

## Phase Relations of the $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ System

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### Introduction

Although in the ternary Cu–Sb–S system tetrahedrite ( $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ ) and famatinite ( $\text{Cu}_3\text{SbS}_4$ ) are common cupro-antimonian sulfide minerals in nature, only chalcostibite ( $\text{CuSbS}_2$ ) is a naturally occurring mineral in the binary  $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$  system. Besides chalcostibite, the mineral species named falkenhaynite and stylopyrite which have a composition of  $3\text{Cu}_2\text{S}\cdot\text{Sb}_2\text{S}_3$  ( $\text{Cu}_3\text{SbS}_3$ ) have been reported almost a century ago.

Falkenhaynite has once been described by Scharizer<sup>1)</sup> in 1890 as a massive gray-black mass of sulfides from the Fiedler vein, Joachimstal, Bohemia and he gave the formula  $\text{Cu}_3\text{SbS}_3$  from rough chemical analysis\*\*. But the veridity of this mineral was denied soon after by Sandberger<sup>2)</sup> (1891), Dana<sup>3)</sup> (1892), and Stevanovic<sup>4)</sup> (1903) as the specimen described by Scharizer might be some impure tetrahedrite or tennantite.

On the other hand stylopyrite, found originally by von Kobell<sup>5)</sup>, from Copiapo, Chile in 1868, has been accepted as mineral species until 1952 despite of some repetition of the argument several times. After the first description by von Kobell, Stevanovic<sup>4)</sup> has reported another occurrence of stylopyrite from Costrovirroyna, Peru in 1903 and Hulin<sup>6)</sup> also found stylopyrite from the Rand silver mine, Randsburg, California in 1925. And many textbooks written by Murdoch<sup>7)</sup> (1916), Davy and Farnham<sup>8)</sup> (1920), Doelter and Leitmeier<sup>9)</sup> (1926) and Palache et al<sup>10)</sup> (1944) listed stylopyrite as species, while “stylopyrite” from Peru by Stevanovic was shown by Schneiderhohn and Ramdohr<sup>11)</sup> to be a mixture of minerals in all respects like tetrahedrite in 1931, and Klochmann and Ramdohr<sup>12)</sup> also doubted Peruvian stylopyrite as probably tetrahedrite of possibly pseudomorphs after pyrostilpnite. In 1951, Milton and Axelrod<sup>13)</sup> studied carefully specimens labelled stylopyrite from Bolivia, Peru, and California by means of ore microscope and X-ray diffraction and showed all specimens of stylopyrite reported before were possibly identified as tetrahedrite or jamesonite. According to their works stylopyrite was listed on the American Mineralogist<sup>14)</sup> as descredited mineral in 1952.

As to synthetic experimental studies, as early as 1912, a phase study of pseudobinary  $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$  has been done by Parravano and de Cesaris<sup>15)</sup>, when synthetic  $\text{Cu}_3\text{SbS}_3$  was mentioned already, but the present authors unfortunately

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\*\* Analysed sample had contained as impurities fairly large quantity of quartz, siderite and chalcopyrite.

have not had a chance to see their original paper. Existence of phase  $\text{Cu}_3\text{SbS}_3$  has been ascertained by the present authors<sup>16)17)</sup> during a preliminary study on the phase equilibrium of the Cu–Sb–S system and also this phase was reported by Godovikov et al<sup>18)</sup>. Ross<sup>19)</sup> (1954) carried out solid diffusion syntheses along the join  $\text{Cu}_2\text{S}$ – $\text{Sb}_2\text{S}_3$  and listed six binary phases of  $3\text{Cu}_2\text{S}\cdot\text{Sb}_2\text{S}_3$  (tetrahedrite),  $5\text{Cu}_2\text{S}\cdot\text{Sb}_2\text{S}_3(?)$ ,  $\text{Cu}_2\text{S}\cdot\text{Sb}_2\text{S}_3$  (chalcostibite),  $4\text{Cu}_2\text{S}\cdot 5\text{Sb}_2\text{S}_3(?)$ ,  $3\text{Cu}_2\text{S}\cdot 4\text{Sb}_2\text{S}_3(?)$ , and  $2\text{Cu}_2\text{S}\cdot 3\text{Sb}_2\text{S}_3(?)$  without comment. Recent phase studies of the system have been reported by Cambi and Elli<sup>20)</sup> (1965) who measured the liquidus temperatures along the join  $\text{Cu}_2\text{S}$ – $\text{Sb}_2\text{S}_3$ , and obtained temperatures in their studies are in good agreement with ours. Skinner, Luce and Makovicky<sup>21)</sup> reported the phase relations of the Cu–Sb–S system quite recently in which phase relations and properties of chalcostibite and  $\text{Cu}_3\text{SbS}_3$  were also mentioned.

## Experimental Procedures

### *Starting Materials*

The primary starting materials used in this experiments were electrolytic copper of 99.99+ % in purity, antimony metal of 99.9+ % in purity, and crystalline sulfur refined as guaranteed reagent from Kanto Chemical Co., purity grade 99.98+ %. Copper chips were reduced in hydrogen atmosphere at about 900°C for 2 hours prior to experiments.  $\text{Cu}_2\text{S}$  and  $\text{Sb}_2\text{S}_3$  which are the endmembers of the system were synthesized first in evacuated silica glass tube from the elements and then they were used as starting materials for the phase study of the binary system.

### *Synthetic Method and Identification of Phases*

Synthetic technique has been described in the preceding papers<sup>22)23)</sup> and then reference should be made to these paper for details. At 500°C and higher temperature, as the reaction rates were sufficiently fast, equilibrium was attained within few days, but below 500°C more than 10 days were necessary for equilibrium. The reaction products of the experiment were identified mainly by the reflecting microscope and X-ray powder diffractometer. In the present study microscopic observation were useful for phase identification because of different in optical properties such as reflection color or anisotropism. Rigaku X-ray diffractometer, Geigerflex was employed for X-ray study and high temperature X-ray study was also performed by using Rigaku high temperature X-ray diffractometer.

