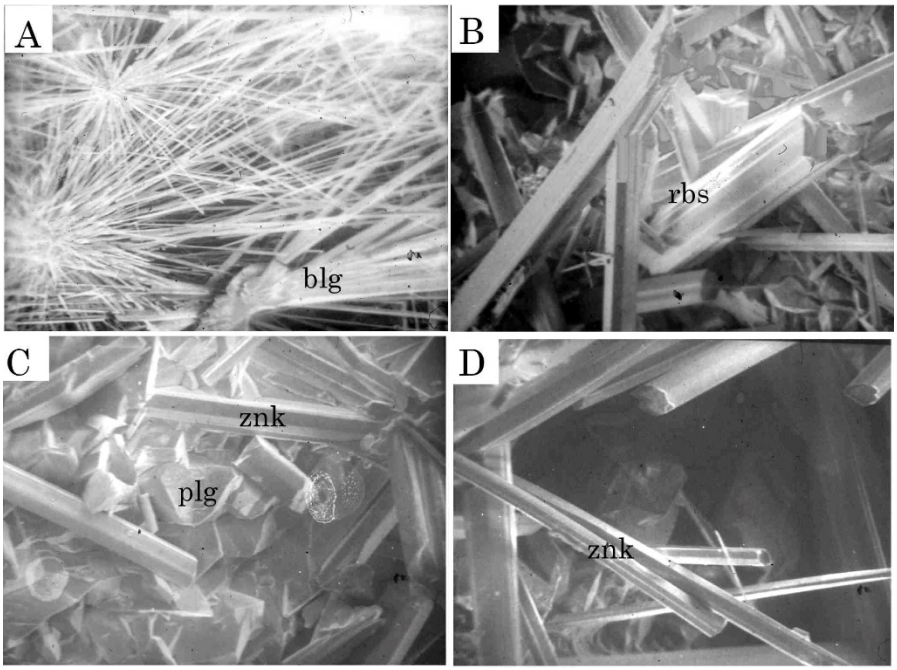

Fig. 1. SEM images of aggregate of acicular crystals synthesized by dry method (width 0.3mm) A: boulangerite (blg) crystals, B: robinsonite (rbs) crystals, C: acicular crystal of zinkenite (znk) and polyhedral crystals of plagionite (plg), D: acicular crystal of zinkenite.

2.2 Hydrothermal synthesis

Mineral synthesis of lead-antimony sulfosalt minerals have been studied by thermal gradient transporting method with 5 m NH_4C1 aqueous solution in gold tube at 300°Cunder pressure of 29 MPa as same method as described by Kitakaze[20] As nutrient materials, mono-phase mineral or their mixture of powdered sulfides synthesized in advance by dry method were employed.

By hydrothermal method, acicular or prismatic crystals as seen in Fig. 2 were synthesized.

