Phase Relations of the Cu_2S-Bi_2S_3 System

Asahiko SUGAKI* and Hiromi SHIMA*

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Introduction

As the copper-bismuth sulfide minerals, wittichenite ($3Cu_2S \cdot Bi_2S_3$), klaprothite ($3Cu_2S \cdot 2Bi_2S_3$), emplectite ($Cu_2S \cdot Bi_2S_3$), cuprobismutite ($Cu_2S \cdot Bi_2S_3$ or $3Cu_2S \cdot 4Bi_2S_3$), and dognacskite ($Cu_2S \cdot 2Bi_2S_3$) have been reported until now in natural occurrence, but the validity of their existence except wittichenite and emplectite has been questioned and discussed many times by numerous workers.

In 1868, Petersen[1] and Sandberger[2] gave a chemical composition of $3Cu_2S \cdot 2Bi_2S_3$ to copper-bismuth sulfide mineral from the Daniel mine, Wittichen, Baden which occurred with chalcopyrite and native bismuth in barite, usually in needle-like crystal. They named it klaprothite. Murdoch[3] concluded that the validity of the species was very doubtful in 1916. Schneiderhöhn and Ramdohr[4] (1931) recognized klaprothite, considering Murdoch's decision incorrect, but Short[5] (1940) had a doubt about it. Moreover, while it was again described in Dana's System of Mineralogy[6] (1944) as a well defined mineral species with orthorhombic form, Nuffield[7] (1947) minutly investigated the specimens by means of X-ray powder photograph and found that they were wittichenite, emplectite, tetrahedrite, or their mixture. However, Ramdohr[8] still suggested a possibility of existence of klaprothite in his new book.

On the other hand, cuprobismutite, found by Hillebrand[9] from the Missouri mine, Hall's Valley, Park Country, Colorado in 1884, was given first $3(Cu, Ag)_2S \cdot 4Bi_2S_3$ of chemical composition by him. The Hillebrand's data were described in the Dana's System of Mineralogy[10] (1892), and Schneiderhöhn and Ramdohr[4] reported another occurrence from Arnsberg, Westphalis, but Short[5] and Palache[11] (1940) afterwards decided that these specimens were emplectite or the mixture of emplectite and bismuthinite, and denied the existence of cuprobismutite. From the results of re-examination on the type specimens from Missouri mine, however, Nuffield[12] (1952) identified cuprobismutite as valid species with chemical composition of $Cu_2S \cdot Bi_2S_3$, and suggested dimorphic relations with emplectite.

Some experimental investigations of this system have been done. Gaudin and Dicke[13] (1939) synthesized artificially Phase A ($Cu_2S \cdot 2Bi_2S_3$), Phase B ($3Cu_2S \cdot 2Bi_2S_3$), and Phase C($3Cu_2S \cdot Bi_2S_3$), and reported that they respectively corresponded to cuprobismutite, klaprothite and wittichenite, but the experi-

* Department of Mining and Mineral Engineering.

ments were carried on in the air and the atomic ratio of these phases does not seem very accurate. Nuffield[7] succeeded in synthesizing wittichenite from the Cu–Bi–S melt, but failed in synthesizing klaprothite and emplectite. He also described[12] a new synthetic phase $3Cu_2S \cdot 5Bi_2S_3$ and a homogeneous phase which has similar X-ray powder pattern of cuprobismutite are produced from the melt. The authors[14] described four synthetic phases of the system, wittichenite, cuprobismutite, $Cu_3Bi_5S_9$ and $CuBi_3S_5$ in 1965. Recently Buhlmann[15] (1971) investigated this system and gave a short paper on the phase relation of this binary system. He does not mention his experiments much in detail but shows only one phase diagram. His result shown in the diagram is almost similar to ours except some of the temperatures of phase changes and detail parts.

Experimental Procedures

Starting Materials:

The primary starting materials used in this experiments were electrolytic copper of 99.99+% in purity, bismuth metal of 99.9+% in purity, and crystlline sulfur refined as guaranteed reagent by Kanto Chemical Co., purity grade 99.98+%. Copper chips were reduced in hydrogen atmosphere at about 900°C for 2 hours prior to experiments. Using these elements the end-members of the system, Cu_2S and Bi_2S_3 were synthesized first in evacuated silica glass tube and then they were used as starting materials for the phase equilibrium study of the binary system.

Method of Synthesis:

Detailed technique of the synthesis has been described in the preceding paper[16]. Carefully weighed amounts of the previously prepared compound, Cu_2S and Bi_2S_3 were sealed into evacuated silica glass or Hario hard glass tube. By inserting a closely fitting glass rod into the tubes, the vapor volume was effectively reduced as described by Kullerud and Yorder[17]. Tubes thus prepared were heated in horizontal or vertical furnaces for various periods and at desired temperatures, controlled within ± 1°C or ± 3°C, depending on the requirment of the experiment. When required, the individual samples were repeatedly ground under aceton and re-heated at a given temperature two or three times to attain equilibrium. Every weighing was performed on an analytical balance, permitting an accuracy of ± 0.05 mg per weighing. The uncertainty in the composition never exceeded 0.1 wt% and was less than 0.05 wt% in most runs. All the runs performed in this study were quenched. The tubes were dropped into ice water and then could be lowered from the furnace temperature to the room temperature in less than 3 seconds.

Identification of Phases:

The reaction products of the experiments were routinely identified at room temperature by reflecting microscope and X-ray powder diffractometer. A

small quantity of the products, generally in powder or sintered mass, were mounted on polyester resin Rigorac and polished smoothly, and then examined under the microscope. Generally, as optical properties of each cuprobismuth sulfide phases are quite similar, they are hardly identified one another, but microscopic observation was usefull to determine homogeneity of products.

The products obtained in all experiments were identified mainly by careful examination of their X-ray powder diffraction patterns. When measurments of d-spacing in high accuracy were required, high purity silicon (99.9999%) was used as an internal standard. Rigaku X-ray diffractometer, Geigerflex was employed in all cases. In some cases, high temperature X-ray technique and single crystal methods were employed. High temperature studies were conducted within nitrogen atmosphere by using Rigaku high temperature X-ray diffractometer and Rigaku continuous cassette moving high temperature camera.

The Differential Thermal Analysis:

The differential thermal analysis (DTA) was very useful for a phase study, especially to know easily the temperature of any phase changing reactions. The apparatus and methods have been described before in detail.[18] All analyses were performed in the evacuated silica glass tubes each having a thermocouple-well of about 5 mm depth at the bottom of the tube. The similar techniques have been used by Jensen[19], Kracek[20], Kullerud and Yund[21], Dunne and Kerr[22], and Moh[23]. In order to check the accuracy of the apparatus and to make a calibration curve to correct the reaction temperature,

Table 1. Calibration of the D.T.A. by melting points of metals

Metal	Melting point (°C)	Heating rate	Temp. at peak beginning (°C)	Deviation (°C)	Cooling analysis (°C)
Tin	231.9	1.25°/min.	233	+1.1	211
		5°/min.	235	+3.1	
		10°/min.	235	+3.1	
Bismuth	271.0	1.25°/min.	271	±0.0	272
		5°/min.	272	+1.0	
		10°/min.	273	+2.0	
Lead	327.3	1.25°/min.	329	+1.7	331
		5°/min.	330	+2.7	
		10°/min.	331	+3.7	
Zinc	419.7	1.25°/min.	421	+1.3	421
		5°/min.	421	+1.3	
		10°/min.	422	+2.3	
Antimony	630.5	1.25°/min.	631	+0.5	571
		10°/min.	632	+1.5	
Aluminium	660.1	1.25°/min.	661	+0.9	660
		5°/min.	663	+2.9	
		10°/min.	664	+3.9	

Table 2. Results of experimental runs at 500°C and 400°C

Cu_2S mol%	Temp. (°C)	Time (days)	Products
100.0	500	5	Cu_2S ss
90.0	500	5	Cu_9BiS_6 ss
85.0	500	5	Cu_9BiS_6 ss
85.0	500	5	Cu_9BiS_6 ss
82.5	500	5	Cu_9BiS_6 ss
80.0	500	5	Cu_9BiS_6 ss+Cu_3BiS_3 ss
75.0	500	5	Cu_9BiS_6 ss+(Cu_3BiS_3 ss)
73.0	500	5	Cu_3BiS_3 ss
70.0	500	5	Cu_3BiS_3 ss+$Cu_3Bi_5S_9$ ss
60.0	500	5	Cu_3BiS_3 ss+$Cu_3Bi_5S_9$ ss
50.0	500	5	Cu_3BiS_3 ss+$Cu_3Bi_5S_9$ ss
40.0	500	5	$Cu_3Bi_5S_9$ ss
37.5	500	5	$Cu_3Bi_5S_9$ ss
30.0	500	5	$Cu_3Bi_5S_9$ ss+$CuBi_3S_5$
25.0	500	5	$CuBi_3S_5$
20.0	500	5	$CuBi_3S_5$+Bi_2S_3
5.0	500	5	$CuBi_3S_5$+Bi_2S_3
0.0	500	5	Bi_2S_3
100.0	400	14	Cu_2S ss
90.0	400	14	Cu_9BiS_6 ss
87.5	400	14	Cu_9BiS_6 ss+Cu_3BiS_3 ss
85.0	400	14	Cu_9BiS_6 ss+Cu_3BiS_3 ss
80.0	400	14	Cu_9BiS_6 ss+Cu_3BiS_3 ss
75.0	400	14	Cu_3BiS_3 ss
60.0	400	14	Cu_3BiS_3 ss+$Cu_{24}Bi_{26}S_{51}$
50.0	400	14	$Cu_{24}Bi_{26}S_{51}$ (+Cu_3BiS_3 ss)
48.0	400	14	$Cu_{24}Bi_{26}S_{51}$
42.9	400	14	$Cu_{24}Bi_{26}S_{51}$+$CuBi_3S_5$
37.5	400	14	$Cu_{24}Bi_{26}S_{51}$+$CuBi_3S_5$
30.0	400	14	$Cu_{24}Bi_{26}S_{51}$+$CuBi_3S_5$
25.0	400	14	$CuBi_3S_5$
20.0	400	14	$CuBi_3S_5$+Bi_2S_3

