Phase relation of some sulfide systems-(2)

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Abstract:

Phase relation studies for binary system of Bi-Se, and ternary systems such as Bi-Sb-S, Bi-Se-S, Co-Sb-S and Fe-Bi-S have been performed by author and some students. Their results are described as mainly phase diagrams and re-determined for some synthetic phases in their systems. .

***Key Words**: Bi-Se system, Bi-Sb-S system, Bi-Se-S system, Co-Sb-S system, Fe-Bi-S system, $FeBi_4S_7$*

Introduction

I have been done the phase equilibrium study of many sulfide systems since 1966 in Yamaguchi University and Tohoku University association with the students in both universities as bachelor thesis, master’s thesis and doctoral thesis. For some sulfide systems, I have been already published in some journals1),2). However, because many experimental results are still unpublished, I have wanted to continue to publish in conjunction with published results2).

The results for binary systems such as Bi-Se and , and ternary systems such as Bi-Sb-S, Bi-Se-S, Co-Sb-S and Fe-Bi-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) and Kitakaze2).

All the run products were examined by reflected light microscope and XRD by diffractometer for determination of phases and phase assemblages. Sometimes, XRD for some synthetic phases were performed using the Guinier method and cell parameters are refined by their data as same as Kitakaze3).

Differential thermal analysis (DTA) in the evacuated silica-glass tube was performed to obtain the temperatures of reactions causing the phase changes.

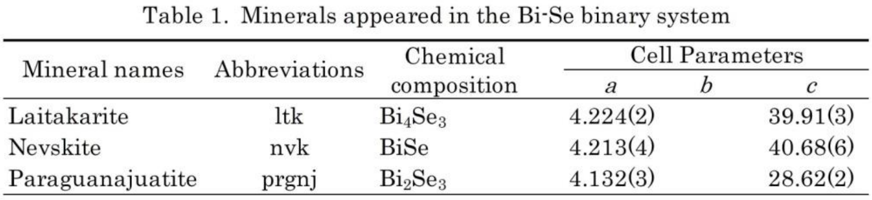
Binary systems

Bi-Se system

Phase relations of the Bi-Se system were studied by Shima and Nakamura4), Chen *et al.*5) , their phase diagrams which is compiled and modified by author.

The phases and crystal data obtained by Guinier method in this system is given in Table 1.

Table 1. Minerals appeared in the Bi-Se binary system



Mineral names	Abbreviations	Chemical composition	Cell Parameters		
			a	b	c
Laitakarite	ltk	Bi_4Se_3	4.224(2)		39.91(3)
Nevskite	nvk	BiSe	4.213(4)		40.68(6)
Paraguanajuatite	prgnj	Bi_2Se_3	4.132(3)		28.62(2)

Phase diagram of the Bi-Se system are shown in Fig. 1. Laitakarite melts has a stoichiometric composition Bi_4Se_3 and melts incongruently at 498℃ to nevskite and liquid. Nevskite has a limited solid solution from 47 to 58 atomic % Se, and melts incongruently to paraguanajuatite and liquid at 596℃. Meanwhile paraguanajuatite which has a stoichiometric composition Bi_2Se_3 is stable up to 701℃ and congruently melts at this temperature. A monotectic reaction between paraguanajuatite and Se-liquid occurs at 618°C

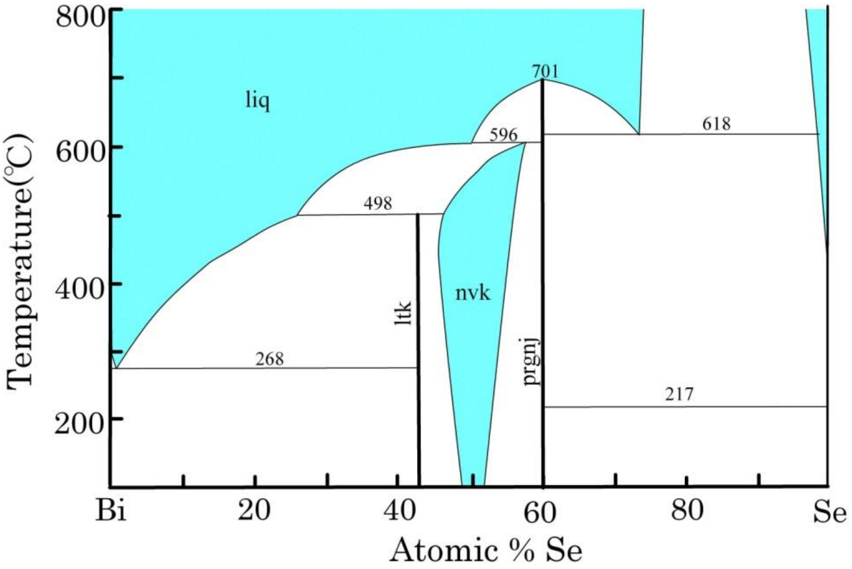


Figure 1. Phase diagram of the Bi-Se binary system. Abbreviation see Table 1.

Ternary systems

Bi-Sb-S system

The phase relations in the Bi_2S_3-Sb_2S_3 join of the Bi-Sb-S system were studied by Sugaki & Shima6) and Sugaki *et al.*7).

The phase diagram of the join compiled from data by author is shown in Fig. 2. There are only bismuthinite (Bi_2S_3) and stibnite (Sb_2S_3) as end members in this join. Both the end members have form a complete solid solution as seen in the diagram below 556°C at which stibnite melts congruently.