### *The Differential Thermal Analysis*

The phase study was mainly done by the differential thermal analysis (DTA). The apparatus and method was identical to those described before in detail<sup>24)</sup> and also similar to the techniques use by Kullerud and Yund<sup>25)</sup> and Moh<sup>26)</sup>. In DTA analysis for the phase study, heating rate has much influence on accuracy,

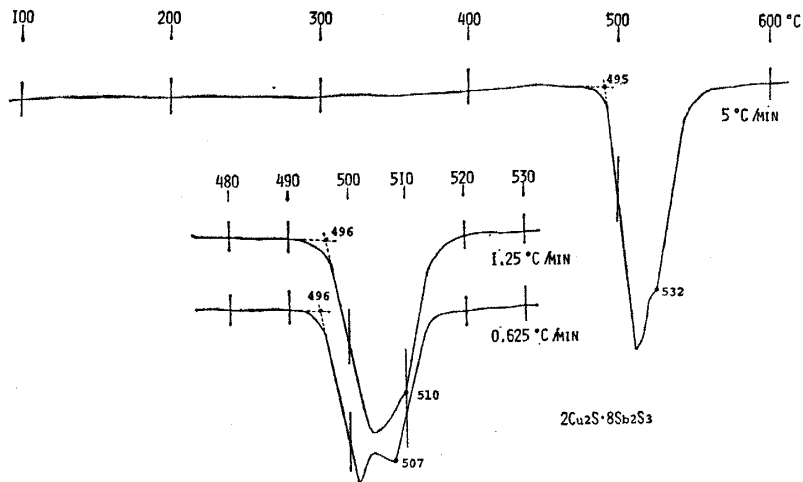


Fig. 1 Effect of heating rate on the DTA curves.

especially on that of the end point temperature of a series of reaction. Besides, if two or more reactions occur within a narrow temperature range on heating, usually the reaction peaks will overlap in high heating rate analysis which makes difficult to read the temperature of each reaction. These are shown clearly in Fig. 1. and then the analysis were done in heating rate of  $0.625^\circ\text{C}/\text{min}$  or  $1.25^\circ\text{C}/\text{min}$ . Accuracy of the experiment would be expected within  $\pm 3^\circ\text{C}$  from the result of measurement on the melting of standard pure metal.

## Experimental Result

### *Preliminary Synthesis and Crystalline Phases*

In order to determine all stable phases in the  $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$  system, preliminary quenching runs were carried out at  $480^\circ\text{C}$  and  $520^\circ\text{C}$ . The experimental results of the runs are compiled in Table 1. Though nothing is mentioned about vapour phase in the table, these solid phases always keep equilibrium with sulfur vapour under their own sulfur pressure.

Four condensed phases of  $\text{Cu}_2\text{S}$ ,  $\text{Cu}_3\text{SbS}_3$ ,  $\text{CuSbS}_2$ , and  $\text{Sb}_2\text{S}_3$  are stable in the binary join. These are all entirely homogeneous under the ore microscopy and their optical properties are shown in Table 2.  $\text{Cu}_2\text{S}$ ,  $\text{CuSbS}_2$  and  $\text{Sb}_2\text{S}_3$  correspond to chalcocite, chalcostibite and stibnite respectively, and their optical properties shown in Table 2 are in good accordance with those described by Uytendogaardt and Burke,<sup>27)</sup> and by Shouten<sup>28)</sup>. Quenched  $\text{Cu}_2\text{S}$  shows X-ray powder pattern of low temperature orthorhombic form because of impossibility to keep high temperature form by quenching, and X-ray powder data of  $\text{CuSbS}_2$  and  $\text{Sb}_2\text{S}_3$  are in good agreement with those of natural chalcostibite and stibnite by Berry and Thompson<sup>29)</sup> respectively. Existence of  $\text{Cu}_3\text{SbS}_3$  has been reported by one of the present authors<sup>16)</sup> in 1967 and later also reported by Godovikov et al.<sup>18)</sup> (1971). Synthesized  $\text{Cu}_3\text{SbS}_3$ , having the same composition with stibnite which has been reported first by von Kobell<sup>5)</sup> (1868), is not confirmed yet to

Table 1. Results of preliminary experimental runs at 480°C and 520°C.

Composition Cu <sub>2</sub> S mol%	Temp. °C	Time hrs.	Products
0.0	480	120	stb. (mono phase)
2.0	480	336	stb ss
4.0	480	336	stb ss + csb
10.0	480	288	stb ss + csb
20.0	480	288	stb ss + csb
30.0	480	288	stb ss + csb
40.0	480	224	stb ss + csb
48.0	480	336	stb ss + csb
50.0	520	360	csb. (mono phase)
51.0	520	408	csb + Cu <sub>3</sub> SbS <sub>3</sub>
55.0	520	288	csb + Cu <sub>3</sub> SbS <sub>3</sub>
60.0	520	148	csb + Cu <sub>3</sub> SbS <sub>3</sub>
70.0	520	169	csb + Cu <sub>3</sub> SbS <sub>3</sub>
73.0	520	408	csb + Cu <sub>3</sub> SbS <sub>3</sub>
75.0	520	360	Cu <sub>3</sub> SbS <sub>3</sub> . (mono phase)
77.0	520	408	Cu <sub>3</sub> SbS <sub>3</sub> + (cc)?
80.0	520	168	Cu <sub>3</sub> SbS <sub>3</sub> + cc
85.0	520	144	Cu <sub>3</sub> SbS <sub>3</sub> + cc
90.0	520	244	Cu <sub>3</sub> SbS <sub>3</sub> + cc
98.0	520	291	Cu <sub>3</sub> SbS <sub>3</sub> + cc
100.0	520	120	cc. (mono phase)

stb: stibnite  
 csb: chalcocostibite  
 cc: chalcocite

Table 2. Optical properties of crystalline phases in the Cu<sub>2</sub>S-Sb<sub>2</sub>S<sub>3</sub> system