Table 3. Stable crystalline phases in the Cu_2S–Bi_2S_3 system

Phases (Composition)		Cu_2S mol%	Minerals
Cu_2S		100.0	chalcocite
Cu_9BiS_6	($9Cu_2S{\cdot}Bi_2S_3$)	90.0	
Cu_3BiS_3	($3Cu_2S{\cdot}Bi_2S_3$)	75.0	wittichenite
$Cu_{24}Bi_{26}S_{51}$	($48Cu_2S{\cdot}52Bi_2S_3$)	48.0	cuprobismutite / emplectite
$Cu_3Bi_5S_9$	($3Cu_2S{\cdot}5Bi_2S_3$)	37.5	
$CuBi_3S_5$	($Cu_2S{\cdot}3Bi_2S_3$)	25.0	
Bi_2S_3		0.0	bismuthinite

pure metals such as tin(Sn), bismuth(Bi), lead(Pb), zinc(Zn), antimony(Sb), and aluminum(Al) were used as an external standard, and the results are shown in Table 1. They show clearly that melting temperatures given from the DTA curves were fairly in good agreement with true melting points of the metals. When the heating rate of the analysis is so slow as 1.25°C/min. or less and the observed temperature is corrected to 1°C lower after the analysis, the accuracy of the reaction temperature measured by the DTA was within ± 1°C for melting of metals. The best results were obtained in our experiment of this system when the heating rates were 0.6°C and 1.25°C per minute and the accuracy would be within ± 3°C. Besides, if more than one reaction occur within a narrow temperature range on heating, the reaction peaks will overlap in the high heating rate analysis. However, the analysis with the low heating rate may separate individual reactions and facilitate to read the reaction temperatures from the DTA curves. Though Zakjarov[24] described the small effect of the sample mass, Shima[25] could not find any effect on the result in the analyses of the sample mass of 0.2 to 1.0 g. The routine analyses were done on the sample of 0.2 to 0.5 g.

Experimental Results

Preliminary Synthesis of Phases:

The primary purpose of this study was to synthesize all stable phases in the Cu_2S–Bi_2S_3 system because of the contradictory results reported by earlier workers. Next, the compositional and thermal stability field of each phases was determined and the phase relations of the system such as solidus and liquidus relations were investigated. Experiments by quenching methods at 500°C and 400°C were made preliminary to establish the stable phases of the system.

The experimental results of the runs are compiled in Table 2. Though in the table nothing is mentioned about vapor phase, these solid phases always keep equilibrium with sulfur vapor under their own sulfur vapor pressur.

As shown in the table six condenced phases of Cu_2S, Cu_9BiS_6, Cu_3BiS_3, $Cu_3Bi_5S_9$, $CuBi_3S_5$, and Bi_2S_3 are stable at 500°C in the binary join, and at 400°C in addition to these six, $Cu_{24}Bi_{26}S_{51}$ becomes stable while $Cu_3Bi_5S_9$ becomes unstable. The seven stable crystalline phases given in Table 3 are all entirely homogeneous under the ore microscope and their optical properties were already reported.[14] [15] Cu_2S, Cu_3BiS_3, $Cu_{24}Bi_{26}S_{51}$, and Bi_2S_3 correspond to chalcocite, wittichenite, cuprobismutite, and bismuthinite respectively, but other three binary compounds have not been found in nature up to date. The X-ray powder diffraction data of four binary phases, Cu_3BiS_3, $Cu_{24}Bi_{26}S_{51}$, $Cu_3Bi_5S_9$, $CuBi_3S_5$ are shown in Tables 4, 5, 6 and 7. As is evident from the Tables 4 and 5, the data of Cu_3BiS_3 and $Cu_{24}Bi_{26}S_{51}$ are in good agreement with those of natural wittichenite and cuprobismutite by Nuffield[7] and Berry and Thompson[26] respectively. Klaprothite, $Cu_6Bi_4S_9$, and dognacskite, $Cu_2Bi_4S_7$ were not stable phases in the system at 400°C and 500°C.

Table 4. The data of X-ray powder diffraction for synthetic Cu_3BiS_3 (wittichenite).

(1)		(2)		
d	I	d	I	hkl
5.66	20	5.68	1	011
5.22	20	5.22	1	020
4.55	55	4.55	4	111
3.85	45	3.83	1	200
3.62	15	3.62	1	121, 210
3.35	20	3.34	1	002, 201
3.18	50	3.19	3	012, 211
3.08	80	3.08	8	220, 102, 031
2.95	35	2.96	1	112
2.86	100	2.85	10	131
2.814	25	2.81	1/2	022
2.648	50	2.66	4	122
2.604	15			
2.578	25	2.58	2	040, 230
2.492	5	2.49	1/2	310
2.401	20	2.39	3	032, 231, 301
2.338	10	2.34	1/2	311
2.301	7	2.28	1/2	141, 320, 132
2.275	2			
2.181	10	2.17	2	013, 321
2.104	5	2.10	1/2	113
2.051	15	2.05	2	330, 023, 042
2.038	10			241
1.997	25	1.989	2	312, 150
1.987	15			123
1.929	10	1.910	1/2	151
1.886	20	1.895	3	322
1.824	30	1.821	3	113, 250
1.812	10			
1.765	25	1.762	3	052

(1) Synthetic Cu_3BiS_3

(2) X-ray powder data for wittichenite by Nuffield[7]

Table 5. The data of X-ray powder diffraction for synthetic $Cu_{24}Bi_{26}S_{51}$

(1)		(2)		
d	I	d	I	hkl
8.22	7			
6.92	9			
6.29	40	6.24	2	$\bar{2}02$
5.63	8			
5.01	25			
4.55	15			
4.37	20			
4.31	25	4.31	3	400
3.85	12			
3.71	50			
3.63	85	3.65	4	111, $\bar{4}03$
3.46	40	3.47	1	402, $\bar{1}12$
3.34	5			
3.11	80	3.23	4	310, $\bar{3}11$, 204
3.17	10			
3.10	100	3.10	10	311, $\bar{1}13$, $\bar{3}12$
3.02	12			
3.00	30			
2.94	10	2.96	1/2b	113, $\bar{6}01$
2.92	25			
2.866	40	2.86	1b	$\bar{6}02$, 312, $\bar{3}13$
2.731	40	2.73	6	601, $\bar{6}03$, $40\bar{5}$
2.645	15			
2.589	12			
2.564	12	2.58	1	$\bar{3}14$, $\bar{5}12$
2.528	10			
2.492	12	2.49	1/2	511, 006
2.443	5			
2.405	12	2.49	1/2	
2.328	7			
2.307	20	2.30	1/2	$\bar{6}05$, 206
2.176	50	2.17	2	$\bar{2}07$, 800
2.132	15			
2.113	12			
2.092	25	2.09	2	710, 801, $\bar{6}06$
2.049	10	2.00	1/2	207, 802
1.959	20	1.961	3	020, $\bar{7}14$
1.943	10			
1.923	9			
1.897	9			

(1) Synthetic $Cu_{24}Bi_{26}S_{51}$ (cuprobimutite)

(2) Data for natural cuprobismutite by Berry and Thompson[27]

Table 6. The data of X-ray powder diffraction for synthetic $Cu_3Bi_5S_9$.

d (meas.)	I	hkl	d (calc.)
7.26	5	002	7.26
6.51	8	200	6.50
6.35	7	$\bar{2}01$	6.37
5.61	18	201	5.58
5.33	5	$\bar{2}02$	5.34
4.49	23	202	4.47
3.84	8	110	3.81
3.63	20	111 004	3.64 3.63
3.60	65	203	3.59
3.467	100	$11\bar{2}$	3.445
3.429	65	$20\bar{4}$	3.440
3.295	30	112 $40\bar{1}$	3.302 3.299
3.251	7	400	3.251
3.176	18	$40\bar{2}$	3.184
3.059	10	401	3.059
2.950	50	204 310 113	2.956 2.931 2.920
2.905	11	005	2.905
2.825	80	$20\bar{5}$ $31\bar{2}$ 311	2.846 2.839 2.809
2.657	17	$40\bar{4}$ $31\bar{3}$	2.667 2.652
2.501	12	403 205	2.502 2.494
2.264	35	115	2.254
2.178	9	$51\bar{2}$	2.176
2.106	25	$60\bar{3}$ 511	2.123 2.108
2.100	25	$51\bar{3}$	2.105
2.094	25	$11\bar{6}$ 601	2.092 2.090
2.077	13	007	2.076
2.011	35	$60\bar{4}$ 512	2.025 2.006
2.002	35	$51\bar{4}$ 405 116	2.002 1.998 1.997
1.987	25	$31\bar{6}$ 602	1.987 1.983
1.866	25		