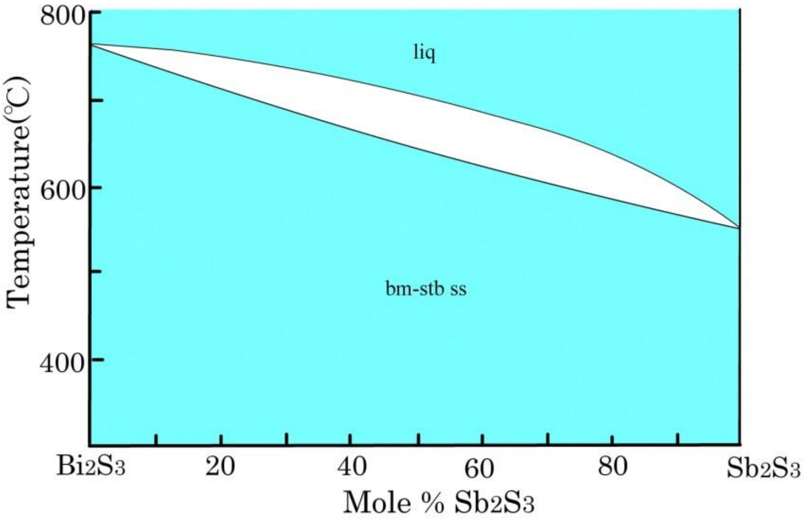


Figure 2. Phase relations of the Bi_2S_3-Sb_2S_3 join in the Bi-Sb-S system.

bm-stb ss: bismuthinite-stibnite solid solution

The phase relations of the isotherm in the Bi-Sb-S system at 400°C are shown in Fig. 3. A univariant assemblage of bismuthinite-stibnite solid solution + (Sb,Bi) alloy + Bi-rich liquid exists. Compositions of bismuthinite-stibnite ss, (Sb,Bi) alloy and Bi-liquid in the assemblage are 75 mole % Sb_2S_3, 75 and 30 atomic % Sb, respectively.

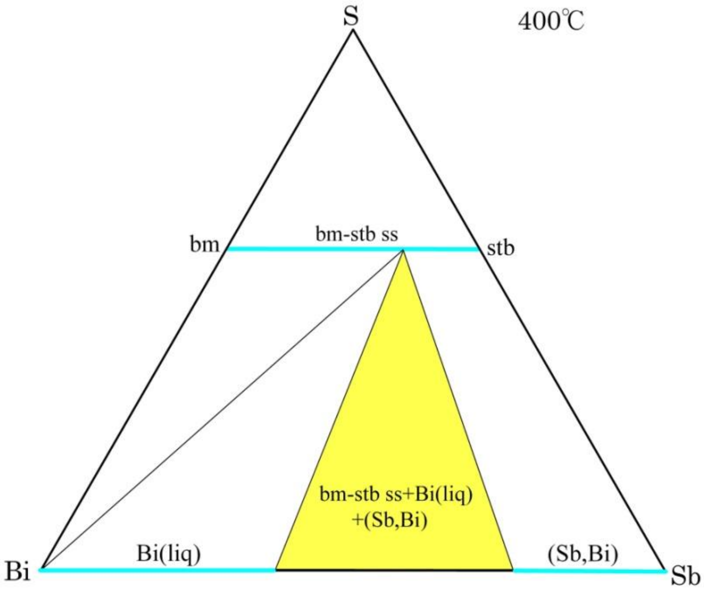


Figure 3. Phase diagram of the Bi-Sb-S system at 400℃.

The isothermal phase relations at 500°C are about same as those at 400°C except the compositions of bismuthinite-stibnite ss, (Sb,Bi) alloy and Bi-liquid in the univariant assemblage change to 62 mole % Sb_2S_3, 91 and 57 atomic % Sb, respectively.

Bi-Se-S system

Phase relation studies in the Bi-Se-S system were performed by Shima and Nakamura[4)], Hanada[8)], Tsuda[9)], and Sanada[10)]. Minerals appeared in this system are given in the Table 2 as minerals with their cell parameters which are obtained by Guinier method by author[3)].

Table 2 Minerals in the Bi-Se-S ternary system

Mineral names	Abbreviations	Chemical composition	Cell Parameters		
			a	*b*	*c*
Laitakarite	ltk	Bi_4Se_3	4.224(2)		39.91(3)
Ikunolite	ikn	$Bi_4(S_{1.5}Se_{1.5})_3$	4.130(5)		39.42(8)
Nevskite	nvk	BiSe	4.213(4)		40.68(6)
Paraguanajuatite	prgnj	Bi_2Se_3	4.132(3)		28.62(2)
Guanajuatite	gnj	$Bi_2(Se_{1.5}S_{1.5})_3$	11.381(9)	11.561(8)	4.053(2)
Bismuthinite	bm	Bi_2S_3	11.120(1)	11.250(1)	3.970(1)

The phase relations of the Bi_4S_3-Bi_4Se_3 pseudo-binary join in the Bi-Se-S system below 550°C are shown in Fig. 4 modified after Tsuda[9)] and author. In this join below 490℃, laitakarite - ikunolite solid solution appears in wide field. The field ranges from 0 to 45 mole % Bi_4S_3 at 490℃, 0 to 65 mole % at 300℃ including ideal formula of ikunolite $Bi_4(Se_{1.5}S_{1.5})_3$. In the Bi_4Se_3 rich region, there are three phases or two phase assemblages appeared outside in this join.