	stibnite Sb <sub>2</sub> S <sub>3</sub>	chalcocostibite Cu <sub>2</sub> S·Sb <sub>2</sub> S <sub>3</sub>	stylotypite 3Cu <sub>2</sub> S·Sb <sub>2</sub> S <sub>3</sub>	chalcocite Cu <sub>2</sub> S
Reflection color	grayish white- brownish gray	galena white- pale brownish gray	grayish white with pinkish tint	bluish gray- grayish white
Reflective pleochroism	distinct	moderate	moderate-weak	weak
Anisotropism	very strong	very strong	strong-moderate	weak
Interference color	dark purplish brown-creamy	dark brown- brownish gray- greenish gray	dark brown-gray with red internal reflection	grayish blue- grayish brown
HNO <sub>3</sub> (1:1)	stains brown	slightly brown	neg. or slightly effective	into blue with eff.
HCl	neg.	neg.	neg.	neg.
KOH	stains reddish brown	neg.	slightly darken	neg.
KCN (20%)	stains brown	neg. -bring out scratches	neg.	immediately changes into black
FeCl <sub>3</sub> (20%)	neg.	neg.	neg.	stains bluish gray
HgCl <sub>2</sub> (sat.)	neg.	tarnish slightly	neg.	stains dark gray

Table 3. X-ray powder diffraction data of low and high temperature polymorph of synthetic  $\text{Cu}_3\text{SbS}_3$ 

(1)			(2)		(3)				(4)	
d(meas.)	I	hkl	d(meas.)	I	d(meas.)	I	hkl	d(calc.)	d(meas.)	I
—	—	012	5.64	4	5.64	3	011	5.56	5.68	1
—	—	020	5.07	4	—	—	—	—	5.22	1
4.50	W	112	4.56	16	4.54	20	111	4.52	4.55	4
4.06	VVW	022	4.08	2	4.06	2	021	4.07	—	—
3.88	M/S	200	3.92	34	3.93	25	200	3.89	3.83	3
3.49	VVW	211	3.53	5	—	—	—	—	—	—
3.355	VVW	202	3.38	6	3.37	7	201	3.35	3.35	20
3.295	W	004	3.32	10	3.31	8	002	3.30	—	—
3.183	M	212	3.21	26	3.20	50	211	3.19	3.19	3
3.092	W	220	3.12	17	3.12	23	220	3.11	—	—
3.037B	S	032	3.06	40	3.05	60	{031 102}	{3.05 3.04}	3.08	8
2.913	W	114	2.935	16	2.917	17	112	2.914	2.96	1
2.828	VS	{132 132}	2.838	100	2.831	100	131	2.840	2.85	10
2.775	VM	024	2.792	6	2.784	18	022	2.780	2.81	0.5
2.617	M	124	2.629	26	2.622	55	122	2.618	2.66	4
2.564	W	{040 230}	2.575	13	2.578	23	{040 230}	{2.580 2.577}	2.58	2
2.531	VW	223	2.548	8	—	—	—	—	—	—
2.469	W	311	2.481	15	—	—	—	—	2.49	0.5
2.429	VW	{302 214}	2.452	5	2.455	2	212	2.444	2.49	0.5
2.385	W	232	2.405	8	2.404	15	231	2.350	2.39	3
2.355	VW	312	2.364	4	2.362	13	311	2.350	2.34	0.5
2.283	W	321	2.295	8	—	—	—	—	2.28	0.5
2.245	VVW	—	2.262	3	—	—	—	—	—	—
2.191	W	{313 322}	2.199	4	2.199	3	321	2.186	2.17	2
2.147B	W	215	2.149	2	—	—	—	—	2.10	0.5
2.050VB	W	304	2.041	13	2.047	18	{241 302}	{2.044 2.039}	2.05	2
2.032VB	VW	234	—	—	—	—	—	—	—	—
—	—	—	2.006	6	2.002	3	—	—	—	—
1.973	VVW	—	1.981	5	1.983	3	—	—	1.989	2
1.955	VW	151	1.965	6	—	—	—	—	—	—
1.917	VVVW	410	1.924	6	1.924	7	410	1.911	1.910	0.5
1.896	W	324	1.903	11	1.904	25	{151 322}	{1.910 1.896}	1.910	0.5
1.853	VW	036	1.860	7	—	—	—	—	1.895	3
1.822	W	420	1.827	6	1.829	8	{250 420}	{1.823 1.820}	1.821	3
1.813	S(M)	136	1.810	20	1.804	33	133	1.803	—	—
1.757	VW	{422 342}	1.762	11	1.764	20	{421 052}	{1.755 1.750}	1.762	3
1.747	W/M	252	1.756	12	1.756	28	251	1.757	—	—
1.703	W	060	1.710	10	1.714	20	060	1.720	1.734	2
1.693	VW	430	—	—	—	—	—	—	—	—
1.675	W	236	1.683	8	1.677	13	—	—	1.681	3

(1) Synthetic  $\text{Cu}_3\text{SbS}_3$  by Skinner<sup>21)</sup> (monoclinic,  $a=7.81\text{\AA}$ ,  $b=10.24\text{\AA}$ ,  $c=13.27\text{\AA}$ ,  $\beta=90^\circ 24'$ )

(2) At room temperature (present study)

(3) At  $200^\circ\text{C}$ , indexed with orthorhombic,  $a=7.78\text{\AA}$ ,  $b=10.32\text{\AA}$ ,  $c=6.60\text{\AA}$ .(4) Natural wittichenite by Berry and Thompson<sup>29)</sup>.

correspond to mineral species "stylotypite". However after deletion by Milton and Axelrod<sup>13)</sup>, mineral of  $\text{Cu}_3\text{SbS}_3$  composition has not been found up to date. Optical properties of synthetic  $\text{Cu}_3\text{SbS}_3$ , shown in Table 2, is somewhat different from those described by Murdoch<sup>7)</sup> and by Davy and Farnham,<sup>8)</sup> and rather resembles tetrahedrite in reflecting color but it is anisotropic and shows red internal reflections. X-ray powder diffraction pattern of quenched  $\text{Cu}_3\text{SbS}_3$  from  $480^\circ\text{C}$  agrees well with that of Godovikov et al<sup>18)</sup> and of Skinner et al<sup>21)</sup> as shown in Table 3 and also is quite similar to that of its bismuth analogue, wittichenite  $\text{Cu}_3\text{BiS}_3$ , except for several additional peaks. As mentioned below this powder pattern is of low temperature form of  $\text{Cu}_3\text{SbS}_3$ .