Table 7. The data of X-ray powder diffraction for synthetic $CuBi_3S_5$

d (meas.)	I	hkl	d (calc.)
6.63	1	$20\bar{1}$	6.62
6.36	4	002	6.36
5.98	11	200	5.96
5.78	4	$20\bar{2}$	5.78
4.68	25	201	4.68
4.24	3	003	4.24
3.82	4	011	3.83
3.64	40	202	3.64
3.50	100	$20\bar{4}$	3.51
3.305	25	$40\bar{2}$	3.307
3.179	15	004	3.179
3.166	10	$40\bar{3}$	3.170
3.093	10	112	3.085
2.983	40	400	2.983
2.962	10	$31\bar{1}$	2.960
2.831	55	310 $20\bar{5}$	2.828 2.822
2.783	5	$31\bar{3}$	2.780
2.661	5	401 113	2.660 2.657
2.536	10	005	2.543
2.406	5	204	2.406
2.339	5	$20\bar{6}$ 402	2.343 2.339
2.291	25	114	2.290
2.266	3	$11\bar{5}$	2.265
2.243	3	$40\bar{6}$	2.248
2.120	30	006	2.120
2.110	25	$60\bar{1}$	2.109
2.055	10	510 403	2.052 2.056
2.020	15	$31\bar{6}$	2.021
2.014	20	020	2.010
2.001	15	$51\bar{5}$	2.003
1.996	10	$20\bar{7}$	1.995
1.988	10	600 021	1.989 1.985
1.972	9	$40\bar{7}$	1.978
1.918	17	222	1.917
1.848	9		
1.819	3		
1.763	5		
1.747	11		
1.719	5		

Results of the Differential Thermal Analysis:

In order to determine the temperature of the phase changing reactions and to construct the binary phase diagram roughly, the DTA were carried out on each of the seven condensed phases and on the mixtures of neighbouring two

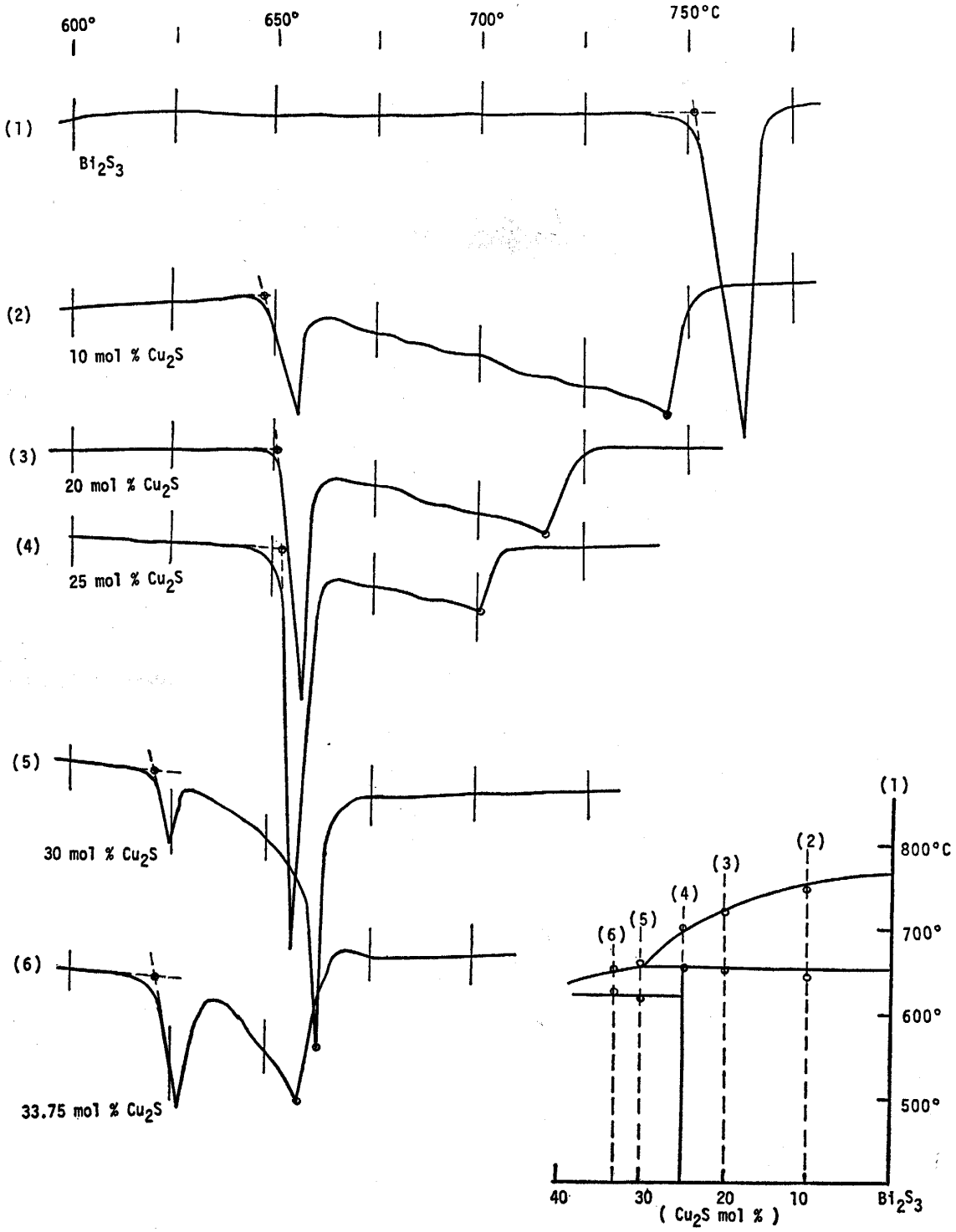

Fig. 1. The DTA curves and schematic phase diagram of the Cu_2S–Bi_2S_3 system (1)

phases which have various bulk compositions. Because of the supercooling phenomena, recorded temperatures of the thermal effects on cooling analysis are usually considerably lower than the true equilibrium temperatures in this system as well as in the system including antimony. As discussed before satisfactory results were given by the heating analysis with rather low heating rate in this system. The results and the schematic phase diagram models expected from the DTA curves are shown in the four figures, 1, 2, 3, and 4.

Fig. 1 shows six DTA curves performed on the samples containing less than 35 percent in Cu_2S molecule. Curve (1) and curve (4) are experiments on condensed homogeneous phases of Bi_2S_3 and $CuBi_3S_5$ respectively, and the former shows congruent melting effect at 756°C. Each five curves except one for Bi_2S_3 has an endothermic peak with two steps but they are clearly divided into two groups. Curves (2), (3), and (4) of the first group show nearly the same beginning temperature of the first endothermic peaks around 650°C which

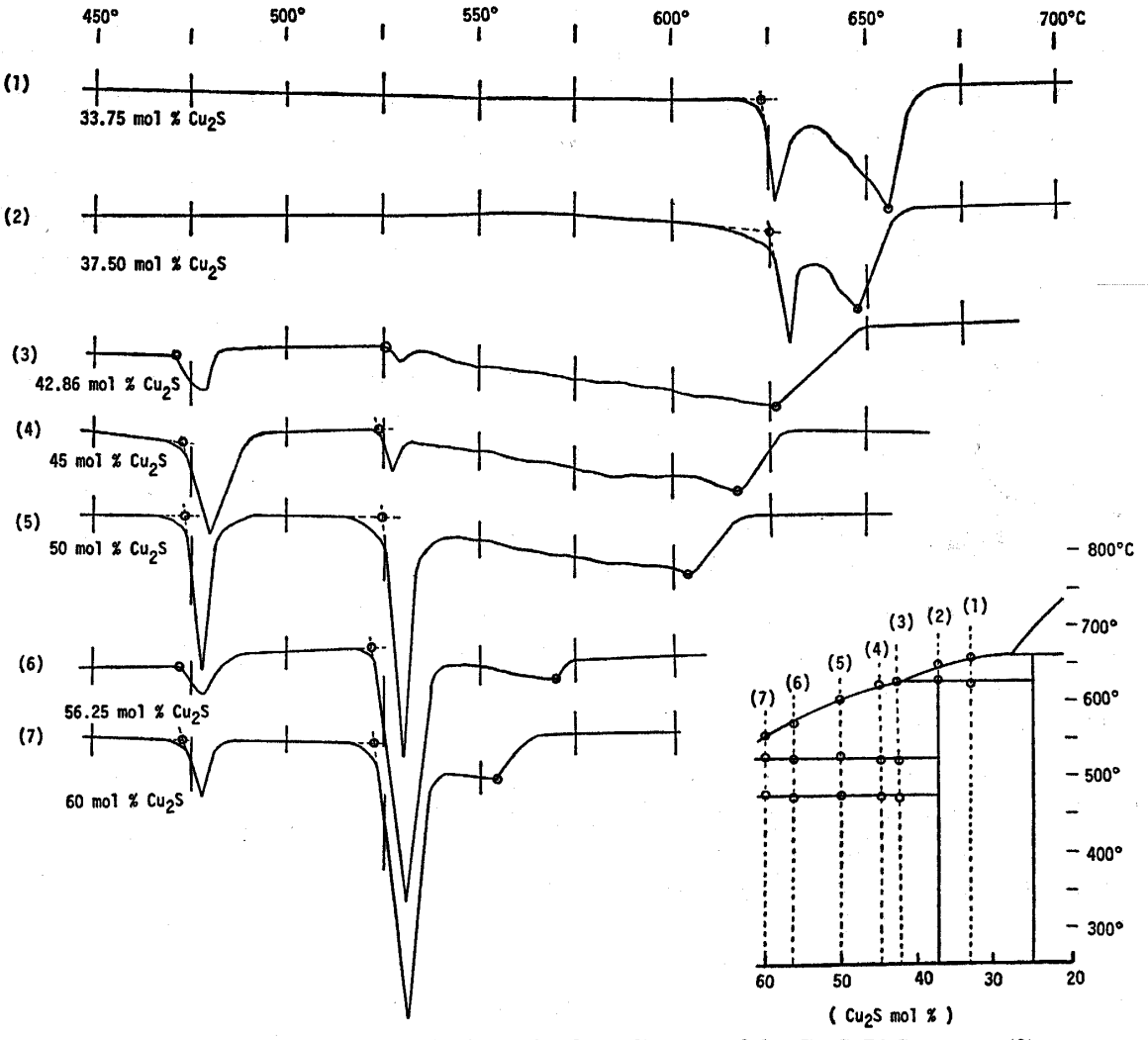

Fig. 2. The DTA curves and schematic phase diagram of the Cu_2S–Bi_2S_3 system (2)