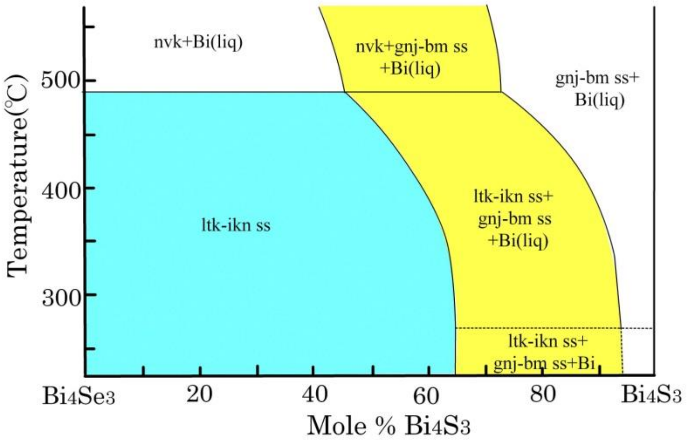


Figure 4. Phase relations of the Bi_4Se_3-Bi_4S_3 join in the Bi-Se-S system.

Abbreviations are same as Table 1, ss: solid solution.

The phase relations of the Bi_2S_3-Bi_2Se_3 join in the Bi-Se-S system below 600°C are shown in Fig. 5 modified after Shima and Nakamura [4)], and Hanada[8)]. Paraguanajuatite contains a limited solid solution than 5 mole % Bi_2S_3 at 500℃, and this area is more wide range according lower temperatures, and an immiscibility field between paraguanajuatite and guanajuatite - bismuthinite solid solution is found. A continuous solid solution between Bi_2Se_2S (33 mole % Bi_2S_3) and Bi_2S_3 at temperatures from 450° to 600°C exists, but reduces its range with lowering temperature.

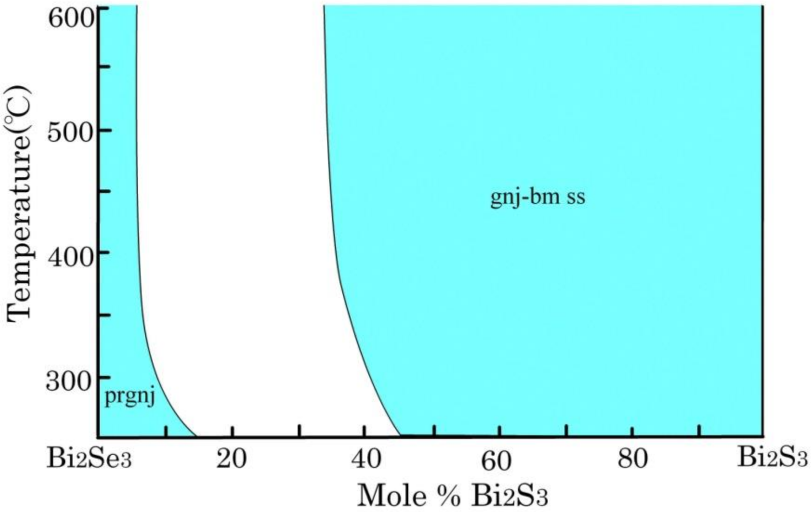


Figure 5. Phase diagram of Bi_2Se_3-Bi_2S_3 join in the Bi-Se-S system.

Abbreviations are same as Table 1, ss: solid solution.

Isothermal phase diagram of Bi-rich portion in the ternary system Bi-Se-S at 550° , 500° and 450°C are shown in Figs. 6, 7 and 8, respectively (Shima and Nakamura$^{4)}$.

At 550°C (Fig. 6), guanajuatite, paraguanajuatite - bismuthinite solid solution, nevskite solid solution appear as stable solid phases. Nevskite has a solid solution field with 17 atomic % S in maximum, and associates with guanajuatite, paraguanajuatite - bismuthinite solid solution and Bi-rich liquid. The univariant assemblages of nevskite solid solution + paraguanajuatite-bismuthinite solid solution + Bi-rich liquid and nevskite solid solution + guanajuatite + paraguanajuatite-bismuthinite solid solution are found in the diagram at 550° and 500℃ (Fig. 7).

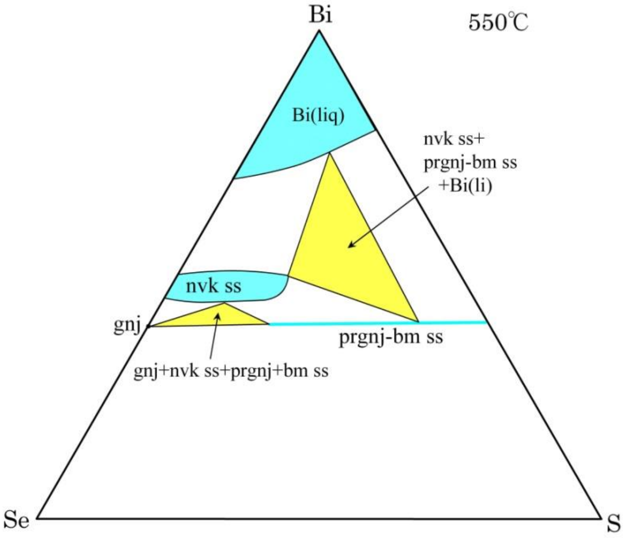


Figure 6. Isothermal section of Bi-rich region in the Bi-Se-S system at 550℃.

Abbreviations are same as Table 1, ss: solid solution.