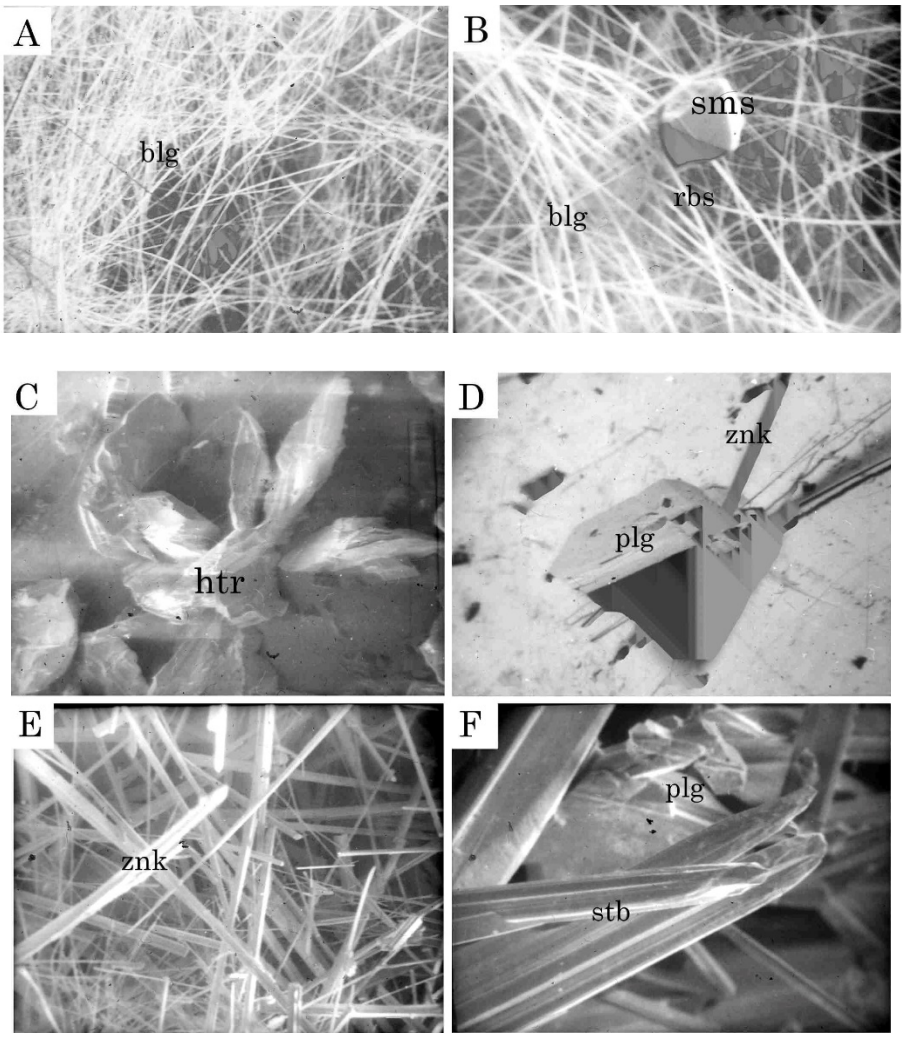

Fig. 2.SEM images for aggregate of euhedral crystals synthesized by hydrothermal method (wide: 0.3mm).

A: Aggregate of acicular boulangerite crystals (350℃), B: acicular crystals of boulangerite associating polyhedral crystal of semseyite (350℃), C: polyhedral crystals of heteromorphite (300℃), D: polyhedral crystal of plagionite associating with acicular zinkenite (350℃), E: aggregate of acicular zinkenite crystals (350℃), D: associating with polyhedral fuloppite and acicular stibnite crystals (280℃).

2.3 Identification of phases

All the run products obtained using the evacuated glass tube method were fine to coarse grained sulfide and their mixture and examined by ore microscope, SEM, and XRD by diffractometer for determination of phases and phase assemblages. Sometimes, the cell parameters for synthetic phases were determined using X-ray single crystal method by precession camera and X-ray single crystal diffractometer.

Their XRD data were obtained by diffractometer and the Guinier camera and cell parameters were refined by their data XRD about same as Kitakaze[21].

3. Phase relation for PbS-Sb_2S_3 pseudo-binary system

The phase relations of PbS-Sb_2S_3 binary join in Pb-Sb-S from 700 to 250°C obtained using the evacuated silica-glass tube method. Reaction products were usually aggregate of acicular

crystal as shown in Fig. 1. Phase relations of PbS-Sb_2S_3 pseudo-binary system are given in Fig. 3. There are consisted with the synthetic phase I, H, F, D and acicular minerals such as boulangerite, robinsonite and zinkenite.