indicate the incongruent melting of $CuBi_3S_5$, and they intersect the liquidus at 743°C, 714°C, and 697°C respectively. Other two runs containning 30.0 mol% and 33.75 mol% Cu_2S, curves (5) and (6), show the thermal effects at 618°C and 620°C which indicate the incongruent melting of the condensed phase $Cu_3Bi_5S_9$, and the bottom points of the second peaks, 659°C and 658°C, represent the completion of melting in their compositions.

The results of the run between 60 mol % and 33 mol % Cu_2S are shown in Fig. 2. The first two runs in the figure, curves (1) and (2), show the similar curves each other, one was performed on the mixture of $CuBi_3S_5$ and $Cu_3Bi_5S_9$ and the other was on stoichiometric composition of $Cu_3Bi_5S_9$, both synthesized at 500°C for 120 hours. The beginning temperatures of the first thermal effect, 620°C and 623°C, correspond to the incongruent melting of $Cu_3Bi_5S_9$. Curves (3) and (4) in Fig. 2 are the results for the experiments on mixtures of $Cu_{24}Bi_{26}S_{51}$ and $Cu_3Bi_5S_9$, and (5), (6), and (7), on mixtures of Cu_3BiS_3 and $Cu_{24}Bi_{26}S_{51}$, synthesized at 500°C and then annealed at 300°C for 21 days. Each curves have two distinct endothermic peaks and a following wide spread peak with gentle slope. The lower sharp peaks begin at the nearly the same temperature of 474 ± 4°C and the intensity of the peaks becomes weaker as the bulk composition is away far from 50.0 mol% Cu_2S. These peaks correspond to breakdown of $Cu_{24}Bi_{26}S_{51}$ into Cu_3BiS_3 and $Cu_3Bi_5S_9$. Eutectic melting of them are indicated by the beginning of the second sharp endothermic peaks at about 523°C and liquidus temperatures, represented on the end-point of the last wide spread endothermic peaks, become lower smoothly like 626°C, 618°C, 602°C, 569°C, and 553°C as increase Cu_2S molecule in the bulk composition.

Fig. 3 shows six DTA curves, five of them performed on mixtures of Cu_3BiS_3 and $Cu_{24}Bi_{26}S_{51}$ and one on stoichiometric Cu_3BiS_3 which were synthesized at 500°C and annealed at 300°C for 21 days. The bulk composition of the samples are 60.0 mole%, 63.75 mol%, 67.5 mol%, 71.25 mol%, 73.03 mol%, and 75.0 mol% Cu_2S. These DTA curves, especially, curves (3), (4), and (5) are very difficult to interprete because complicate reactions occur successively within a narrow temperature range. Although the decomposition effect of $Cu_{24}Bi_{26}S_{51}$ is observed in the five curves except the run containning 75.0 mol% Cu_2S, the intensity of the peaks of this reaction decrease extremely in curves (4) and (5), because of the small quantity of the phase $Cu_{24}Bi_{26}S_{51}$. Liquidus temperatures come closer to the beginning temperature of melting according as bulk composition comes near the eutectic point, then the eutectic point of Cu_3BiS_3 and $Cu_3Bi_5S_9$ is expected to situate at the composition between 67.5 mol% and 63.75 mol% Cu_2S from the curves. Experiment of the stoichiometric composition of Cu_3BiS_3 is shown as curve (6) in Fig. 4, showing incongruent melting, however as mention below, the compositional range of Cu_3BiS_3 solid solution shifts successively towards less Cu_2S molecule on heating, then the beginning of the endothermic peak is not sharp.

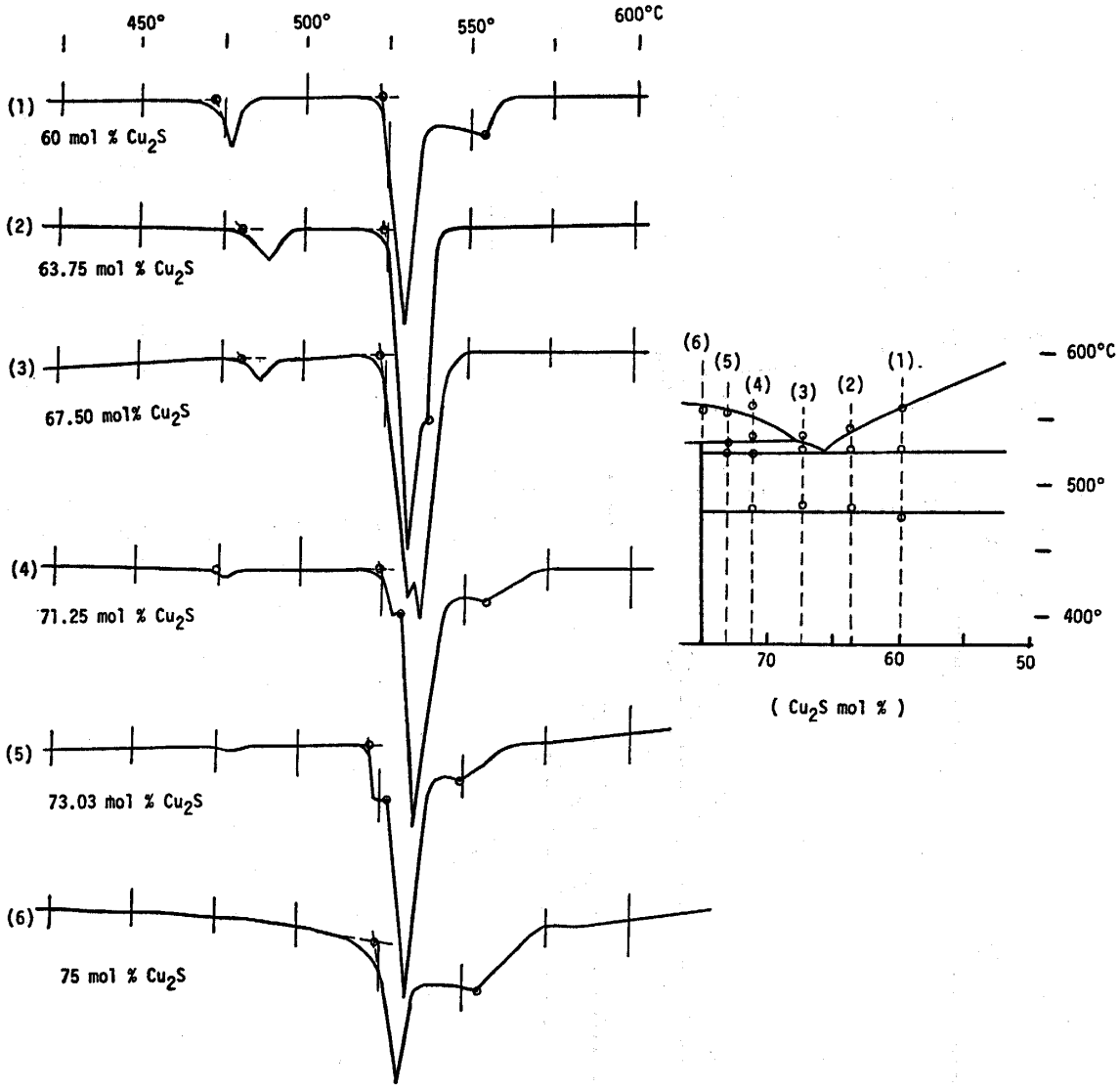

Fig. 3. The DTA curves and schematic phase diagram of the Cu_2S–Bi_2S_3 synstem (3)

Fig. 4 shows the experimental results for bulk compositions of 77.5 mol%, 80.0 mol%, and 85.0 mol% Cu_2S. Before the analysis, sample synthesized at 500°C were annealed at 300°C at least for 20 days and then the starting sample consists of Cu_2S solid solution and Cu_3BiS_3. Their heating analysis curves are characterized by extremely gentle endothermic reactions which suggest thermal reaction accompanying with increasing temperature such as solid solution reaction. For example, the experiment containning 77.5 mol% Cu_2S shows very gentle endothermic reaction from about 400°C on heating which suggested that Cu_3BiS_3 molecule solves gradually into Cu_9BiS_6 solid solution. The reaction completes at 525°C, meaning solvus, and then the solid solution begins to melt at about 535°C, showing again a gentle endothermic peak from this temperature on the DTA curve. Liquidus is intersected at about 564°C. As the compositions come closer to Cu_2S the solvus, indicated at the point of the bottom of the