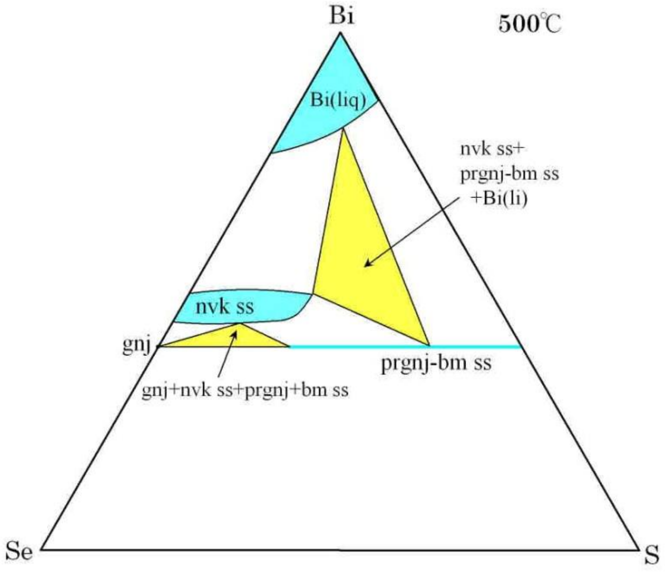


Figure 7. Isothermal phase relations of Bi-rich region in the Bi-Se-S system at 500℃.

Abbreviations are same as Table 1, ss: solid solution.

At 492°C, S-free laitakarite is crystallized. It forms a solid $Bi_4(Se,S)_3$ solution ranging from 0 to 24 atomic % S including laitakarite composition (Bi_4SeS_2, 14.3 atomic % S) and ikunolite composition ($Bi_4S_{1.5}Se_{1.5}$) at 450°C (Fig. 8), then called as laitakarite-ikunolite solid solution. The phase associates with nevskite phase solid solution, paraguanajuatite-bismuthinite solid solution and Bi-rich liquid, but does not coexist with guanajuatite.

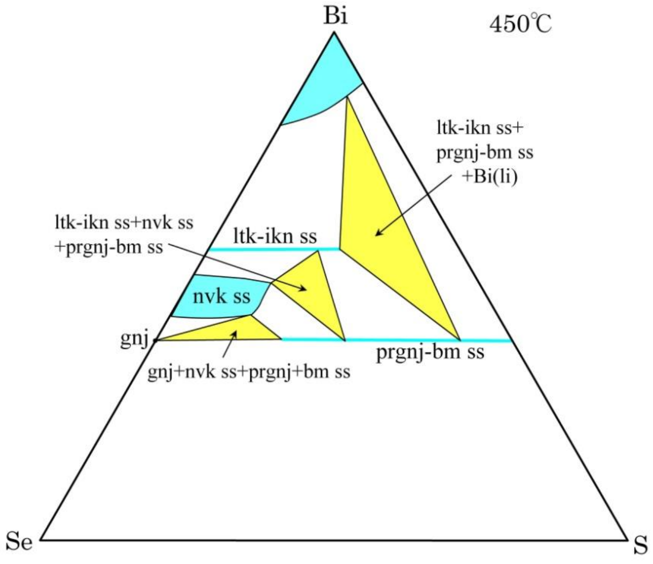


Figure 8. Isothermal phase relations in the Bi-rich region in the Bi-Se-S system.

Abbreviations are same as Table 1, ss: solid solution.

There are three univariant assemblages of laitakarite-ikunolite solid solution + paraguanajuatite - bismuthinite solid solution + Bi-rich liquid, laitakarite-ikunolite solid solution, nevskite solid solution + paraguanajuatite - bismuthinite solid solution and guanajuatite + nevskite solid solution + paraguanajuatite - bismuthinite solid solution in Fig. 8.

Below 450℃, the phase relations at 400, 350 and 300℃ were performed by Tsuda[10)], their phase diagrams modified by author are shown in Figs. 9, 10 and 11, respectively. Univariant assemblages are about same to 450℃, except their change of compositions for solid solution.

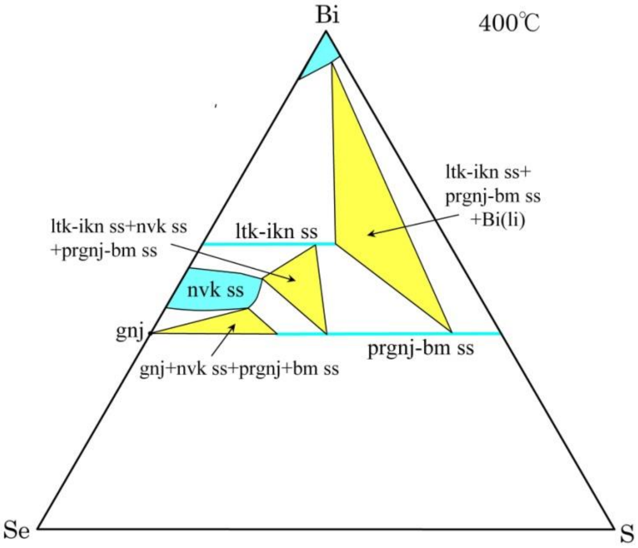


Figure 9. Phase relations in the Bi-rich region in the Bi-Se-S system at 400℃.