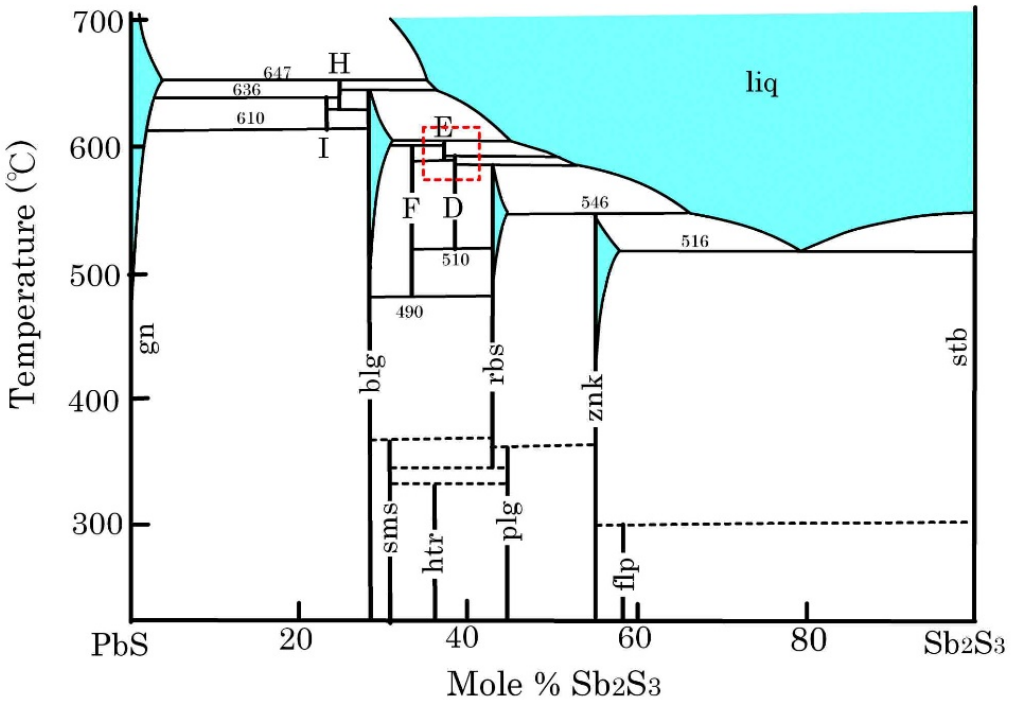

Fig. 3. Phase diagram of PbS-Sb_2S_3 pseudo-binary join in the Pb-Sb-S ternary system. Blur area: mono-phase regions. Abbreviations are seen in Table 1.

Synthetic phase I decomposes to galena and phase H galena at 636°C, and below 610℃ to galena and boulangerite. It has an ideal composition of $Pb_{16}Sb_{10}S_{31}$, and corresponding to phase I by Kitakaze[3] and by Kitakaze *et al.*[11] Cell parameters determined by precession camera and refined by XRD using least square method as seen in Table 1.

Synthetic phase H with composition of $Pb_3Sb_2S_6$ is stable at temperatures from 625 to 647℃, at which it melts incongruently to galena and liquid. It is corresponding to phase H by Kitakaze[3], Cu-free meneghinite by Wang[16], Kitakaze *et al.*[11) 15)] and Sugaki et al.[14] Cell parameters determined by the single crystal methods and refined using XRD by least square method as seen in Table 1. These data are good agreement with those of phase H by Kitakaze[3], Cu-free meneghinite by Wang[12] and Kitakaze *et al.*[11) 14) 15)] Although this phase is stable above 625℃ in the PbS-Sb_2S_3 join, it may be stable to room temperature with some amount of Cu content as meneghinite.

Boulangerite with ideal composition of $Pb_5Sb_4S_{11}$ melts incongruently to phase H and liquid at 640℃, at which it has limited solid solution to Sb_2S_3 rich side. Refined cell parameters using XRD is given in Table 1.

Phase F with ideal compositing of $Pb_2Sb_2S_5$ stables at temperatures from 490 to 584℃. But below 490℃, it has more sulfur-rich composition than PbS-Sb_2S_3 join (Yamamoto *et al.* [12] and Sugaki *et al.*[13]), and then disappears from the join although it is appeared at about 390℃ as ternary phase. Refined cell parameters using XRD is given in Table 1. This phase having

composition of $Pb_2Sb_2S_5$ may be corresponding to plumosite, but this mineral was not been précised crystallographic data, so this identification is doubtful.

Relations between phase E and phase D are somewhat complicate, then their relations are shown in Fig. 4 enlarged of red squares area of Fig. 3.

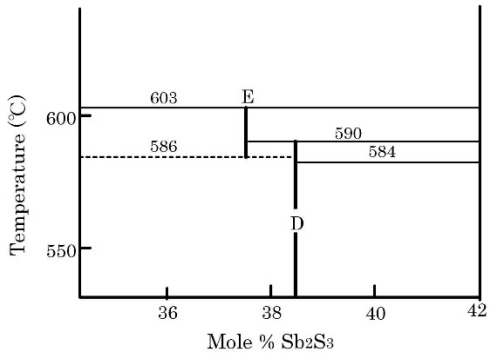

Fig. 4. Relation ship between phase E and phase D at red square area in Fig. 3.