### Results of the Differential Thermal Analysis

The DTA were carried out on each of the four condensed phases and on the mixture of neighbouring two phases which have various bulk compositions. As discussed before satisfactory results were given by heating analysis with heating rate as low as  $0.625^\circ\text{C}/\text{min}$  or  $1.25^\circ\text{C}/\text{min}$ . The results of the DTA are shown

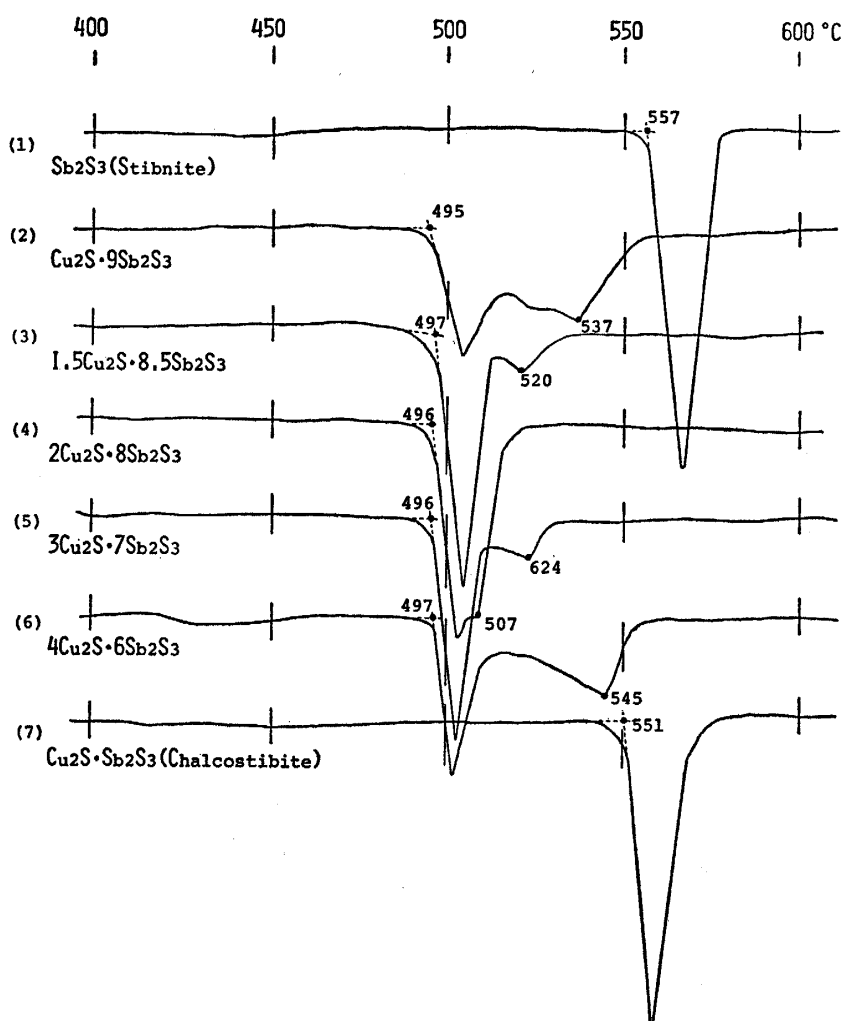


Fig. 2 The DTA curves for phase study on the  $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$  system (1).

in Fig. 2 and Fig. 3. Fig. 2 shows seven DTA curves performed on the sample containing less the 50% in  $\text{Cu}_2\text{S}$  molecular. Curve (1) and (7) are results of analyses on condensed homogeneous phases of  $\text{Sb}_2\text{S}_3$  and  $\text{CuSbS}_2$  respectively and they show both congruent melting effect at  $557^\circ\text{C}$  and  $551^\circ\text{C}$ . The congruent melting temperature of stibnite at  $557^\circ\pm 3^\circ\text{C}$  and chalcocostibite at  $551^\circ\pm 3^\circ\text{C}$  agree well with  $556^\circ\text{C}$  by Barton<sup>30)</sup> and  $553^\circ\pm 2^\circ\text{C}$  by Skinner et al<sup>21)</sup>. Other five curves have double endothermic peak which begin nearly the same temperature of  $496^\circ\pm 1^\circ\text{C}$  and these DTA curves show a typical eutectic relations. Nearly the same beginning temperature of the first endothermic peaks around  $496^\circ\text{C}$  indicate the eutectic melting of  $\text{Sb}_2\text{S}_3$  and  $\text{CuSbS}_2$ , and the end points of the second endothermic reaction of each curve show liquidus point at  $537^\circ\text{C}$ ,  $520^\circ\text{C}$ ,  $507^\circ\text{C}$ ,  $624^\circ\text{C}$ , and  $545^\circ\text{C}$  respectively.

