Phase relation of some sulfide system-(1)

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Abstract:

Phase relation studies for binary system of Fe-S and Ni-S, and ternary system such as Ag-Au-S, Ag-Au-Se, Ag-Se-S and Ag-Sn-S have been performed. Their results are described as mainly phase diagrams.

***Key Words**: Fe-S system, Ni-S system, Ag-Au-S system, Ag-Au-Se system, Ag-Se-S, Ag-Sn-S system*

Introduction

I have been doing the experimental studies on the phase equilibrium for sulfide or sulfosalt systems since 1966 in Yamaguchi University and Tohoku University association with Dr. Sugaki and students in both universities as bachelor thesis, master's thesis and doctoral thesis. For some sulfide systems, I have been already published in some journals. However, because many experimental results are still unpublished, I have wanted to continue to publish in conjunction with published results.

The results for binary systems such as Fe-S and Ni-S, and ternary systems as Ag-Au-S, Ag-Au-Se, Ag-Se-S and Ag-Sn-S are described in this time.

Experimental Procedures

Synthetic experiments were carried out by the silica-glass tube method which is about same described by Kitakaze *et al*.[1].

All the run products were examined by reflected light microscope and XRD for determination of phases and phase assemblages. Sometimes, high-temperature XRD methods by high-temperature diffractometer or high-temperature Debye-Scherer camera were using the determination for unquenchable high-temperature phases, and rarely high-temperature precession method was used for determination of structure type such as pyrrhotite type phases. XRD for some synthetic phases were performed using the Guinier method and cell parameters are refined by their data as same as Kitakaze[2].

Differential thermal analysis (DTA) in the evacuated silica-glass tube was performed to obtain the temperatures of reactions causing the phase changes such as liquids, solidus, eutectic, peritectic, eutectoid, peritectoid, polymorphic phase transitions and tie-line changes in the phase diagram.

Binary systems

Fe-S system

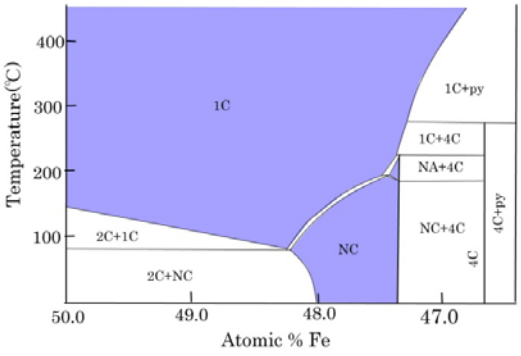

Figure 1. Phase diagram on pyrrhotite below 450℃ after Sugaki *et al*.[3]. Abbreviations; 2C: troilite (FeS), NC: hexagonal pyrrhotite ($Fe_{1-x}S$), NA: intermediate pyrrhotite ($Fe_{1-x}S$), 1C: high-form pyrrhotite ($Fe_{1-x}S$), 4C: monoclinic pyrrhotite (Fe_7S_8).

Ni-S system

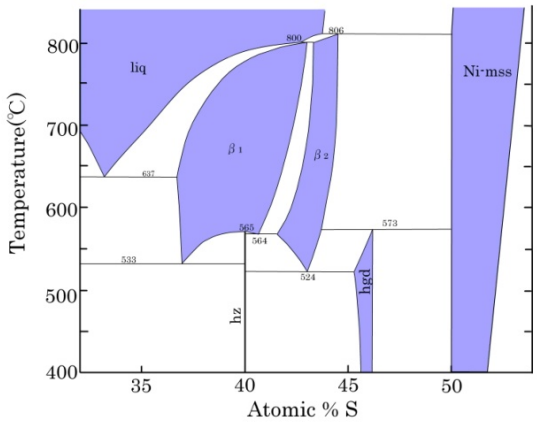

Figure 2. The phase diagram for the composition range from 32.0 to 54.0 atomic % S in the Ni－S binary at temperatures from 400° to 825℃ after Kitakaze *et. al.*[1]. Symbols: β_1: phase β_1 (Ni_3S_2 SS), β_2: phase β_2 (Ni_4S_3 SS), hz: heazlewoodite (Ni_3S_2), hgd: high-form godlevskite (Ni_7S_6), Ni-mss: Ni monosulfide SS ($Ni_{1-x}S$), liq: liquid, SS: solid solution.