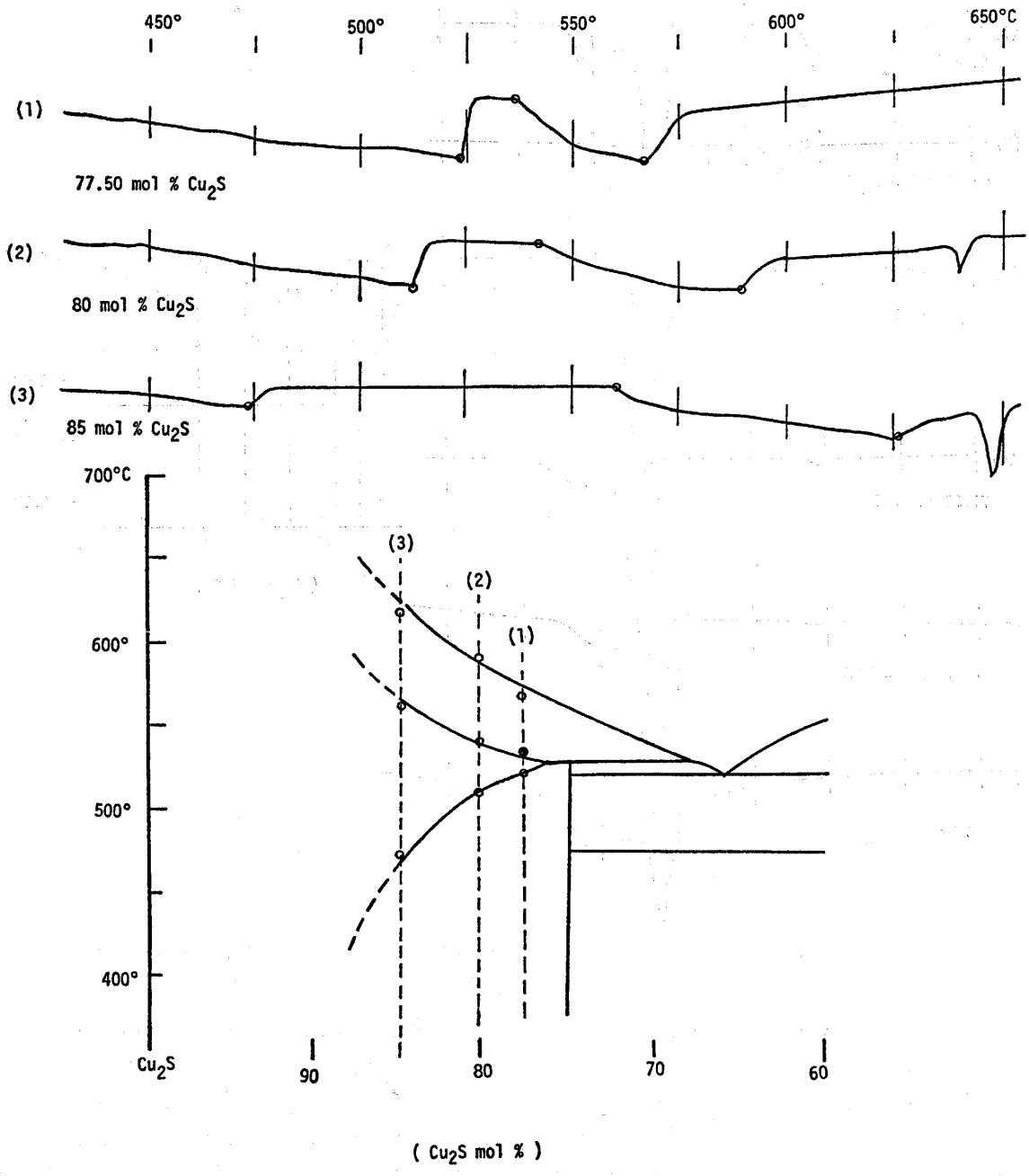

Fig. 4. The DTA curves and sche matic phase diagram of the Cu_2S–Bi_2S_3 system (4)

first gentle peak, becomes lower and lower as 525°C, 511°C, and 473°C, while the solidus, represented as the beginning point of the second gentle peak, becomes higher and higher like 535°C, 539°C, and 578°C.

Results of twenty thermal analyses are summerized in Table 8.

Table 8. Results of the differential thermal analysis for the Cu_2S–Bi_2S_3 system

Cu_2S mol%	T_1	T_2	T_3	T_4	T_5	T_6	T_7	T_8
0.00	756°C							
10.00	743	648°C						
20.00	714	649						
25.00	697	651						
30.00	659		618°C					
33.75	658		620					
37.50	647		623					
42.50	626				525°C	470°C		
45.00	618				523	471		
50.00	602				524	473		
56.25	569				523	470		
60.00	553				523	474		
63.75	536				525	478		
67.50	535				524	478		
71.25	552			530°C	521	475		
73.03	547			526				
75.00	551			524				
77.50	563						535°C	525°C
80.00	588						539	511
85.00	626						578	473
mean value		649°C	620°C	527°C	523°C	474°C		

T_1: Liquidus
T_2: Incongruent of $CuBi_3S_5$
T_3: Incongruent of $Cu_3Bi_5S_9$
T_4: Incongruent of Cu_3BiS_3
T_5: Eutectic of Cu_3BiS_3–$Cu_3Bi_5S_9$
T_6: Decomposition of $Cu_{24}Bi_{26}S_{51}$
T_7: Solidus of Cu_9BiS_6
T_8: Solvus of Cu_9BiS_6

Quenching Experiments for Phase Relations:

Since the DTA is essentially on the dynamic analysis, it does not theoretically represent the true equilibrium relations. Then it is necessary to examine the results of the DTA study critically by means of the other method. Several quenching and additional investigations are performed.

Determination of Some Melting Relations: In the last section liquidus, solidus, and some subsolidus relations in the system were determined by means of the DTA. Several quenching runs were done to make sure some melting relations and the results are listed in Table 9. Copper-bismuth sulfide melt cannot be quenched to "glass" as widely known in the common metallic system. Then, the evidence of melting was based on a change in the appearance of the material

Table 9. Results of experimental runs for melting relations.

Cu_2S mol%	Temp. °C	Time, hours	Products
20.0	600	76	$CuBi_3S_5+Bi_2S_3$
	625	48	$CuBi_3S_5+Bi_2S_3$
	650	48	Bi_2S_3+L
25.0	635	48	$CuBi_3S_5$
	650	48	Bi_2S_3+L
37.5	550	120	$Cu_3Bi_5S_9$ ss
	630	216	$CuBi_3S_5+L$
	675	72	L
40.0	550	120	$Cu_3Bi_5S_9$ ss
	600	72	$Cu_3Bi_5S_9$ ss+L
50.0	520	120	Cu_3BiS_3 ss+$Cu_3Bi_5S_9$ ss
	550	120	$Cu_3Bi_5S_9$ ss+L
	625	120	L
60.0	515	120	Cu_3BiS_3 ss+$Cu_3Bi_5S_9$ ss
	530	96	$Cu_3Bi_5S_9$ ss+L
	550	96	$Cu_3Bi_5S_9$ ss+L
	556	120	L
75.0	500	120	Cu_3BiS_3 ss(+Cu_9BiS_6 ss)
	535	2	Cu_9BiS_6 ss+L
	580	2	L
80.0	575	2	Cu_9BiS_6 ss+L

from a porous and coarse mass or aggregate of powder to a smooth, rounded, non-porous globules. Partial melting such as eutectic or peritectic, common in this system, in which the crystalline phase is in equilibrium with the melt at the run temperature, is not easily determined. It can be only deduced from grain size and textural relations in the quenched sample under microscopic observation. The stable crystalline phase at the run temperature is characteristically coarser grained and surrounded by the finer grained material representing the crystallized liquid.

Experiments on the bulk compositions of 20.0 mol% and 25.0 mol% Cu_2S show the incongruent melting of $CuBi_3S_5$ occur between 635°C and 650°C which is consistent with 649°C given by the DTA, and $Cu_3Bi_5S_9$ melts incongruently at 620°C$\pm$5°C. Solidus of eutectic melting between Cu_3BiS_3 ss and $Cu_3Bi_5S_9$ ss should be between 520°C and 530°C from the result of quenching runs on the composition of 50.0 mol% and 60.0 mol% Cu_2S, and at the temperature of 556°C just above 553°C given from the DTA for the liquidus of 60.0 mol% Cu_2S composition only liquid phase could observed. From the results of the quenching and the DTA experiments eutectic point between Cu_3BiS_3 ss and $Cu_3Bi_5S_9$ ss is at 523$\pm$5°C and about 65 mol% Cu_2S in composition. As shown

in Table 9, the quenching experiments support the results from the DTA investigation.