Phase E with $Pb_7Sb_8S_{19}$is stable only in the temperature range from 586℃ to 603℃, at which it melts incongruently to boulangerite and liquid. Below 586℃, its composition is changing to more Sb rich side, then disappeared from PbS-Sb_2S_3 join, and stables to about 390℃ as ternary phase. Cell parameters of this phase determined by single crystal method and refined by XRD using least squares method as seen in Table 1.

Robinsonite with ideal composition with $Pb_4Sb_6S_{13}$ is stable below 584℃. It melts incongruently to phase D and liquid and has limited solid solution from 42.86 to 55.25 mole % Sb2S3 at 540℃. This mineral is stable to about 350℃ in this join, but it composition is change to more metal rich at about 320℃. Cell parameters synthesized at 500℃ are determined by XRD using X-ray single crystal method (Table 1).

Zinkenite with ideal composition of $Pb_9Sb_{22}S_{42}$ incongruently melts to robinsonite and liquid and has eutectic with stibnite at 516℃. It has limited solid solution of 2.0 mole % Sb_2S_3 at 516℃, and stables to room temperature. Refined cell parameters for the mineral is shown in Table 1.

Below 400℃, many minerals appeared in this join. There are acicular group minerals such as boulangerite, robinsonite and zinkenite and plagionite group minerals such as semseyite, heteromorphite, plagionite and fuloppite synthesized by dry and hydrothermal methods.

At 350℃, assemblages of boulangerite + semseyite, semseyite + robinsonite, robinsonite + plagionite and plagionite + zinkenite are appeared in this join. But at 300℃, robinsonite disappeared from the join because its composition changes to more metal-rich side at 320℃. And fuloppite is not appeared in this join.

4. Ternary phase relations of Pb-Sb-S system

Phase relations at 600℃

Phase diagram at 600℃ is given in Fig. 5. There are boulangerite with limited solid solution area, phase E, phase F and galena are appeared stable phase, and wide region of sulfide liquid in Sb-rich side associating with phase I. There are 5 univariant assemblages at this temperature.

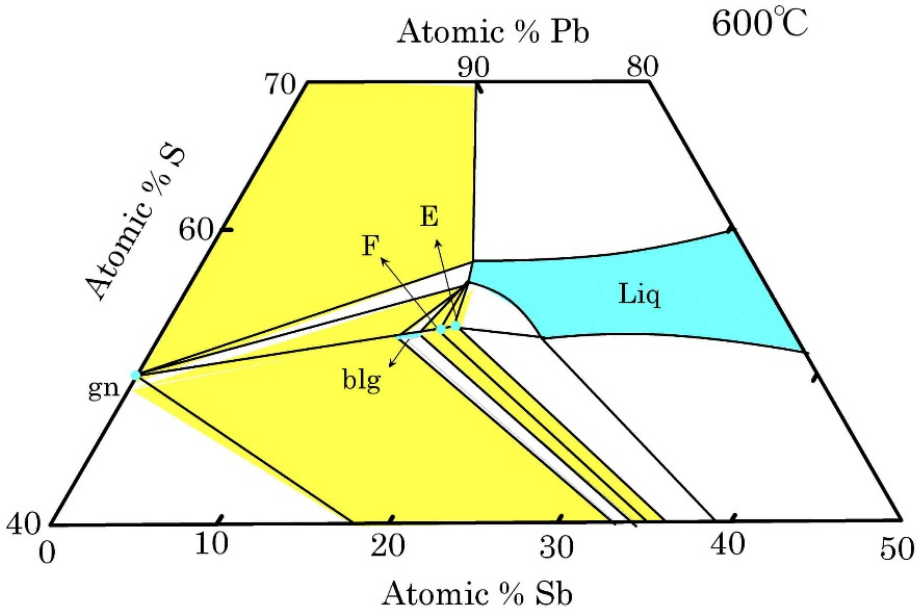

Fig. 5. Phase diagram for central portion of Pb-Sb-S ternary system at 600℃. Abbreviation is same to Table 1.

Phase relations at 500℃

Phase relations at 500℃ is shown in Fig. 6. Galena, boulangerite, phase F, Phase D, robinsonite, zinkenite and stibnite appear as stable phases in the ternary diagram, but phase D is more metal-rich composition than PbS-Sb_2S_3 join. Synthetic phase E disappears at this temperature because decomposed to phase F and D at 510℃. Sulfide liquids remain as separate two regions of sulfur rich and metal rich sides. There are 16 univariant assemblages.