The results of the analyses on the samples less than 50% in  $\text{Sb}_2\text{S}_3$  molecular are shown in Fig. 3. Curve (1) is the results on  $\text{CuSbS}_2$  also shown already as curve (7) in Fig. 2. Curve (6) is the analysis on another binary condensed phase  $\text{Cu}_3\text{SbS}_3$  that shows congruent melting reaction at  $613^\circ\text{C}$ . The curves

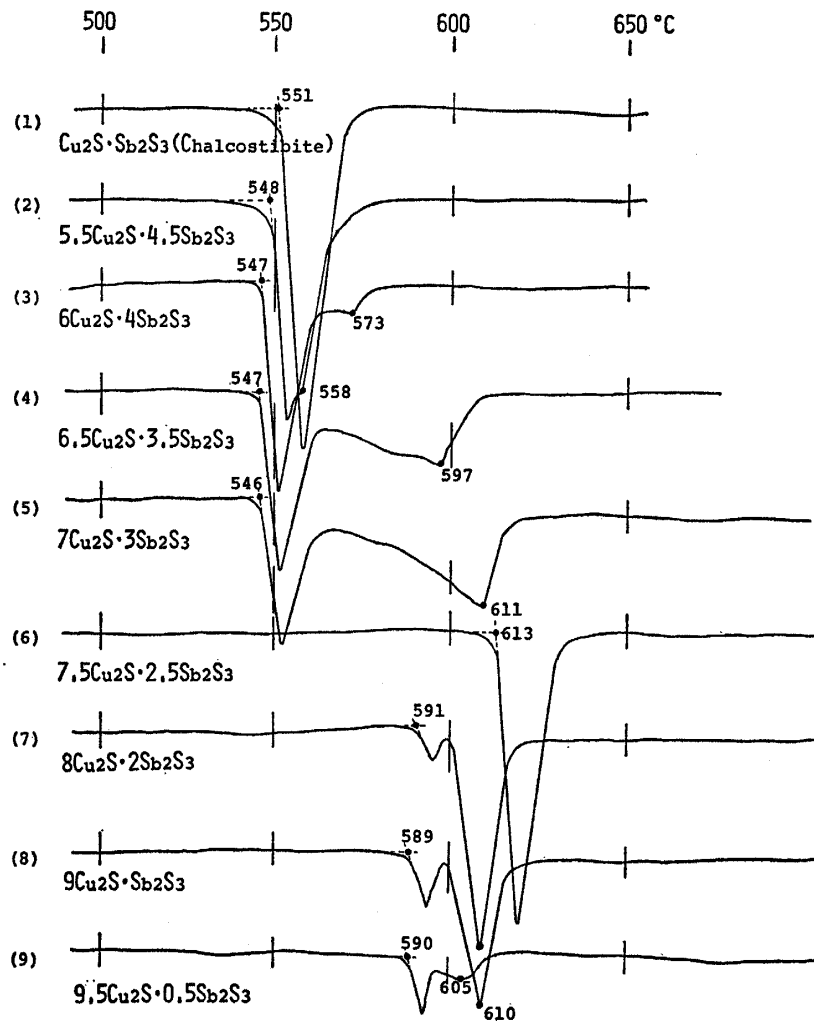


Fig. 3 The DTA curves for phase study on the  $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$  system (2).

in the figure are clearly divided into two groups at  $\text{Cu}_3\text{SbS}_3$  composition. The first group of curves (2), (3), (4), (5) shows nearly the same beginning temperatures of the first endothermic peaks at  $548^\circ\text{C}$ ,  $547^\circ\text{C}$ ,  $547^\circ\text{C}$ , and  $546^\circ\text{C}$  severally which may correspond to the eutectic melting of  $\text{CuSbS}_2$  and  $\text{Cu}_3\text{SbS}_3^*$ . Eutectic points should be between 50 mol% and 55 mol% in  $\text{Cu}_2\text{S}$  molecule and their liquidus temperatures, represented on the end point of the second endothermic peak with gentle slope, become higher smoothly like  $558^\circ\text{C}$ ,  $573^\circ\text{C}$ ,  $597^\circ\text{C}$  and  $611^\circ\text{C}$  as increase  $\text{Cu}_2\text{S}$  molecule in the bulk composition. Other three of the second group, curves (7), (8), and (9) are experiments on the mixture sample of  $\text{Cu}_3\text{SbS}_3$  and  $\text{Cu}_2\text{S}$ . Though these curves don't clearly show definite phase relations, the same beginning temperature of the first endothermic peak at  $590^\circ\text{C}$  possibly correspond to eutectic melting between  $\text{Cu}_2\text{S}$  and  $\text{Cu}_3\text{SbS}_3$ .

The results of fifteen thermal analysis are summarized in Table 4.

Table 4. Results of the differential thermal analysis for the  $\text{Cu}_2\text{S}$ - $\text{Sb}_2\text{S}_3$  system

$\text{Cu}_2\text{S}$ mol%	$T_1$	$T_2$	$T_3$	$T_4$
0.0	$557^\circ\text{C}$			
10.0	537	$495^\circ\text{C}$		
15.0	520	497		
20.0	507	496		
30.0	524	496		
40.0	545	497		
50.0	551			
55.0	558		548	
60.0	573		547	
65.0	597		547	
70.0	611		546	
75.0	613			
80.0	613			589
90.0	610			591
95.0	605			590
mean value		$496^\circ\text{C}$	$547^\circ\text{C}$	$590^\circ\text{C}$
$T_1$ : Liquidus				
$T_2$ : Eutectic of stibnite-chalcostibite				
$T_3$ : Eutectic of chalcostibite- $\text{Cu}_3\text{SbS}_3$				
$T_4$ : Eutectic of $\text{Cu}_3\text{SbS}_3$ -chalococite?				