Ternary systems

Ag-Au-S system

The minerals and phases within the Ag-Au-S system are given together with their crystal data and thermal stabilities in Table 1. Besides gold and silver including electrum, argentite and acanthite, uytenbogaadtite, petrovskaite as minerals, and primitive cubic (pc), body-centered cubic (bcc) and face-centered cubic (fcc) phases as synthetic phase in the system. Within them argentite, pc, bcc and fcc phases are unquenchable high-temperature form. Thus, to obtain their crystal data and phase relations, DTA and high-temperature XRD methods had to be used.

Table 1. Minerals and phases appeared in the Ag-Au-S system

Minerals and phases	Symbols	Compositions	Thermal stability Low limit	High limit	
Acanthite	ac	Ag_2S		179	Inversion to high form (bcc)
Argentite	bcc	Ag_2S	179	593	Inversion to fcc
High-form argentite	fcc	Ag_2S	593	834	Congruent melting
Uytenbogaadtite	uty	Ag_3AuS_2	-	180	Inversion to high form (pc)
High-form uytenbogaadtite	pc	$(Ag,Au)_2S$	180	400?	Decomposed to fcc + pc
Petrovskaite	ptr	AgAuS	-	296	Inversion
High-form petrovskaite	fcc	$(Ag,Au)_2S$	296	745	Congruent melting

The phase relations along the Ag_2S-Au_2S join in the Ag-Au-S system are shown in Figure 3 by the data compiled from Graf [4], Kitakaze *et al.*[5], Sugaki *et al.*[6], Barton [7] and Pal'yanova *et al.*[8].

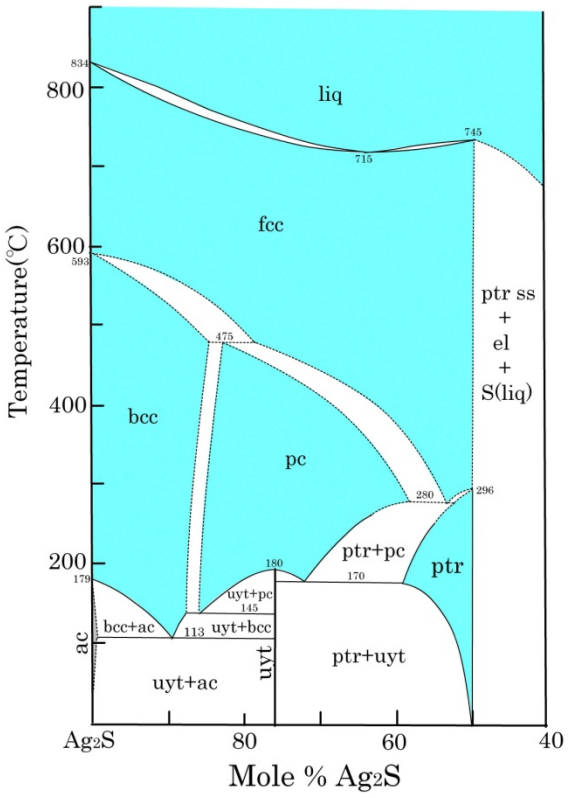

Figure 3. Phase diagram for Ag_2S rich potion of Ag_2S-Au_2S join in the Ag-Au-S system compiled after Graf [3], Kitakaze *et al*, [4], Sugaki *et al.*[5], Barton[6] and Pal'yanova *et al.*[7]. See Table 1 for symbols.

Phase relations in the ternary Ag-Au-S system at 500, 250 and 150℃ were studied by Kitakaze *et. al.*[5] and Sugaki *et al.*[6], and compiled their data as showing in Figures 4, 5 and 6.