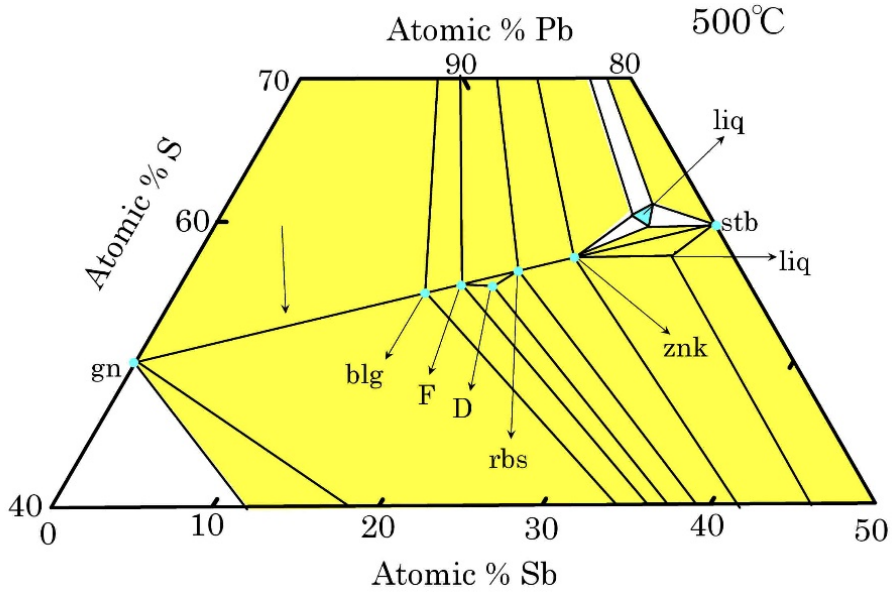

Fig. 6. Phase relations of central portion of Pb-Sb-S ternary system at 500℃.

Phase relations at 400℃

Ternary phase diagram for 400℃ is shown in Fig. 7. Stable phases such as galena, phase F, phase D, robinsonite, zinkenite and stibnite are appeared. But, phases F and D are not belonging in PbS-Sb_2S_3 join because former is changing to sulfur-rich composition and later to metal rich composition at 490℃ and 510℃, respectively. Sulfide liquid disappears at this temperature. There are 13 univariant assemblages at this temperature.

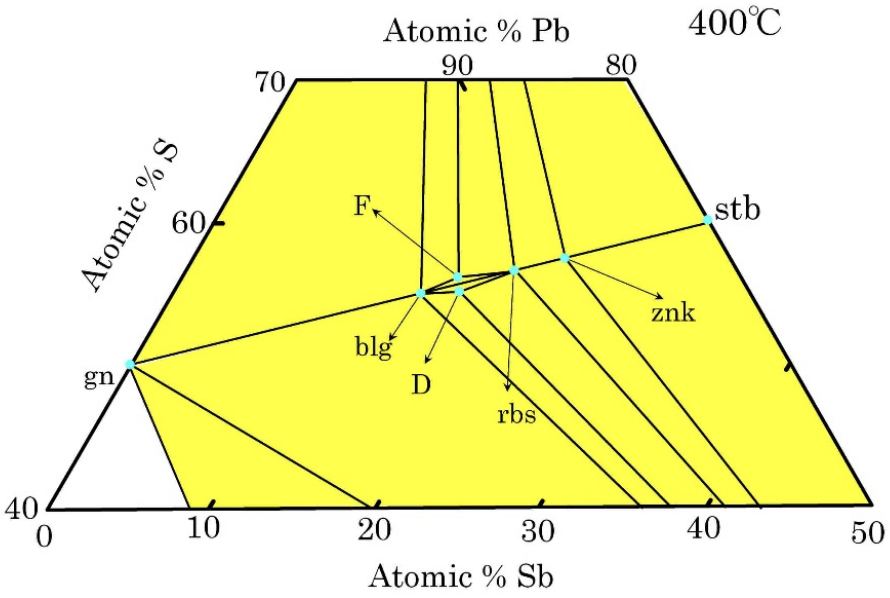

Fig. 7. Phase diagram for central portion of Pb-Sb-S ternary system at 400℃.