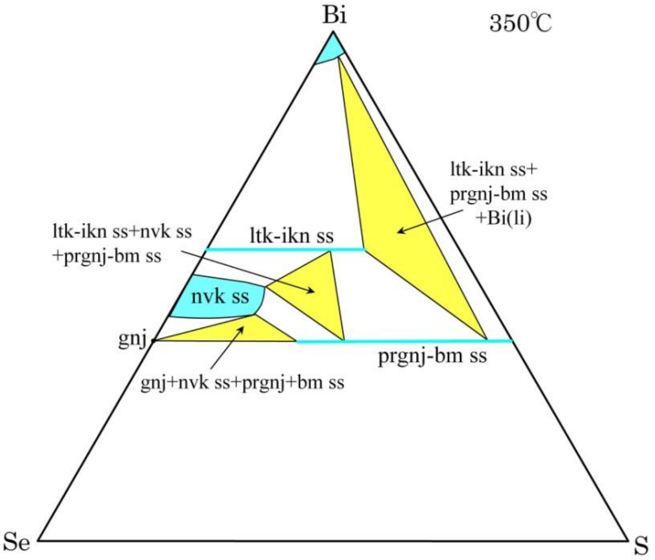


Figure 10. Isothermal section in the Bi-rich region in the Bi-Se-S system at 350℃.

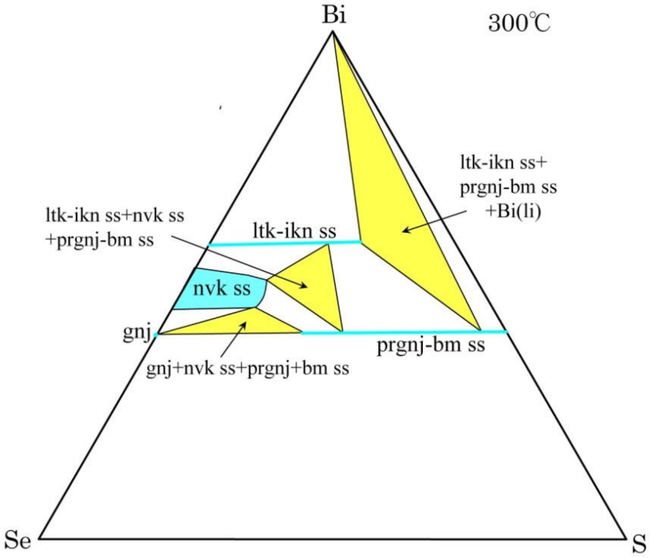


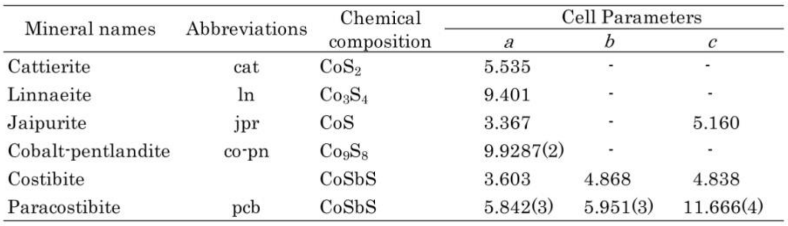
Figure 11. Isothermal section in the Bi-rich region in the Bi-Se-S system at 300℃.

Co-Sb-S

There are few equilibrium works of the Co-Sb-S system especially on ternary phase relation by Kitakaze *et al.*, (unpublished). In this ternary system, cattierite, linnaeite, jaipurite and cobalt-pentlandite belonging in Co-S binary system, and paracostibite as ternary minerals are appeared as the synthetic minerals.

Their chemical composition and cell parameters are given in Table 3.

Table 3. Minerals, their chemical composition and cell parameters in the Co-Sb-S system



Mineral names	Abbreviations	Chemical composition	Cell Parameters		
			a	*b*	*c*
Cattierite	cat	CoS_2	5.535	-	-
Linnaeite	ln	Co_3S_4	9.401	-	-
Jaipurite	jpr	CoS	3.367	-	5.160
Cobalt-pentlandite	co-pn	Co_9S_8	9.9287(2)	-	-
Costibite		CoSbS	3.603	4.868	4.838
Paracostibite	pcb	CoSbS	5.842(3)	5.951(3)	11.666(4)

Paracostibite is high temperature polymorph of costibite (CoSbS) (Cabri *et al.*[11]), and melts incongruently to phase $Co_{1-x}S$ and liquid at 876±5°C. But, they did not succeed to transform to costibite from paracostibite by annealing cool down to 100°C (Cabri *et al*,[11]).

Isothermal sections (Kitakaze *et al.*, [12] at 600° and 500°C are shown in Fig. 11 and 12. Binary phases such as CoSb, $CoSb_2$ and $CoSb_3$ are stable up to 1195°, 902° and 770°C, respectively.

In the 600°C isotherm, many phases such as cattierite, linnaeite, phase $Co_{1-x}S$ and cobalt-pentlandite along the Co-S join, phases CoSb, $CoSb_2$ and $CoSb_3$ along the Co-Sb system are observed in the system. As shown in Fig. 12, paracostibite which exists in central portion of the diagram stably assembled with linnaeite, cobalt-pentlandite, cobalt, phase CoSb, phase $CoSb_2$ phase $CoSb_3$, antimony, and sulfide-liquid. Then, nine univariant around CoSbS. Univariant assemblages of cattierite + linnaeite + sulfide-liquid and cattierite + assemblages which include paracostibite are found sulfide-liquid + sulfur-liquid are also found adding to those include paracostibite.