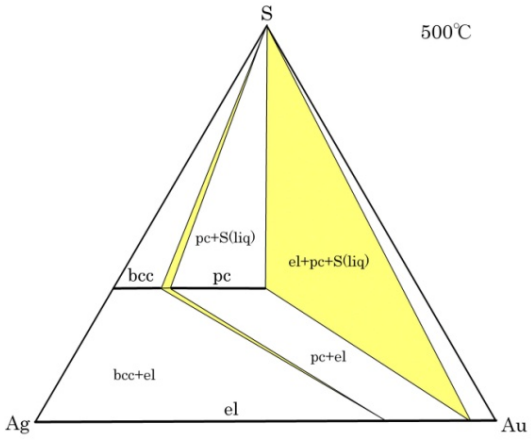

Figure 4. The phase diagram in the Ag-Au-S system at 500℃ complied after Kitakaze et *al.* [5] and Sugaki *et al.*[6] . See Table 1 for symbols, el: electrum, S(liq): sulfur liquid.

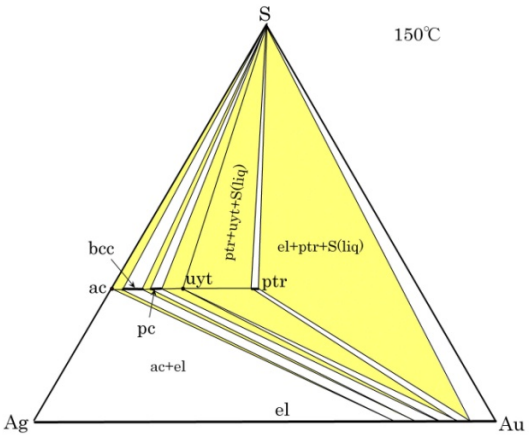

Figure 6. The phase diagram in the Ag-Au-S system at 150℃ complied after Kitakaze *et. al.* [5] and Sugaki *et. al.*[6] . See Table 1 for symbols, el: electrum, S(liq): sulfur liquid.

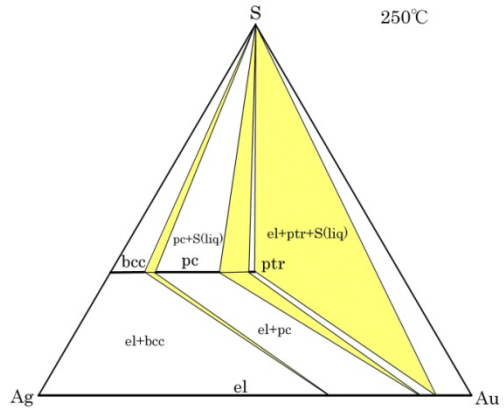

Figure 5. The phase relations of the Ag-Au-S system at 250℃ complied after Kitakaze *et. al.*[4] and Sugaki *et. al.* [5] . See Table 1 for symbols, el: electrum, S(liq): sulfur liquid.

Ag-Au-Se system

The phase relations of the Ag-Au-Se system were studied by Iijima[9] using the evacuated glass-tube method, DTA and high-temperature XRD. The phase diagram for Ag_2Se rich potion of Ag_2Se-Au_2Se join in this system compiled after his data is shown in Figure 7. In this join, there are four solid phases as naumannite (Ag_2Se), fischesserite (Ag_3AuSe_2), synthetic phase X (AgAuSe: correspond to Se-rich Petrovskaite) and bcc (correspond to high-form of naumannite and fischesserite) . The synthetic phase AgAuSe was also found by Nekrasov *et al.*[10], but was not synthesized by Echmaeva and Osadchi[11]

The phase relations of the Ag-Au-Se ternary system also performed by Iijima[9] and obtained the isothermal diagrams at 500, 250 and 150℃ showing in Figure 8, 9 and 10. In the ternary system, synthetic AuSe appears in addition with above four phases, this phase also has been reported by Rabenau *et al.*[11], Karakaya and Thompson[12] and Echmaeva and Osadchi[13].