Phase relations at 370℃

Phase relations at 370℃ is shown in Fig. 8. Boulangerite, semseyite, robinsonite, plagionite zinkenite and stibnite are stable phase at this temperature. Semseyite and plagionite as stable phases appear at this temperature. Synthetic phases F and D appeared at 400℃ are decomposed about 380℃, then disappeared from the diagram. There are 13 univariant assemblages.

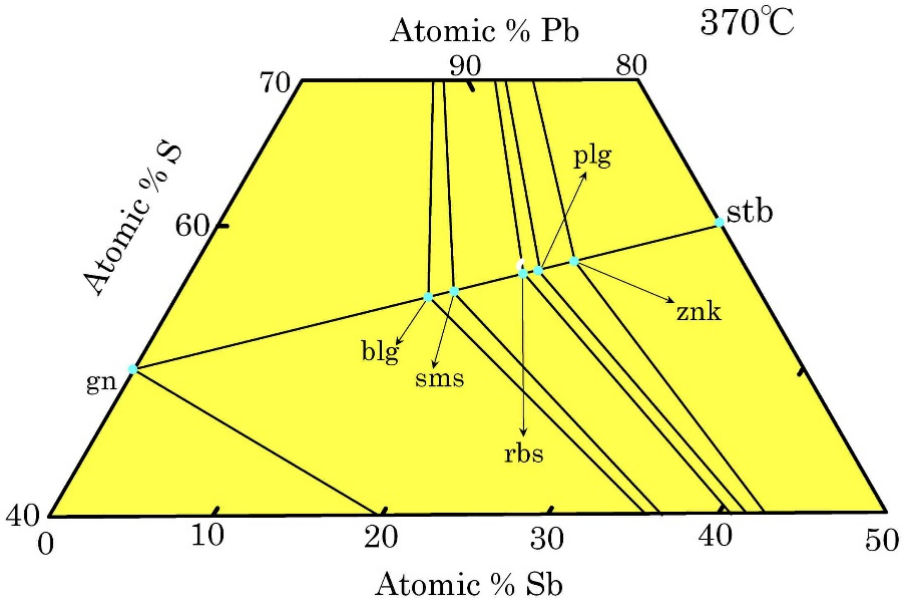

Fig. 8. Phase relations of Pb-Sb-S ternary system at 370℃.

Phase relations at 300℃

Schematic phase diagram at 300℃ is shown in Fig. 9. Heteromorphite firstly appears as stable phase at this temperature. Then, there are 8 stable phases such as boulangerite, semseyite, heteromorphite, robinsonite plagionite, zinkenite and stibnite. But robinsonite composition changes to metal-rich side from PbS-Sb_2S_3 join.

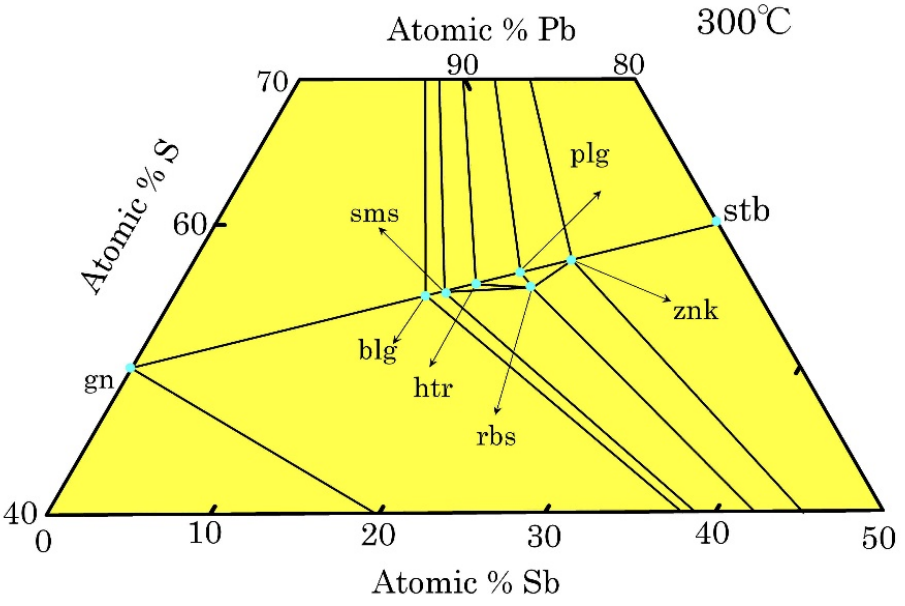

Fig. 9. Phase relations of central portion of ternary Pb-Sb-S system at 300℃.