### Quenching Experiment of Phase Relations

The almost satisfactory results on the phase relations of the binary system  $\text{Cu}_2\text{S}$ - $\text{Sb}_2\text{S}_3$  were given by the DTA. It is still necessary to examine the result by means of the other method because the DTA is essentially on the dynamic

\* Skinner et al suggest a different interpretation, and discussion on this will be done later.



analysis. Several quenching experiments were performed to make sure the phase relation and some of the results are listed in Table 5. As Copper antimonian

Table 5. Results of quenching experimental runs

Composition $\text{Cu}_2\text{S}$ mol%	Temp. °C	Time days	Quenched products
10.0	551	7	Liq
	542	6	Liq
	530	7	Stb+Liq
20.0	510	10	Liq
	500	7	Stb+Liq
	490	7	Stb+Csb
25.0	518	7	Liq
	510	7	Liq
	502	7	Csb+Liq
	485	12	Csb+Stb
40.0	551	7	Liq
	540	6	Csb+Liq
	502	7	Csb+Liq
	485	12	Csb+Stb
55.0	580	5	Liq
	565	5	Liq
	551	7	Liq + ( $\text{Cu}_3\text{SbS}_3$ )
	540	7	$\text{Cu}_3\text{SbS}_3$ + Csb
65.0	620	5	Liq
	600	5	Liq
	585	5	$\text{Cu}_3\text{SbS}_3$ + Liq
	551	7	$\text{Cu}_3\text{SbS}_3$ + Liq
	530	7	$\text{Cu}_3\text{SbS}_3$ + Csb
85.0	660	5	Cc + Liq?
	620	5	Cc + Liq?

sulfide melt also could not be quenched to "glass" similarly in other sulfide system such as the Cu-Bi-S, system, identification of melt, especially in the case of melt in which the crystalline phase exist in equilibrium with at the run temperature, was not easy. It can be only deduced from grain size, material form, and textural relations in quenched samples under ore microscopic observation. All the quenching experiments shown in Table 5 are not in conflict with the result of the DTA and support positively the results from the DTA investigation. Experiments on the bulk composition of 20.0 mol% and 25.0 mol%  $\text{Cu}_2\text{S}$  show that the eutectic melting begins between 500°C and 490°C, 502°C and 485°C respectively which are consistent with 496°C given by the DTA. And they also indicate the eutectic point must be between these two composition. Eutectic point should be nearly 22.5 mol%  $\text{Cu}_2\text{S}$  at 496°C.

Solidus of the eutectic melting\* between  $\text{CuSbS}_2$  and  $\text{Cu}_3\text{SbS}_3$  should be

\* see later discussion

between 551°C and 540°C from the result of quenching runs on the composition of 55.0 mol%  $\text{Cu}_2\text{S}$  which support the result of 547°C from the DTA. Eutectic point between  $\text{CuSbS}_2$  and  $\text{Cu}_3\text{SbS}_3$  is possibly 53.0 mol%  $\text{Cu}_2\text{S}$  at  $547^\circ \pm 3^\circ\text{C}$  from the fact  $\text{Cu}_3\text{SbS}_3$  is in equilibrium with liquid at 551°C on 55.0 mol% run.

#### *High Temperature X-ray Study for $\text{Cu}_3\text{SbS}_3$*

As mentioned previously, X-ray powder diffraction pattern of  $\text{Cu}_3\text{SbS}_3$  quenched from 480°C is very similar to that of wittichenite but is not identical. Skinner et al<sup>21)</sup> mention that  $\text{Cu}_3\text{SbS}_3$  at high temperature cannot be quenched but invert into low temperature metastable polymorph. Then some high temperature X-ray investigation was practiced on  $\text{Cu}_3\text{SbS}_3$ . X-ray powder data of  $\text{Cu}_3\text{SbS}_3$  at room temperature and at 200°C are already shown in Table 3 comparing with those of low form  $\text{Cu}_3\text{SbS}_3$  by Skinner et al<sup>21)</sup> and of wittichenite by Berry and Thompson<sup>29)</sup>. High temperature form has orthorhombic symmetry,  $a=7.68 \text{ \AA}$ ,  $b=10.33 \text{ \AA}$ ,  $c=6.70 \text{ \AA}$ , which is the same structure as that of wittichenite  $\text{Cu}_3\text{BiS}_3$ , while low temperature polymorph has monoclinic symmetry,  $a=7.81 \text{ \AA}$ ,  $b=10.24 \text{ \AA}$ ,  $c=13.27 \text{ \AA}$ ,  $\beta=90^\circ 24'$  as shown before by Skinner et al<sup>21)</sup>. As c-dimension of low monoclinic form is twice of that of high orthorhombic form, value of  $l$  indexed in monoclinic cell must be twice of that in orthorhombic cell. And then some reflection which have odd number  $l$  index appearing in low form must disappear in high form as shown in Table 3.

The intensity of the characteristic reflection (311) in low temperature form is measured carefully with elevating temperature from room temperature up to 200°C, and the results plotted in diagram are shown in Fig. 4. which indicate the reversible inversion taking place at around 120°C. This inversion temperature is essentially identical to that of  $122^\circ \pm 2^\circ\text{C}$  by Skinner et al<sup>21)</sup>.

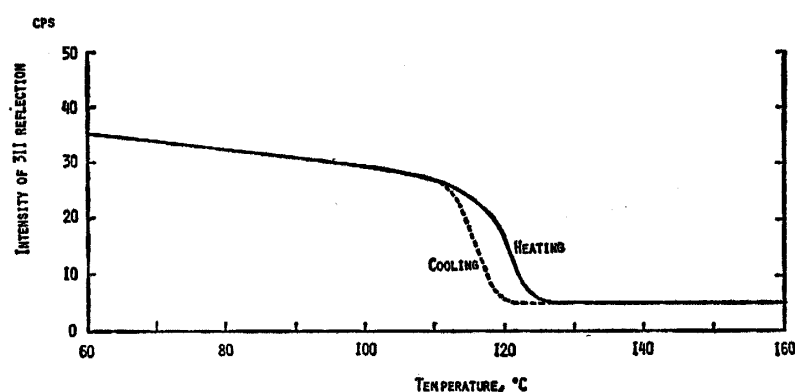


Fig. 4 Intensity change of the reflection (311) which is characteristic in low temperature monoclinic form of  $\text{Cu}_3\text{SbS}_3$  on heating.

### **Summary of Phase Relation and Discussions**

The summarized phase diagram of the  $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$  system is shown in

Fig. 5 and the temperatures of the phase changing reactions are listed in Table 6.