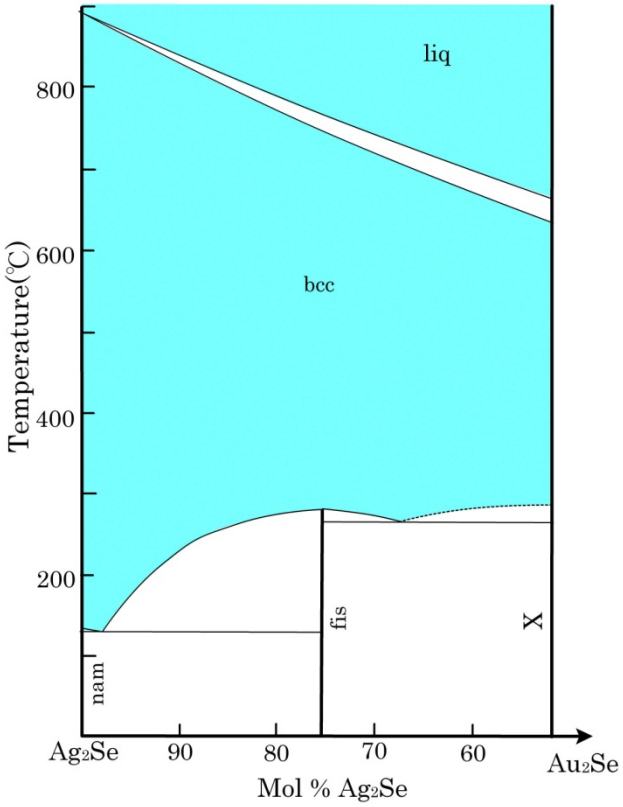

Figure 7. Phase diagram for Ag_2Se rich potion of Ag_2Se-Au_2Se join in the Ag-Au-Se system compiled after Iijima[8]. Abbreviations; num: naumannite, fis: fischesserite, bcc: solid solution of high-form for naumannite and fischesserite, X: synthetic phase X with AgAuSe .

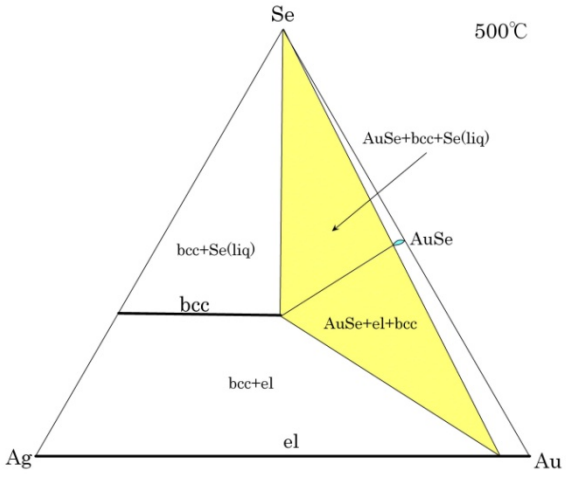

Figure 8. Isothermal diagram of Ag-Au-Se system at 500℃ compiled after Iijima[8]. Abbreviations are same to Figure 7. el: electrum, Se(liq): liquid Se.

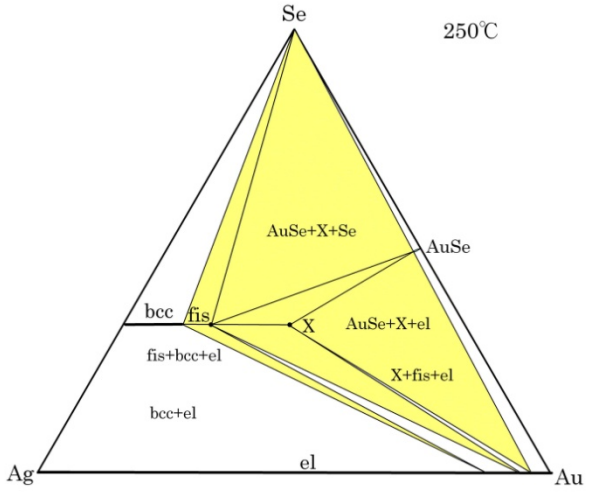

Figure 9. Isothermal phase diagram of Ag-Au-Se system at 250℃ compiled after Iijima[8]. Abbreviations are same to Figure 8.