Although phase relations at 280℃ are not obtained. But assemblage between fuloppite and stibnite was synthesized hydrothermally (Sugaki *et al.* [8]) as seen in Fig. 2, the fuloppite may be stable below about 280℃.

References

1) Robinson, S.C. (1948) Synesis of lead sulphantimonides. Econ. Geol., **43**, 293-312.

2) Jambor, J.L. (1968) New lead sulfantimonides from Madoc, Ontario, Part 3, Synthesis, paragenesis, origin. Can. Miner., **9**, 05-521.

3) Kitakaze, A. (1968) Mineral synthesis and its phase relations in PbS-Sb_2S_3 system.(unpub.) M.S. Thesis Yamaguchi Univ. (in Japanese).

4) Jambor, J.L. (1968) New lead sulfantimonides from Madoc, Ontario, Part 3, Synthesis, paragenesis, origin. Can. Miner., **9**, 505-521.

5) Salanci, B. and Moh, G. (1970) The pseudobinary join galena-anitmonite, PbS-Sb_2S_3. Neues Jahrb. Miner. Mh., **1970**, 524-528.

6) Craig, J.R., Chang, L.L.Y. and Lees, W.R. (1973) Investigations in the Pb-Sb-S system. Can. Miner., **37**, 438-446.

7) Garvin, P.L. (1973) Phase relations in the Pb-Sb-S system. Neues Jahrb. Miner. Abh., **118**, 235-267.

8) Wang, N. (1976) A study along the PbS-Sb_2S_3. Neues Jahr. Mine. Abh., **1976**, 79-81.

9) Wang, N. (1976) Phases along the PbS-Sb_2S_3 join Neues Jahr. Mine. Abh., **128**, 167-175.

10) Salanci, B. and Klein, D. (1979) Beitrage zunm System Pb-Sb-S. Chem. Erde, **38**, 105-114.

11) Kitakaze, A., Sugaki, A. & Shima, H. (1995) Study of the minerals on the PbS-Sb_2S_3 join, Part 1: Phase relation above 400℃. Miner. Jour., **17**, 282-289.

12) Yamamoto、T., Sugaki, A., Shima, H. & Kitakaze, A. (1973) Phase relation of Pb-Sb-S system (1). Jour. Japan. Miner. Petrol. Econ. Geol., **68**, 94 (Abstr. In Japanese).

13) Sugaki. A., Shima, H., Kitakaze, A. & Yamamoto, T. (1973) Phase relations of Pb-Sb-S system (2). Annual Meeting Abstr. Miner. Soc. Japan 46 (Abstr. In Japanese).

14) Sugaki, A., Shima, H. & Kitakaze, A. (1969) Crystal data for synthetic phases in PbS-Sb_2S_3 system. Jour. Japan. Assoc. Mineral. Petrol. Econ. Geol., 61, 172-173 (Abstr. In Japanese).

15) Kitakaze, A., Sugaki, A. & Shima, H. (1973) Synthetic sulfide minerals (V). Tech. Rept. Yamaguchi Univ., **1**, 182-192.

16) Wang, N. (1977) Synthesis and crystal data of a Cu-free “meneghinite”. Can. Miner., **15**, 115-116.

17) Kitakaze, A., Sugaki, A. & Shima, H. (1975) Pb-Sb sulfosalt mineral synthesized by hydrothermal method (1). Abstr. Annual Meeting Miner. Soc. Japan 114 (Abstr. In Japanese).

18) Sugaki, A., Shima, H. & Kitakaze, A. (1975) Pb-Sb sulfosalt mineral synthesized by hydrothermal method (2). Abstr. Joint Meeting 104 (Abstr. In Japanese).

19) Nakamura, M. (1977) Study of lead-sulfosalt minerals, especially PbS-Sb_2S_3-As_2S_3 system. M.S. Thesis Yamaguchi Univ. (in Japanese).

20) Kitakaze, A. (2018) Phase relations of some sulfide systems (4) Especially Cu-Fe-S system. Mem. Fac. Eng. Yamaguchi Univ., **68,** 55-76.

21) Kitakaze, A. (1996) Cell Parameters Refinement Using Guinier Method (in Japanese). Jour. Miner. Soc. Japan, **25**, 69-7

(Received.November.30.2020)