Stability of $Cu_3Bi_5S_9$ Solid Solution: The phase, $Cu_3Bi_5S_9$, has been recognized by Nuffield[7] (1947) during his study on cuprobismuth sulfosalts minerals. The phase has a fairly wide solid solution range at the higher temperature but is not stable at room temperature. Table 10 shows the results of several experiments in order to examine thermal and compositional stability of $Cu_3Bi_5S_9$. The phase is stable only above 442°±3°C to 620°±5°C which is incongruent melting temperature of $Cu_3Bi_5S_9$. Below 442°C $Cu_{24}Bi_{26}S_{51}$ and $CuBi_3S_5$ are stable instead of $Cu_3Bi_5S_9$ in this composition, but the breakdown reaction on cooling is sluggish. The extents of the solid solution field of $Cu_3Bi_5S_9$ were determined by constructing curves of d-value versus composition. The d(311) reflection of $Cu_3Bi_5S_9$ which synthesized at in various compositions at 500°C was measured precisely by the X-ray diffractometer with 1/4° per minute of goniometer rotation rate. An appropriate amount of silicon (99.9999% in purity) was mixed with sample and use as an internal standard. Results of measurement are listed in Table 11 and shown in Fig. 5. As clearly shown in Fig. 5, the solid solution area of $Cu_3Bi_5S_9$ extends from 37.5 mol% to 41.25 mol% Cu_2S at 500°C. Maximum composition in Cu_2S mol% of the solid solution is 43.05 mol% Cu_2S at 523°±5°C that is the temperature of eutectic melting between Cu_3BiS_3 and $Cu_3Bi_5S_9$.

Table 10. Results of experimental runs for the stability of $Cu_3Bi_5S_9$ solid solution.

Cu_2S mol%	Temp. °C	Time, hours	Products
35.00	500	120	$Cu_3Bi_5S_9$ ss+$CuBi_3S_5$
37.00	500	120	$Cu_3Bi_5S_9$ ss+$CuBi_3S_5$
37.50	400	182	$Cu_{24}Bi_{26}S_{51}$+$CuBi_3S_5$
	500	120	$Cu_3Bi_5S_9$ ss
	600	78	$Cu_3Bi_5S_9$ ss
	625	216	$CuBi_3S_5$+L
39.10	500	120	$Cu_3Bi_5S_9$ ss
40.00	430	168	$Cu_{24}Bi_{26}S_{51}$+$CuBi_3S_5$
	440	168	$Cu_{24}Bi_{26}S_{51}$+$CuBi_3S_5$
	445	144	$Cu_{24}Bi_{26}S_{51}$+$Cu_3Bi_5S_9$ ss
	450	144	$Cu_{24}Bi_{26}S_{51}$+$Cu_3Bi_5S_9$ ss
	500	120	$Cu_3Bi_5S_9$ ss
	550	120	$Cu_3Bi_5S_9$ ss
	600	78	$Cu_3Bi_5S_9$ ss+L
40.70	500	120	$Cu_3Bi_5S_9$ ss
42.86	500	120	$Cu_3Bi_5S_9$ ss (+Cu_3BiS_3 ss)
	550	120	$Cu_3Bi_5S_9$ ss+L
45.00	500	120	$Cu_3Bi_5S_9$ ss+Cu_3BiS_3 ss

Table 11. Results of measurement on $Cu_3Bi_5S_9$ ss d (311) spacing.

Comp. Cu_2S mol%	Temp. (°C)	d (311) (A)	Phase present
30.00	500	2.8250	$Cu_3Bi_5S_9$ ss + $CuBi_3S_5$
35.00	500	2.8253	$Cu_3Bi_5S_9$ ss + $CuBi_3S_5$
37.50	500	2.8248	$Cu_3Bi_5S_9$ ss
39.10	500	2.8214	$Cu_3Bi_5S_9$ ss
40.70	500	2.8179	$Cu_3Bi_5S_9$ ss
42.86	500	2.8169	$Cu_3Bi_5S_9$ ss + Cu_3BiS_3 ss
45.00	500	2.8170	$Cu_3Bi_5S_9$ ss + Cu_3BiS_3 ss

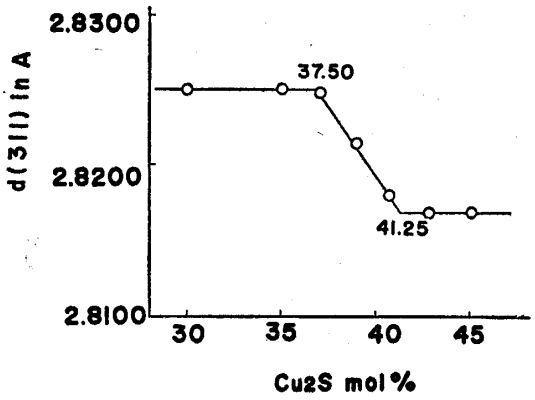

Fig. 5. Determination for the solid solution limit of $Cu_3Bi_5S_9$ ss. Relations of d-value versus Cu_2S mol% at 500°C

Phase Relations of Cuprobismutite and Emplectite: Table 12 shows results of some experiments to examine the phase relations of cuprobismutite and emplectite. All experiments on the mixture of Cu_2S and Bi_2S_3 in the ratio of 1 : 1 which corresponds to emplectite in natural occurrence produced always cuprobismutite

Table 12. Results of experimental runs for cuprobismutite and emplectite.

Composition Cu_2S mol%	Starting materials	Temp. (°C)	Time (days)	Products
50.0	$Cu_2S + Bi_2S_3$	480	7	wt + $Cu_3Bi_5S_9$
50.0	$Cu_2S + Bi_2S_3$	460	7	cpb (+wt)
50.0	$Cu_2S + Bi_2S_3$	400	14	cpb (+wt)
*50.0	$Cu_3BiS_3 + Cu_3Bi_5S_9$	250	14	emp (+wt)
49.0	$Cu_2S + Bi_2S_3$	400	21	cpb (+wt)
48.0	$Cu_2S + Bi_2S_3$	400	21	cpb
48.0	$Cu_3BiS_3 + Cu_3Bi_5S_9$	400	14	cpb
47.0	$Cu_2S + Bi_2S_3$	400	26	cpb (+$Cu_3Bi_5S_9$)

* Starting materials pressed by the oil press at 1 ton/cm² to make compressed sylindrical block before heating.

wt: wittichenite cpb: cuprobismutite

emp: emplectite

taking with a small quantity of wittichenite (Cu_3BiS_3) above 400°C, and emplectite never appeared as a stable phase at high temperature. From the results of the experiment shown in Table 12 the composition of cuprobismutite seems to be 48 mol% Cu_2S, and then chemical formula of this phase should be written as $Cu_{24}Bi_{26}S_{51}$. Cuprobismutite decomposes at 473°±5°C as determined by means of the DTA before, and quenching results does not contradict it.

Table 13. The data of X-ray diffraction for synthetic emplectite

(1)		(2)		
d	I	d	I	hkl
7.31	45	7.255	36	002
5.64	11	5.644	4	101
5.04	7	5.028	3	
4.70	34	4.681	29	102
4.55	9			
3.97	9	3.962	5	
3.83	6			
3.63	12	3.625	10	004
3.57	26			
3.53	12			
3.23	100	3.216	100	111
3.13	86	3.119	77	104
3.07	78	3.064	60	200
3.05	79	3.046	83	013
3.01	15			
2.95	7	3.000	16	201
2.858	18			
2.831	20	2.823	18	202
2.730	7	2.721	7	113
2.644	9			
2.600	7	2.588	7	203
2.522	8	2.515	4	
2.417	5	2.417	8	006
2.335	46	2.331	48	204
2.298	9	2.290	8	212
2.254	18	2.248	17	106
2.166	39	2.160	42	213
1.961	18	2.027	5	301
1.895	7	1.899	6	206
1.859	23	1.856	29	215

(1) Synthetic emplectite

(2) Natural emplectite by Buhlmann[26] (Tannenbaum, Saxony)

Only one experiment was successful to synthesize emplectite as also shown in Table 12. Cu_3BiS_3 and $Cu_3Bi_5S_9$ were weighed exactly to make a bulk composition to 50 mol% Cu_2S, mixed throughly, and then made a sylindrical compressed piece, 5 mm$\phi \times$6 mm in size, by the simple squeeze type oil press at one ton/cm^2 of pressur. The piece sealed into an evacuated glass tube and heated at 250°C for 26 days. X-ray powder pattern of product, shown in Table 13, is in good agreement with one of natural emplectite described by Buhlmann[26]. The DTA curve of synthesized emplectite shows a weak endothermic peak beginning at about 360°C before melting. It is quite easy to conclude that this peak represents the transformation from emplectite to cuprobismutite if they are surely in dimorphous relation as mentioned by Nuffield[12] and Buhlmann[15], but any positive evidence to interprete this peak has not been obtained yet. Active investigations by means of high temperature X-ray diffraction are being continued now to elucidate the relationship between both phases. Anyway, emplectite supposed to be certainly stable up to 360°C, while cuprobismutite which is synthesized at higher temperature and then kept in vacuum almost 5 years at room temperature has not changed at all. There are still many problems which must be solved as for the relationship between emplectite and cuprobismutite.

Examination of Klaprothite and Dognacskite: In order to ascertain the reliability of the existence of klaprothite and dognacskite, several quenching runs were practised and the results are shown in Table 14. No compound with the composition of $3Cu_2S{\cdot}2Bi_2S_3$ and $Cu_2S{\cdot}2Bi_2S_3$, corresponding to the composition reported for klaprothite and dognacskite respectively, was synthesized at any temperature, and quenching products were always mixtures of two phases. From consideration of the results, it seems most reasonable to conclude that klaprothite and dognacskite are untrueworthy species as minerals.

Table 14. Results of experimental runs for klaprothite and dognacskite.