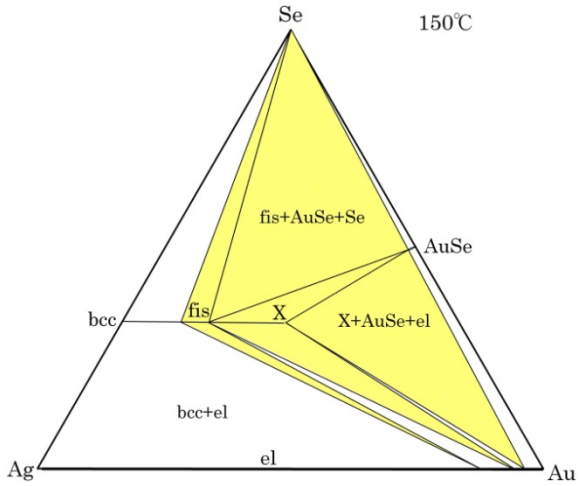

Figure 10. The phase diagram of Ag-Au-Se system at 150℃ compiled after Iijima[8]. Abbreviations are same to Figure 7.

Ag-Se-S system

The minerals belonging in the Ag-Se-S system are acanthite, low- and high-argentite, aguilarite and low- and high-naumannite. All phases within the Ag_2S-Ag_2Se join in the system.

The phase relations of the Ag_2S-Ag_2Se join in the Ag-Se-S system were studied by Iijima *et al.* [13], Petruck *et al.* [14], Sugaki & Kitakaze [15], Bontschwa -Mladenowa and Zaneva [16] and Pal'yanova *et al.* [17]. The phase diagram compiled from the data by Iijima *et al.* [13] and Sugaki & Kitakaze [15] using the evacuated glass-tube method, DTA and high-temperature XRD is

shown in Figure 10.

Acanthite (ac) with monoclinic form inverts to unquenchable low-argentite with body-centered cubic (bcc) form at 179℃, and the bcc form changes to unquenchable face-centered cubic (fcc) lattice at 593℃. Wares low-naumannite having orthorhombic cell transforms to high-temperature form with unquenchable bcc cell at 130℃, and the bcc melts congruently at 889℃.

Aguilarite forms a widely continuous solid solution with acanthite ranging from 0 to 73 mole % Ag_2Se at 80℃. Also low-naumannite has a limited solid solution with 81 to 100 mol. % Ag_2Se at 80℃. There is immiscibility field from 73 to 81 mole % Ag_2Se at 80℃. As mentioned above, aguilarite is corresponding to Se-rich portion of the continuous solid solution between acanthite and aguilarite, and is not an independent phase that is different by Petruk *et al.* [15].

Eutectoid reaction between acanthite-aguilarite solid-solution and naumannite solid-solution occurs at 80 ℃ and 75 mole % Ag_2Se, and aguilarite solid-solution transforms to bcc phase at this temperature or above the continuous solid-solution of the bcc phase between Ag_2S and Ag_2Se in the join at temperatures from 179° to 593℃.

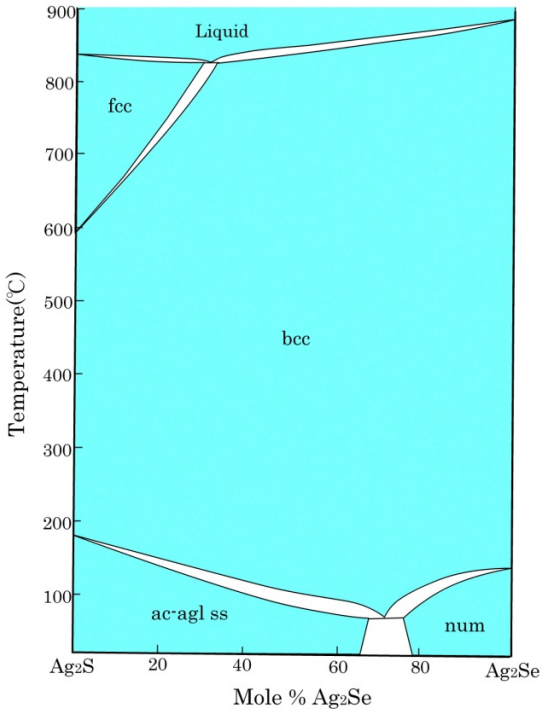

Figure 11. Phase diagram of Ag_2S-Ag_2Se join in the Ag-Se-S system compiled after Iijima *et. al.*[14] and Sugaki and Kitakaze[16]. Abbreviations are ac: acanthite, agl: aguilarite, num: naumannite, bcc: high-form acanthite (argentite)-high-form naumannite solid solution