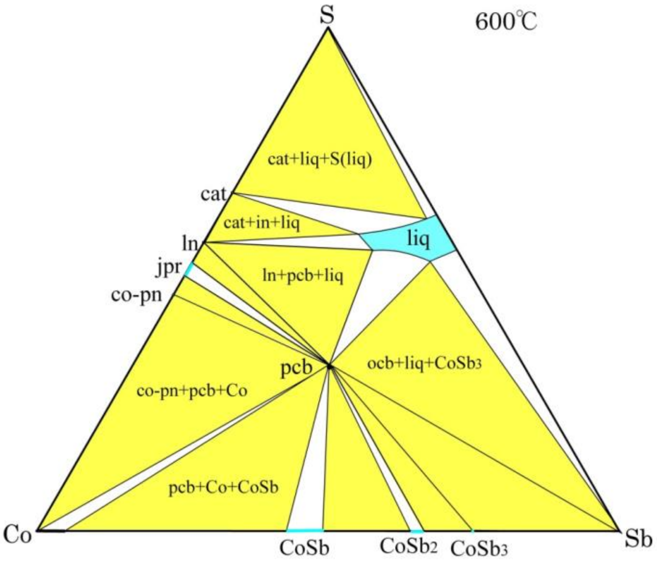


Figure 11. Phase diagram of the Co-Sb-S system at 600℃.

Abbreviations are same to table 1.

The phase relation at 500°C (Fig. 12*)* is similar to that at 600°C. But stibnite is found in 500°C isotherm, because it melts congruently at 546°C. Paracostibite has tie lines with linnaeite, cobalt-pentlandite, cobalt, $Co_{1-x}S$, phase CoSb, phase $CoSb_2$, phase $CoSb_3$, antimony and stibnite, and it is surrounded by nine univariant assemblages. It does not have tie line with cattierite because of existence of the tie line between linnaeite and stibnite, paracostibite cannot assemble with cattierite. Univariant assemblages of cattierite + linnaeite + stibnite and cattierite + stibnite + sulfur-liquid are also found adding to those include paracostibite.

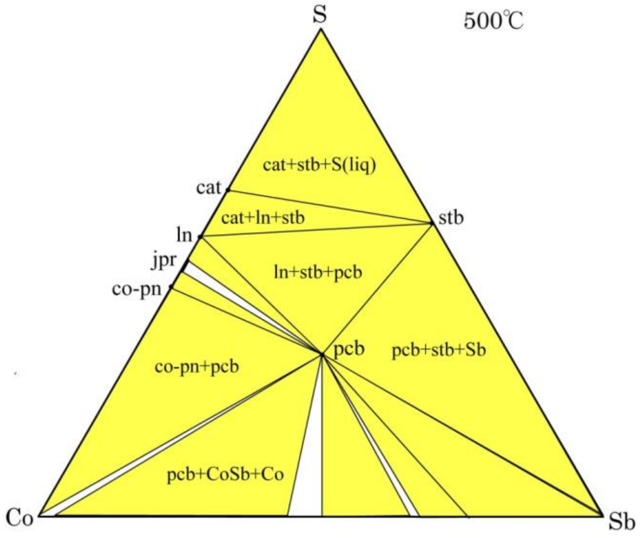


Figure 12. Isothermal section in the Co-Sb-S system at 500℃.

Abbreviations are same to table 1.

Fe-Bi-S system

Phase relations in the Fe-Bi-S system have been investigated by Sugaki et al., Craig et al. and Shima et al (1977). Synthetic phase $FeBi_4S_7$ was found in the join FeS-Bi_2S_3 of the system, as shown in Fig. 13. It is stable in the temperature range between 623°±3°C and 726°±3°C, which is the congruent melting point, and is decomposed to the assemblage of pyrrhotite + bismuthinite + bismuth-rich liquid at temperatures below 623 °C. Therefore, phase $FeBi_4S_7$ cannot be expected to be found in nature. The phase is monoclinic, a=12.7739(6)A, b=3.9618(5)A, c=11.8081(5)A, β =104.48(4)° calculated by least squares method using XRD data obtained by the Guinier camera. Its density measured by Barman balance is 6.39 g/cm^3 and calculated density, 6.41 g/cm^3 as Z=2.

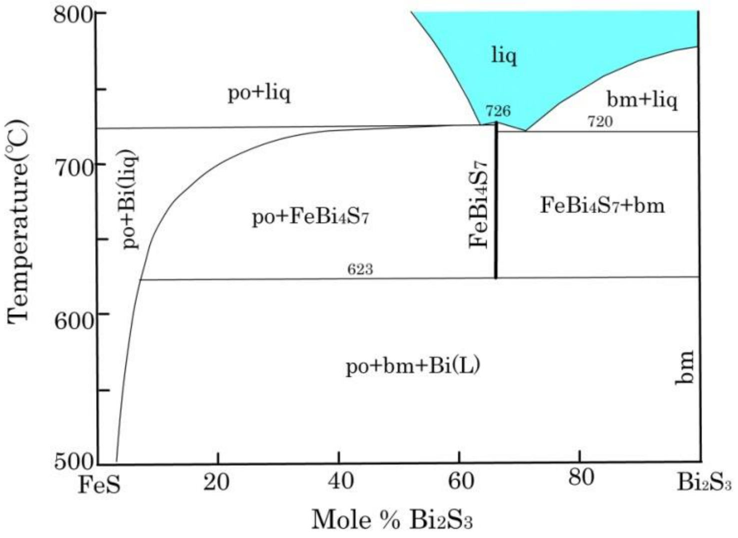


Figure 12. Phase relations of FeS-Bi_2S_3 join in the Fe-Bi-S system.