Composition Cu_2S mol%	Starting materials	Temp. (°C)	Time (days)	Products
32.0	$Cu_2S+Bi_2S_3$	500	5	$Cu_3Bi_5S_9$ ss+$CuBi_3S_5$
33.0	$Cu_2S+Bi_2S_3$	500	5	$Cu_3Bi_5S_9$ ss+$CuBi_3S_5$
33.3	$Cu_2S+Bi_2S_3$	500	5	$Cu_3Bi_5S_9$ ss+$CuBi_3S_5$
33.3	Cu_3BiS_3 ss+$CuBi_3S_5$	400	14	$Cu_3Bi_5S_9$ ss+$Cu_{24}Bi_{26}S_{51}$
33.3	Cu_3BiS_3 ss+$CuBi_3S_5$	300	32	$Cu_3Bi_5S_9$ ss+$Cu_{24}Bi_{26}S_{51}$
60.0	$Cu_2S+Bi_2S_3$	500	5	Cu_3BiS_3 ss+$Cu_3Bi_5S_9$ ss
60.0	$Cu_3BiS_3+Cu_{24}Bi_{26}S_{51}$	500	5	Cu_3BiS_3 ss+$Cu_3Bi_5S_9$ ss
60.0	$Cu_2S+Bi_2S_3$	400	14	Cu_3BiS_3 ss+$Cu_{24}Bi_{26}S_{51}$
60.0	$Cu_3BiS_3+Cu_{24}Bi_{26}S_{51}$	300	32	Cu_3BiS_3 ss+$Cu_{24}Bi_{26}S_{51}$
60.0	$Cu_3BiS_3+Cu_{24}Bi_{26}S_{51}$	200	88	Cu_3BiS_3 ss+$Cu_{24}Bi_{26}S_{51}$

Stability of Cu_3BiS_3 Solid Solution: Synthetic Cu_3BiS_3 is identical with natural wittichenite in every respect as shown in the case of X-ray powder pattern of Table 4. Though the phase has the composition of Cu_3BiS_3 at room temperature, compositional stability range of Cu_3BiS_3 shifts towards Cu_2S poor composition at higher temperature. Extent of the solid solution field of Cu_3BiS_3 were determine by X-ray method. The d(131) spacing of Cu_3BiS_3 solid solution synthesized at 500°C in several different compositions were carefully measured and plotted versus composition as shown in Table 15 and Fig. 6. From the d versus composition curve, solid solution of Cu_3BiS_3 extends from 73.5 mol% to 71.5 mol% Cu_2S at 500°C. Cu_3BiS_3 ss melts incongruently at 527°±5°C at nearly 72.5 mol% Cu_2S.

Table 15. Results of measurement of d (131) spacing on Cu_3BiS_3 ss.

Composition Cu_2S mol%	Temp. (°C)	d (131) (A)	Phase present
70.0	500	2.8545	Cu_3BiS_3 ss+Cu_9BiS_6
72.0	500	2.8557	Cu_3BiS_3 ss
72.5	500	2.8565	Cu_3BiS_3 ss
73.0	500	2.8583	Cu_3BiS_3 ss
73.5	500	2.8595	Cu_3BiS_3 ss
77.5	500	2.8595	Cu_3BiS_3 ss+$Cu_3Bi_5S_9$ ss

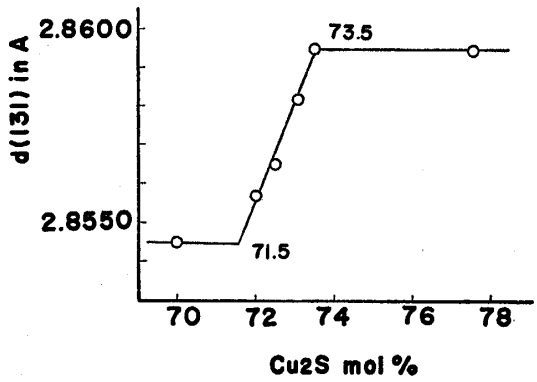

Fig. 6. Determination for the solid solution limit of Cu_3Bi_3S. Relations of d-value versus Cu_2S mol% at 500°C.

High Temperature X-ray Study for Cu_2S Rich Portion:

Among the Cu_2S–Bi_2S_3 system the portion near Cu_2S is the most difficult to make clear the phase relations, because of difficulty of quenching to keep the phases at run temperature, and less reproducibility of X-ray powder pattern. In this paper Cu_9BiS_6 phase (which has fairly wide solid solution field at high temperature) is supposed to be an independent phase from Cu_2S solid solution, but both of them are supposed to have a very similar structure at the high temperature, then it is still difficult to identify both phases from each other.

Some high temperature X-ray investigation was practiced. Fig. 7 shows

high temperature X-ray diffraction pattern of two high temperature modifications of chalcocite I (cubic) and II (hexagonal) and Cu_9BiS_6 phase. As shown in the figure, two reflections between 25° and 30° in 2θ of Cu_9BiS_6 seem to correspond to (111) and (200) reflection of cubic phase of chalcocite and other two between 45° and 50° in 2θ, to (110) and (103) reflections of hexagonal phase of chalcocite. Quenched products from the temperature above 400°C usually

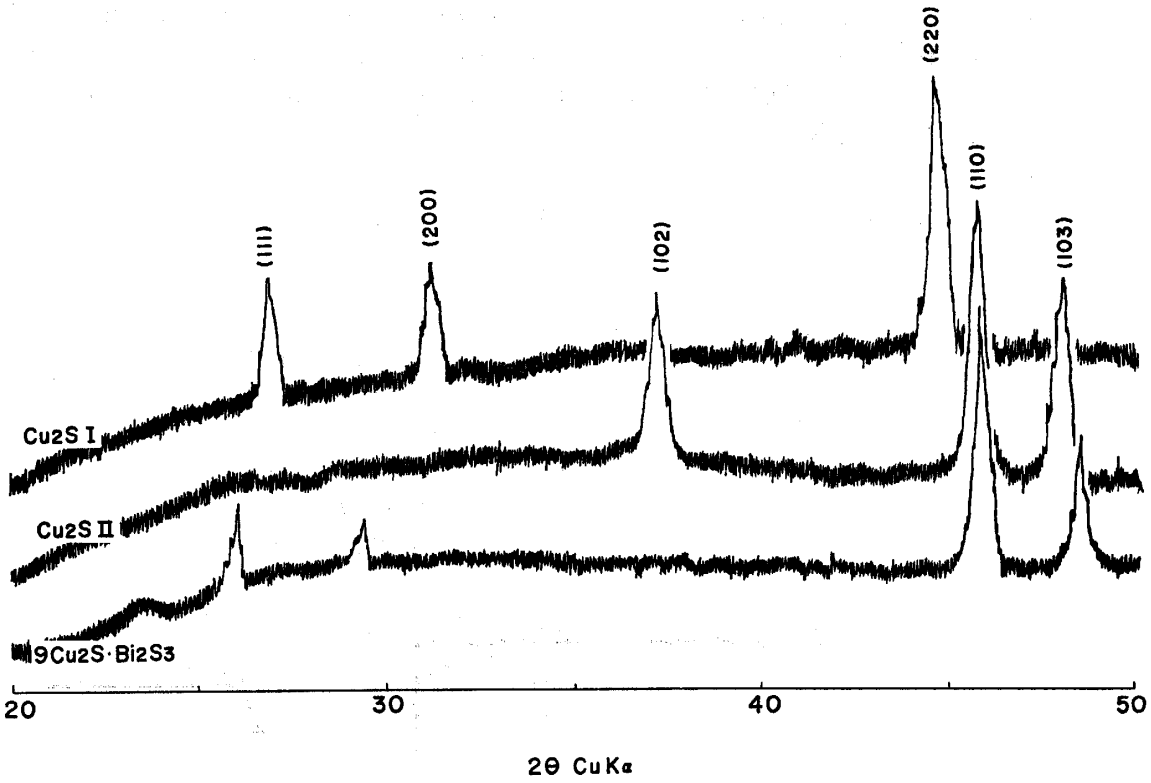

Fig. 7. High temperature X-ray diffraction patterns of Cu_9BiS_6 and chalcocite

Table 16. Results of high temperature X-ray study on Cu_9BiS_6 solid solution.

Composition Cu_2S mol%	room temp.**	298°C	350°C	400°C	480°C
100.0	Cc III	Cc II			Cc I
97.5	Cc III + Cu_9BiS_6*			Cc II	Cc I
95.0	Cu_9BiS_6*	Cc II + wt	Cc II ? + wt		
90.0	Cu_9BiS_6*	Cc II + wt		Cu_9BiS_6(+wt)	Cu_9BiS_6
85.0	Cu_9BiS_6*			Cu_9BiS_6 + wt	Cu_9BiS_6

Cc III : chalcocite orthorhombic low form
Cc II : chalcocite hexagonal high temp. form
Cc I : chalcocite cubic high temp. form
Cu_9BiS_6* : quenched pattern of Cu_9BiS_6
wt : wittichenite
** : X-ray diffraction was taken at room temperature on the quenched sample from 500°C.

indicates several weak additional reflections. Results of high temperature X-ray studies are listed in Table 16. Experiments on the composition containing 97.5 mol% Cu_2S give only X-ray patterns of chalcocite, hexagonal pattern at 390°C and cubic pattern at 480°C. Then considering the evidence chalcocite solid solution dissolves Bi_2S_3 molecule at least 2.5 mol%. Small quantity of wittichenite coexists with chalcocite II below 350°C at the composition of 95.0 mol% Cu_2S. In experiments on the composition of 90.0 mol% Cu_2S chalcocite II and wittichenite assemblage at lower temperature change into Cu_9BiS_6 and wittichenite assemblage at 400°C, and the homogeneous Cu_9BiS_6 at 480°C with ascending temperature. On the basis of these data, it seems reasonable to assume that Cu_9BiS_6 is independent phase from chalcocite and stable only above the temperature between 350°C and 400°C. Cu_9BiS_6 melt incongruently at nearly 650°±10°C. From results of high temperature X-ray investigations, quenching runs, and DTA experiments, solid solution field of Cu_9BiS_6 extends to 87 mol% Cu_2S at 450°C, 82 mol% Cu_2S at 500°C and about 78 mol% Cu_2S in maximum at 526°C.