Ag-Sn-S system

The phase relation studies and mineral synthesis in Ag-Sn-S system were performed by Kitazawa *et al.*[18] and Sugaki *et al.*[19]. According their results, there are recognized canfieldite (Ag_8SnS_6), synthetic phases X (Ag_2SnS_3) and Y ($Ag_4Sn_3S_8$) as ternary compounds in the Ag-Sn-S system besides herzenbergite (SnS), ottemanite (Sn_2S_3) and berndtite (SnS_2) in the Sn-S join and silver (phase α) and phase ζ (Ag-Sn alloy) in the Ag-Sn join. The crystal data and thermal stability of the ternary phases in the present system are summarized in Tables 1 and 2, respectively.

Table 2. Cell parameters of minerals and synthetic phases in the Ag-Sn-S system after Sugaki *et al.*[20]

Minerals and phases	Compositions	Crystal system	Cell parameters			
			a(Å)	b(Å)	c(Å)	β(°)
Canfieldite	Ag_8SnS_6	Orth	15.3050	7.5531	10.7046	-
Phase X	Ag_2SnS_3	Mon	6.6280	11.4740	13.2310	97.97
Phase Y	$Ag_4Sn_3S_8$	Cub	10.7972	-	-	-
Berndtite	SnS_2	Hex	3.6476	-	5.8970	-
Ottemannite	Sn_2S_3	Orth	8.8180	14.0350	3.7460	-
Hezenbergite	SnS	Orth	4.3291	11.1923	3.9838	-

Table 3. Thermal stability range of phases in the Ag-Sn-S system after Kitazawa *et al.*[18]

Minerals and phases	Symbols	Compositions	Thermal stability		Reaction
			Low limit	High limit	
Acanthite	ac	Ag_2S		179	Inversion to high form (bcc)
Argentite	bcc	Ag_2S	179	593	Inversion to fcc
High-form argentite	fcc	Ag_2S	593	834	Congruent melting
Canfieldite	cf	Ag_8SnS_6	-	174	Inversion to high form
High-form cabfieldite		Ag_8SnS_6	174	855	Congruent melting
Phase X	X	Ag_2SnS_3	-	646	Incongruent melting
Phase Y	Y	$Ag_4Sn_3S_8$	258	676	Incongruent melting
Berndtite	brn	SnS_2	-	692	Inversion to high form
High-form berndtite	h-brn	SnS_2	692	865	Congruent melting
Ottemannite	ott	Sn_2S_3	-	668	Inversion to high form
High-form ottemannite	h-ott	Sn_2S_3	668	759	Incongruent melting
Hezenbergite	hz	SnS	-	597	Inversion to high form
High-form hezenbergite	h-hz	SnS	597	874	Congruent melting

The phase diagram of the Ag_2S-SnS_2 join obtained by Kitazawa *et al,* [18] using the evacuated silica

glass-tube method and differential thermal analysis is shown in Figure 12.

Canfieldite has two polymorphs of high- and low-phases with an inversion point, 174°C. This high-form is unquenchable, and melts congruently at 855°C. The synthetic phases X and Y were also are not yet confirmed as a natural phase. According to them, the phase X melts incongruently to phase Y and liquid at 646°C. Whereas phase Y also melts incongruently to SnS_2 and liquid at 676°C. There are present two eutectic points at 767°C and 7 mol % SnS_2 between Ag_2S and high-canfieldite and at 644°C and 45 mole % SnS_2 between high-canfieldite and phase X. Phase Y is not stable below 258℃, and then break down to Phase Y and herzenbergite.