Abbreviations are po: pyrrhotite, bm: bismuthinite

The isothermal sections of the system Fe-Bi-S at temperatures below 623°C become simple phase relation because its phase disappears. The phase relations of the ternary Fe-Bi-S system were studied by Sugaki *et al*.[12)13)] and Shima *et al*. [14)]). They are relatively simple because phase $FeBi_4S_7$ is only one as the ternary compound, but only in a limited temperature range as described above. Figure 13 shows the phase relations of the isothermal diagram in the Fe-Bi-S system at 750°C. There are only two sulfide phases, hexagonal pyrrhotite (1C) and bismuthinite, and liquid phase in the ternary diagram. Bismuthinite cannot assemble with pyrrhotite and pyrite because it is surrounded with the liquid phase. The liquid phase which develops into a sulfur-rich middle portion from the Bi-S join extends to the Bismuth (liq) corner along the join.

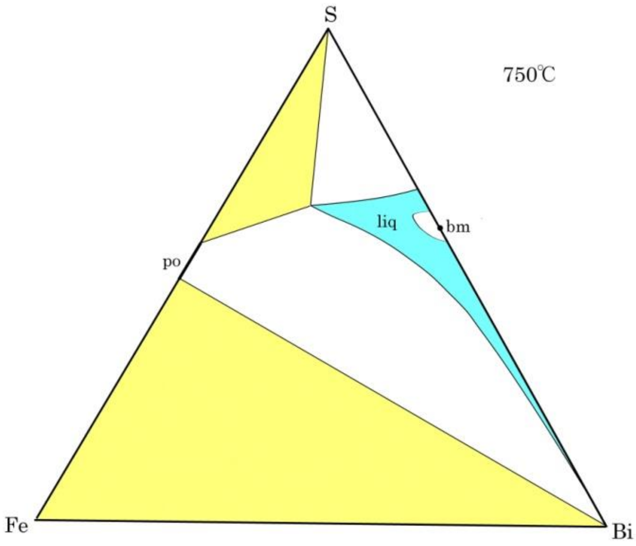


Figure 13. Phase relations of Fe-Bi-S system at 750℃.

Abbreviations are same to Fig. 12.

Pyrite appears at 743°C, and associates with the liquid phase, pyrrhotite and sulfur (liq) at 740°C. The phase $FeBi_4S_7$ crystallizes at 726°C, assembling with pyrrhotite and liquid phase as seen in Fig. 13 at 725℃.

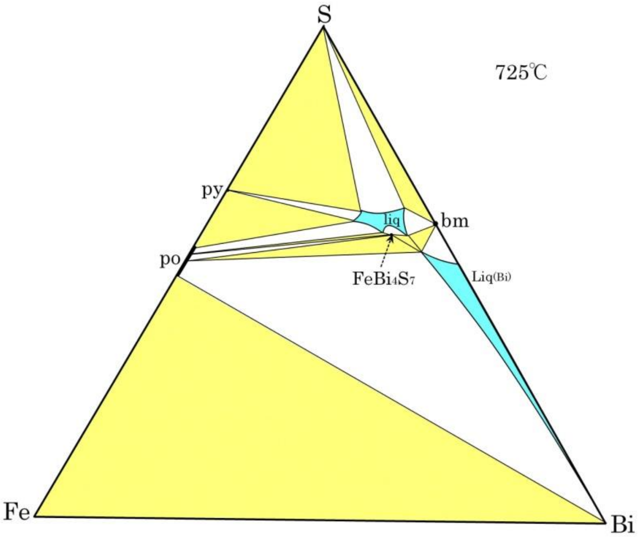


Figure 14. Phase relations of Fe-Bi-S system at 725℃.

Abbreviations are same to Fig. 12 and py: pyrite.

The phase liquid is divided to two liquid phases, sulfide-liquid, and Bi-rich liquid, and the sulfur-rich liquid of them retreats to the inside of the ternary from the join. Accordingly, bismuthinite assembles with Bi (liq), sulfide-liquid and Sulfur (liq). The isothermal phase relations of the system at 700°C are shown in Fig. XX. As seen in the figure, the sulfide-rich liquid phase found at 725°C disappears at this temperature, but the Bi-liquid phase corresponding to Bismuth (liq) in the figure still remains as nearly linear form extending to the bismuth corner. There are five univariant assemblages as follows: pyrite + bismuthinite + S(liq), pyrite + pyrrhotite + bismuthinite, bismuthinite + $FeBi_4S_7$ + Bi(liq), pyrrhotite + $FeBi_4S_7$ + Bi (liq) and pyrrhotite + iron + Bi(liq).

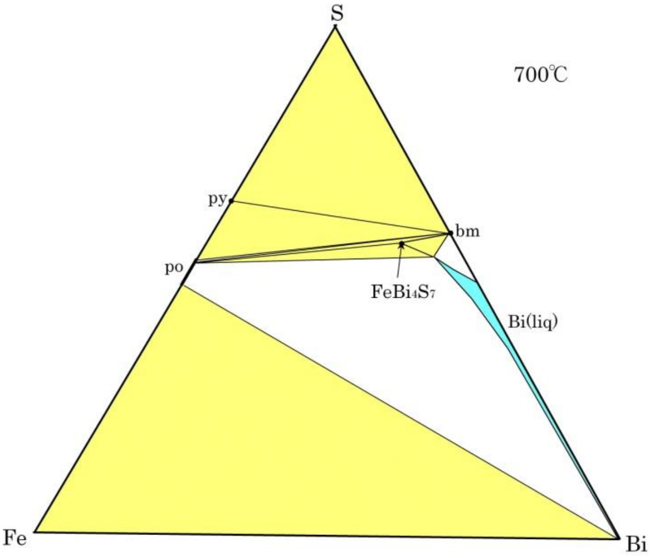


Figure 15. Phase relations of Fe-Bi-S system at 700℃.