Summary and Discussions

The summarized phase diagram of the Cu_2S–Bi_2S_3 system is shown in Fig. 8, and the temperatures of the phase changing reactions are listed in Table 17.

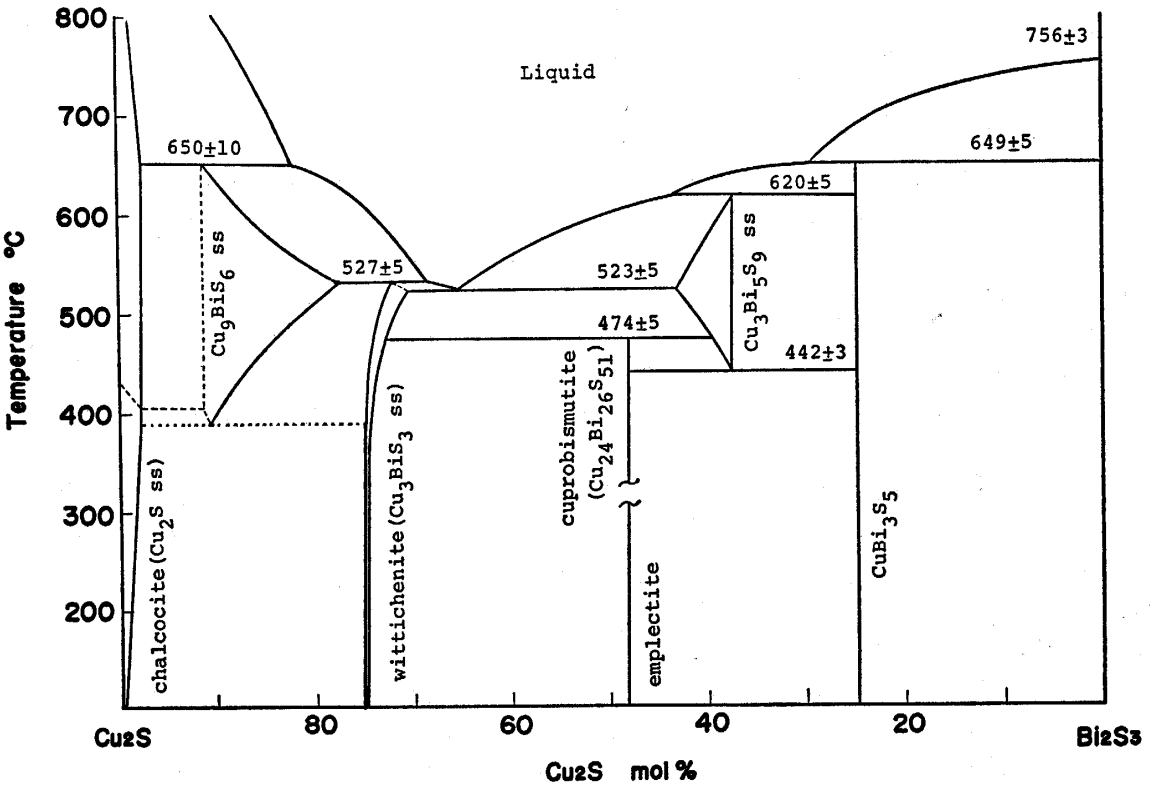

Fig. 8. Phase diagram of the Cu_2S–Bi_2S_3 system

Table 17. List of the reaction temperature in the Cu_2S–Bi_2S_3 system.

Congruent melting of Bi_2S_3	756°±3°C
Incongruent melting of $CuBi_3S_5$	649°±5°C
Incongruent melting of $Cu_3B_5S_9$	620°±5°C
Lower stability limit of $Cu_3Bi_5S_9$	442°±5°C
Decomposition of $Cu_{24}Bi_{26}S_{51}$	474°±5°C
Incongruent melting of Cu_3BiS_3	527°±5°C
Eutectic of Cu_3BiS_3–$Cu_3Bi_5S_9$	523°±5°C
Incongruent melting of Cu_9BiS_6	650°±10°C
Lower stability limit of Cu_9BiS_6	350°−400°C

Crystalline phases in the system are Cu_2S(chalcocite), Cu_9BiS_6, Cu_3BiS_3 (wittichenite), $Cu_{24}Bi_{26}S_{51}$ (cuprobismutite), $CuBiS_2$ or $Cu_{24}Bi_{26}S_{51}$ (emplectite), $Cu_3Bi_5S_9$, $CuBi_3S_5$, and Bi_2S_3 (bismuthinite). Among them Cu_9BiS_6, $Cu_3Bi_5S_9$, and $CuBi_3S_5$ have not been found in nature, and the former two phases, Cu_9BiS_6 and $Cu_3Bi_5S_9$, could not be expected to be found in nature hereafter because of their unstability at low temperature as shown in Fig. 8, while $CuBi_3S_5$ phase has a possibility in future. $CuBi_3S_5$ is stable below 649°±5°C and the phase melts in congruently at this temperature to Bi_2S_3 and liquid.

$Cu_3Bi_5S_9$ is stable in temperature range between 442°±5°C and 620°±5°C which is incongruent melting point of this phase. Buhlmann[15] gives 688°±5°C in his phase diagram to the temperature of incongruent melting of $Cu_3Bi_5S_9$. His diagram shows a little lower temperature than our results in general, but the difference of both data does not exceed 10 degrees and within allowance of the measurements. Incongruent melting temperature of $Cu_3Bi_5S_9$ is only the big discrepancy between both results. $Cu_3Bi_5S_9$ dissolves a considerable amount of Cu_2S molecule, and solid solution limit is the composition of 43.5 mol% Cu_2S in maximum at 523°C. Phase relations of cuprobismuthite and emplectite still have a problem which has to be elucidated. Cuprobismutite that was once reported as $4Cu_2S{\cdot}3Bi_2S_3$ by Hillebrand[9] has a composition of 48 mol% Cu_2S and 52 mol% Bi_2S_3 and decomposes at 473°±5°C into Cu_3BiS_3 and $Cu_3Bi_5S_9$. Lower stability limit of cuprobismutite has not been determined but after 5 years kept in vacuum at room temperature cuprobismutite has not changed at all. X-ray powder pattern of synthesized phase is shown in Table 6 with those of natural cuprobismutite by Berry and Thompson[27]. On the other hand emplectite, of which accurate composition is not determined yet, was synthesized at 250°C for 26 days from a compressed cylindrical block sample, mixture of Cu_3BiS_3 and $Cu_3Bi_5S_9$, 50 mol% Cu_2S in bulk composition. The DTA curve of synthesized emplectite shows weak endothermic thermal effect beginning at about 360°C, and before it no effect is seen. It seems to be sure emplectite is stable below about 360°C, but is not sure to transform into cuprobismutite above this temperature as suggested by Nuffield[12] and Buhlmann[15].

Buhlmann suggested 290°C as transformation temperature from emplectite to cuprobismutite, then even if the endothermic effect at 360°C is supposed to represent the transition, 70 degrees difference is inconsistent. There is still high possibility that emplectite and cuprobismutite are in dimorphous relations, but conclusion will be laid until after more detailed investigation. Even though they are dimorphous, transformation from cuprobismutite to emplectite should be sluggish because if has never been succeeded to synthesize emplectite by means of annealing cuprobismutite formed at higher temperature.

Synthetic wittichenite, Cu_3BiS_3, has identical properties in every respects with natural wittichenite. X-ray powder diffraction data are shown in Table 4 comparing with those of natural wittichenite by Nuffield[7]. At high temperature compositional stability range of Cu_3BiS_3 solid solution shifts towards less Cu_2S molecule, and this phase melts incongruently at 527°±5°C in 73.0 mol% Cu_2S. The eutectic point between Cu_3BiS_3 ss and $Cu_3Bi_5S_9$ ss is 527°± 5°C at about 65 mole% Cu_2S.

Klaprothite and dognacskite have not appeared in the study. Both minerals having $Cu_6Bi_4S_9$ and $Cu_2Bi_4S_7$ in composition could not be expected to be found in nature hereafter. However, about klaprothite Springer[28] suggested quite recently some possibility of dimorphous relation with emplectite and of identical species with cuprobismutite.

Cu_9BiS_6, supposing to have the similar structure of high temperature forms of chalcocite, is stable below 650°C and above around 400°C, but lower stability limit has not been determined. Cu_9BiS_6 dissolves considerable amount of Bi_2S_3 molecule and solid solution field extends to 87 mol% Cu_2S at 450°C, 78 mol% Cu_2S in maximum at 527°C.

The properties of the crystalline phases, such as optical and crystallographic, will be described minutely in another paper.

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