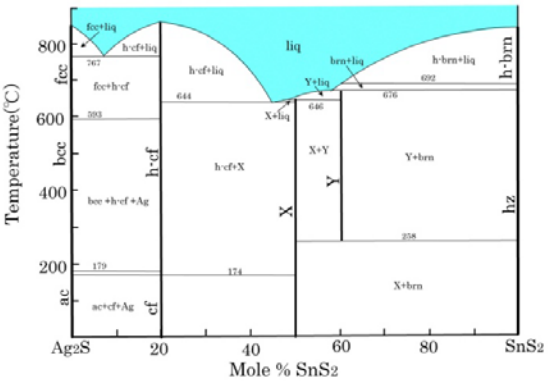

Figure 12. Phase diagram of Ag_2S-SnS_2 join in the Ag-Sn-S system compiled after Kitazawa *et al.* [18]. Abbreviations see Table 3. liq: sulfide liquid.

Binary joins of Ag_2S-Sn_2S_3 and Ag_2S-SnS in the system were obtained by Kitazawa *et al.*[18] using the DTA and high-temperature XRD, and are shown in Figures 13 and 14.

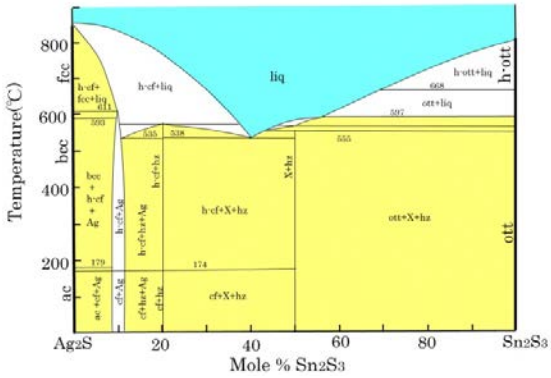

Figure 13. Phase relation of Ag_2S-Sn_2S_3 join in the ternary Ag-Sn-S system compiled after Kitazawa *et al.*[18]. Abbreviations are same to Figure 12.

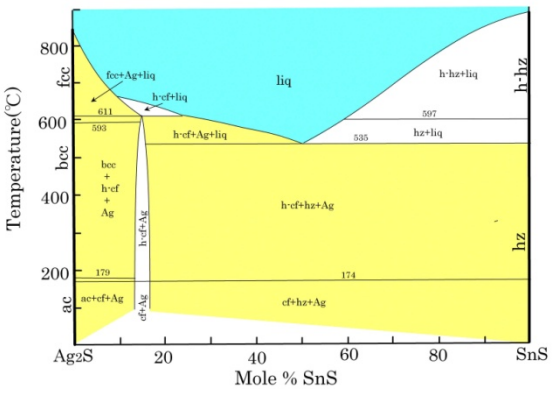

Figure 13. Phase relation of Ag_2S-SnS join in the ternary Ag-Sn-S system compiled after Kitazawa *et al.*[18]. Abbreviations are same to Figure 12.

From the experimental results by Kitazawa *et al.*[19], isothermal phase diagram of the ternary system at 600°C is shown in Figure 14. At this temperature, a ternary liquid field is stably present in a central portion of the diagram, coexisting with Ag, high-canfieldite, phase X, berndtite, ottemannite and herzenbergite. High-canfieldite assembles with argentite(bcc), silver, phase X, ternary liquid and sulfur liquid, but not associate with phase Y, berndtite, ottemannite, herzenbergite, phase ζ (Ag-Sn alloy) and Ag-Sn liquid.