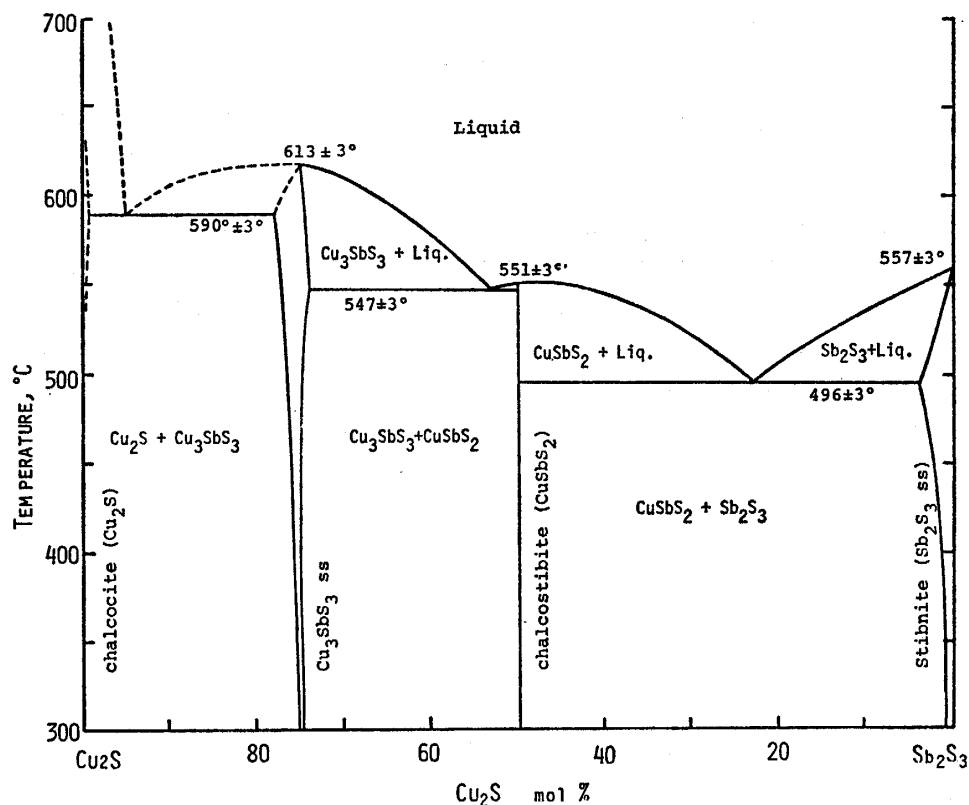


Fig. 5 Phase diagram of the  $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$  system.

Table 6. List of the reaction temperature in the  $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$  system.

Congruent melting of $\text{Sb}_2\text{S}_3$	$557 \pm 3^\circ\text{C}$
Congruent melting of $\text{CuSbS}_2$	$551 \pm 3^\circ\text{C}$
Congruent melting of $\text{Cu}_3\text{SbS}_3$	$613 \pm 5^\circ\text{C}$
Inversion of $\text{Cu}_3\text{SbS}_3$	$120 \pm 5^\circ\text{C}$
Eutectic of $\text{Sb}_2\text{S}_3-\text{CuSbS}_2$	$496 \pm 3^\circ\text{C}$
Eutectic* of $\text{CuSbS}_2-\text{Cu}_3\text{SbS}_3$	$547 \pm 5^\circ\text{C}$

\* There is possibility this reaction is not eutectic but also other tie line change reaction.

Crystalline phases in the system are only four,  $\text{Cu}_2\text{S}$  (chalcocite),  $\text{Cu}_3\text{SbS}_3$ ,  $\text{CuSbS}_2$  (chalcostibite), and  $\text{Sb}_2\text{S}_3$  (stibnite).

The melting temperature of stibnite was known to be at  $546^\circ\text{C}$  by Hansen and Anderco<sup>31)</sup> (1958) but in this study was determined at  $557 \pm 3^\circ\text{C}$  which agree well with that of Barton's work<sup>30)</sup> (1971). Stibnite could contain a small amount of Cu as much as about 2 mol%  $\text{Cu}_2\text{S}$  at  $480^\circ\text{C}$ .

Previous worker's data about the congruent melting temperature of chalcostibite are  $535^\circ\text{C}$  by Wernick and Benson<sup>32)</sup> (1957),  $552.6^\circ\text{C}$  by Cambi and Elli<sup>20)</sup>

(1965), and  $553^\circ \pm 2^\circ\text{C}$  by Skinner et al.<sup>21)</sup> (1972), compared to our value of  $551^\circ \pm 3^\circ\text{C}$ . Last three values except Wernick and Benson's one show good agreement each other. There is no evidence from our experiment to suggest chalcostibite has a measurable solid solution field about the ideal composition  $\text{CuSbS}_2$ .

Although Skinner et al.<sup>21)</sup> suggest stibnite and chalcostibite assemblage change into antimony metal and liquid at  $476.5^\circ \pm 2^\circ\text{C}$ , no evidence supporting this tie line change could not be found in our experiments even from ternary phase study. The DTA curves also indicate that no phase changing reaction can be expected below  $496^\circ\text{C}$ , the beginning temperature of distinct endothermic reactions which are seen in common on every curves between  $\text{Sb}_2\text{S}_3$  and  $\text{CuSbS}_2$ . Supposing that this endothermic reaction correspond to the tie line change, obtained temperature in our analyses is almost 20 degree higher than that of Skinner's value. The endothermic reaction rather seems to be a beginning of the melting reaction of stibnite and chalcostibite and both phase possibly melt in eutectic relations. The eutectic point between them is  $496^\circ \pm 3^\circ\text{C}$  at about 22.5 mol%  $\text{Cu}_2\text{S}$ .

$\text{Cu}_3\text{SbS}_3$  melts also congruently at  $613^\circ \pm 3^\circ\text{C}$  which is nearly the same but a little higher than  $607.5^\circ \pm 3^\circ\text{C}$  of the value of Skinner et al.<sup>21)</sup> Cambi and Elli<sup>20)</sup> (1965) mention about tetrahedrite occurring along the join  $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ , having a melting point at  $610^\circ\text{C}$ , but it supposed to be  $\text{Cu}_3\text{SbS}_3$  phase and its melting temperature.  $\text{Cu}_3\text{SbS}_3$  has a small solid solution field along the join  $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$ , which extends from 74 mol% to 77 mol%  $\text{Cu}_2\text{S}$  at  $480^\circ\text{C}$ .