Abbreviations are same to Fig. 14.

Phase $FeBi_4S_7$ disappears at 623°C as described above. The phase relations of the Fe-Bi-S system at 600°C are as given in Fig. xx. There is found no sulfide with ternary compound in the isothermal diagram, and the univariant assemblages of pyrite + bismuthinite + S(liq), pyrrhotite + pyrite + bismuthinite, pyrrhotite + bismuthinite + Bi(liq) and pyrrhotite + iron + Bi(liq) exist as stable associations. Pyrite cannot accompany by Bi(liq). These assemblages and tie lines are stable until about 300°C (Fig. xx) or below.

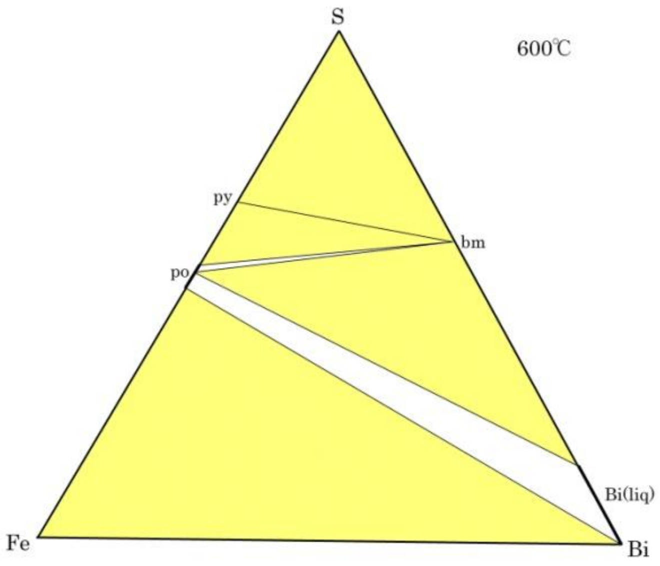


Figure 16. Phase relations of Fe-Bi-S system at 600℃.

Abbreviations are same to Fig. 14.

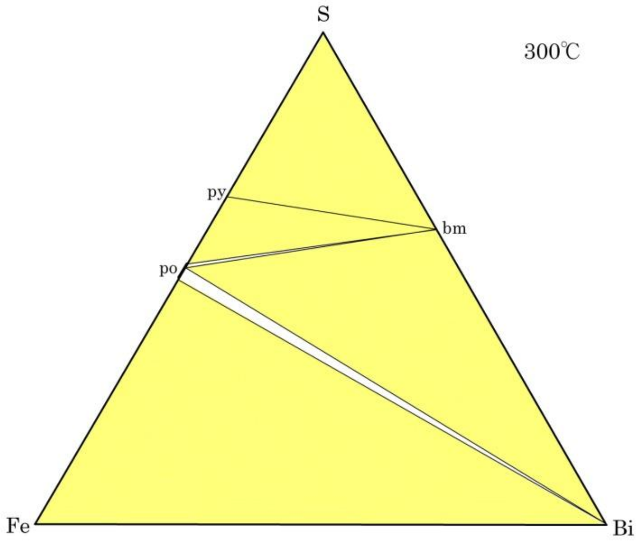


Figure 17. Phase relations of Fe-Bi-S system at 300℃.

Abbreviations are same to Fig. 14.

However, the tie line between pyrrhotite and bismuthinite is replaced with the tie line between pyrite and Bi at about 250°C as shown in Fig. 18. Monoclinic pyrrhotite also appears around this temperature. As its results the five univariant assemblages of pyrite + bismuthinite + S(1iq), pyrite + bismuthinite + Bi, pyrite + monoclinic pyrrhotite (4C) + Bi(liq), monoclinic pyrrhotite + hexagonal pyrrhotite (1C) + Bi(liq), and hexagonal pyrrhotite (1C) + iron + Bi(liq). Bismuth can assemble with all the phases except S(liq).

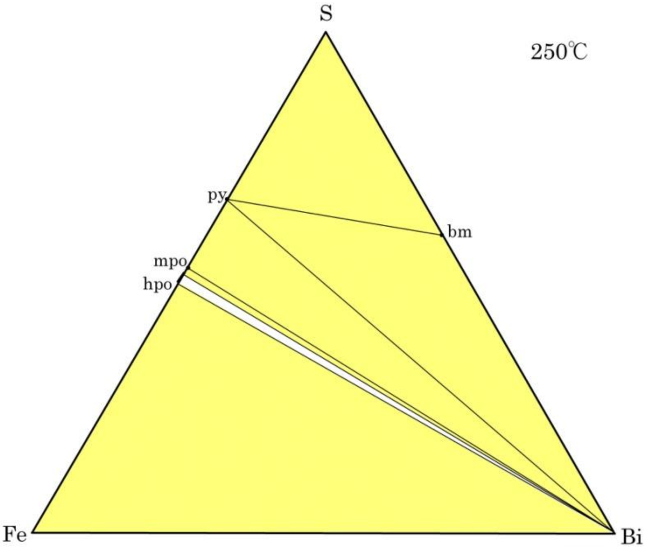


Figure 18. Phase relations of Fe-Bi-S system at 250℃.

Abbreviations are same to Fig. 14.

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