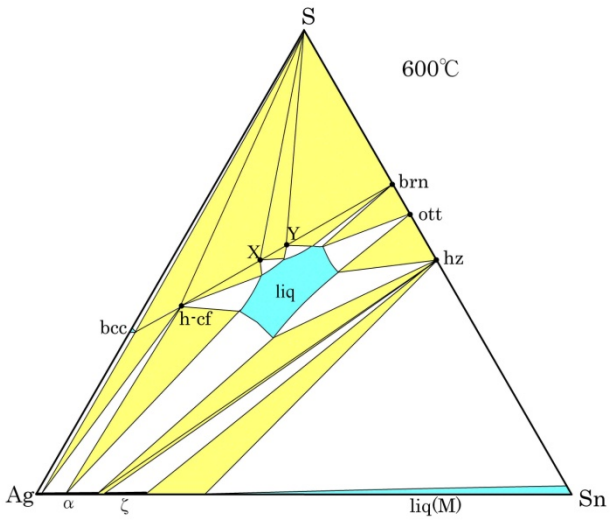

Figure 14. Isothermal phase diagram of Ag-Sn-S system at 600℃, compiled after Kitazawa *et al.*[18]. Abbreviations see Table 3, α : Ag rich Ag-Sn alloy, ζ : Ag-Sn alloy, liq: sulfide liquid, liq(M): Ag-Sn metal liquid, S(liq): sulfur liquid.

The isothermal phase relations of the system at 500°C are shown in Figure 15 (Kitazawa *et al.*[19]). According to this figure, silver metal can coexist with

high-canfieldite, whereas the Sn-rich part of silver solid solution α (Ag-Sn alloy), and Ag-Sn (liquid) coexist with herzenbergite. Herzenbergite also assembles stably with the ternary phases such as high-form canfieldite, phase X, and phase Y.

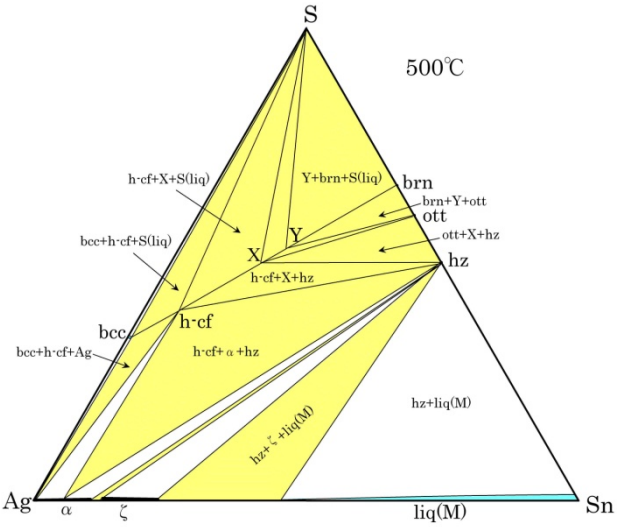

Figure 15. Isothermal phase diagram of Ag-Sn-S system at 500℃ compiled after Kitazawa *et al.*[19]. Abbreviations see Figure 14.

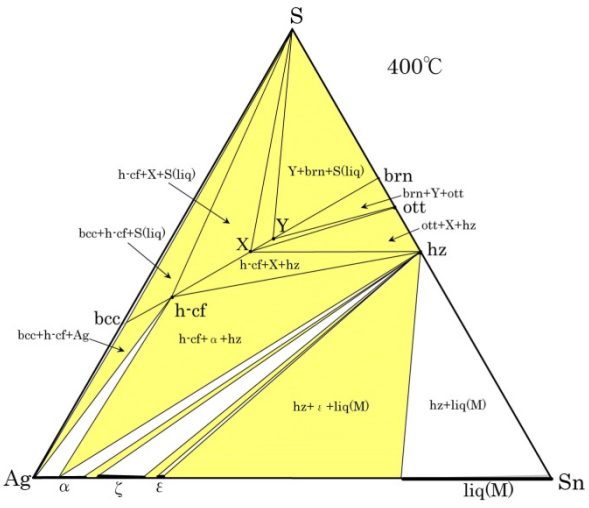

Figure 16. Isothermal phase diagram of Ag-Sn-S system at 400℃ compiled after Kitazawa *et al.*[18]. Abbreviations see Figure 14.

According to Kitazawa *et al.*[19], the tie-line between phase X and ottemannite occurs stably below 555°C instead of the tie line between phase Y and herzenbergite. The tie-line of phase X and ottemannite still is stable at 400°C as seen in Figure 16 (Kitazawa *et al.* [19]). The stabilities and phase relations of phase X and phase Y in the ternary system below 400°C are not clarified in detail at present.

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