$\text{Cu}_3\text{SbS}_3$  has two modifications which invert reversely at about  $120^\circ\text{C}$ . High temperature polymorph has orthorombic symmetry of wittichenite type structure, while low temperature polymorph is monoclinic. Skinner et al.<sup>21)</sup> also suggest that  $\text{Cu}_3\text{SbS}_3$  is only stable above  $359^\circ\text{C}$ , but now the authors do not have any positive data about this. Though no change was observed when  $\text{Cu}_3\text{SbS}_3$  synthesized at higher temperature than  $400^\circ\text{C}$  was annealed at  $200^\circ\text{C}$  as long as 10 days, it is not clear whether  $\text{Cu}_3\text{SbS}_3$  is a stable phase below  $400^\circ\text{C}$  or not.

The eutectic point between chalcostibite and  $\text{Cu}_3\text{SbS}_3$  should be  $547^\circ \pm 3^\circ\text{C}$  at about 53 mol%  $\text{Cu}_2\text{S}$ , if both phases melt in eutectic relations as shown in the phase diagram of Fig. 5. However Skinner et al. suggest that this is not a eutectic but the reaction chalcostibite +  $\text{Cu}_3\text{SbS}_3$  going to famatinite + liquid at  $543^\circ \pm 2^\circ\text{C}$ . Anyway the reaction temperature is so close to the melting temperature of chalcostibite,  $551^\circ\text{C}$ , that it might be difficult to make clear the relations, and the possibility of Skinner's interpretation is also present. In this case the  $\text{Cu}_2\text{S}-\text{Sb}_2\text{S}_3$  system becomes a pseudobinary.

Melting relation of  $\text{Cu}_2\text{S}$  rich area have not been revealed yet and more detailed experiments have to be carried out.

### References

- 1) Scharizer: *Jahrbuch, d.k.k. Geolog. Reichsanst.*, **40**, 433 (1890)
- 2) Sandberger: *Jb. Mineral.*, **1**, 274 (1891)
- 3) E. Dana: "Dana's system of mineralogy" John Wiley & Sons, N. Y. (1892)
- 4) S. Stevanovic: *Zeit. für Krist.*, **37**, 235 (1903)
- 5) F. von Kobell: *Ber. Akad. Muenchen*, **1**, 163-168 (1865)
- 6) C. D. Hulin: "Geology and ore deposits of the Randsburg Quadrangle" California state Min. Bur., Bull. **95**, (1925)
- 7) J. Murdoch: "Microscopic determination of the opaque minerals" N.Y. (1916)
- 8) W. M. Davy and C. M. Farnham: "Microscopic examinations of the ore minerals" McGraw Hill N. Y. (1920)
- 9) C. Doelter and H. Leitmeier: "Handbuch der Mineralchemie" **4**, (1926)
- 10) C. Palache, H. Berman and C. Frondel: "Dana's system of mineralogy" 7th ed., Vol. **1**, John Wiley & Sons N.Y. (1944)
- 11) H. Schneiderhöhn and P. Ramdohr: "Lehrbuch der Erzmikroskopie" Bd. **II**, Berlin (1931)
- 12) P. Ramdohr: "Klockmann's Lehrbuch der Mineralogie" 7th ed., Stuttgart (1948)
- 13) C. Milton and J. M. Axelrod: *Amer. Mineral.*, **36**, 696-703 (1951)
- 14) *American Mineralogist*, **37**, 362 (1952)
- 15) N. Parravano and P. de Cesaris: *Atti. Acad. Lincei*, (5) **21**, 797 (1912)
- 16) H. Shima: *Jour. Mineral. Soc. Japan*, **8**, 357 (1967) Abs. (in Japanese)
- 17) A. Sugaki, H. Shima and A. Kaneyasu: *Mining Geology*, **19**, 75 (1969) Abs. (in Japanese)
- 18) A. A. Godovikov, N. A. Ilyasheva, and S. N. Nenasheva: *Soc. Mining Geol., Japan Spec. Issue* **2**, 32-34 (1971)
- 19) V. Ross: *Econ. Geol.*, **49**, 734-752 (1954)
- 20) L. Cambi and M. Elli: *Chimica Industria*, **47**, 2 (1965)
- 21) B. J. Skinner, F. D. Luce and E. Makovicky: *Econ. Geol.*, **67**, 924-938 (1972)
- 22) A. Sugaki and H. Shima: *Mem. Fac. Eng. Yamaguchi Univ.*, **15**, 15-32 (1965)
- 23) A. Sugaki, and H. Shima: *Tech. Rept. Yamaguchi Univ.*, **1**, 45-70 (1972)
- 24) A. Sugaki, and H. Shima: *Mem. Fac. Eng. Yamaguchi Univ.*, **16**, 99-108 (1965) (in Japanese)
- 25) G. Kullerud and R. A. Yund: *Jour. Petr.*, **3**, 126-175 (1962)
- 26) G. H. Moh: *Neues Jb. Mineral. Abh.*, **111**, 227-263 (1969)
- 27) W. Uytendogaardt and E. A. J. Burke: "Tables for microscopic identification of ore minerals" Elsevier Amsterdam (1971)
- 28) C. Schouten: "Determination tables for ore microscopy" Elsevier Amsterdam (1962)
- 29) L. G. Berry and R. M. Thompson: "X-ray powder data for ore minerals" *Geol. Soc. Amer.*, N. Y. (1962)
- 30) P. B. Barton Jr.: *Econ. Geol.*, **66**, 121-132 (1971)
- 31) M. Hansen and K. Anderko: "Constitution of binary alloys" McGraw Hill N.Y. (1958)
- 32) J. H. Wernick and K. E. Benson: *Jour. Chem. Phys. Solid.* **3**, 157-159 (1957)