

## Synthetic Sulfide Minerals (II)

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### I. Introduction

Mineral synthesis has been carried out in many laboratories with various objects, such as, for instance, production of minerals with desirable physical properties or understanding of the geological conditions under which certain minerals have formed. The present authors have been studying the phase relations between several sulfide minerals in order to estimate the genetic conditions of ore deposits. First of all, it is required in this works to synthesize minerals which have stoichiometric composition. In the present paper, the methods of sulfide mineral synthesis and properties of synthesized minerals are described. Simple sulfides such as CuS, Cu<sub>2</sub>S, Fe<sub>1-x</sub>S, MnS, Bi<sub>2</sub>S<sub>3</sub> and Sb<sub>2</sub>S<sub>3</sub> were already described in the last report<sup>1)</sup>, and this paper contains eight complex sulfide minerals, such as CuFeS<sub>2</sub> (chalcopyrite), Cu<sub>5</sub>FeS<sub>4</sub> (bornite), Cu<sub>3</sub>BiS<sub>3</sub> (wittichenite), CuBiS<sub>2</sub> (cuprobismuthite or emplectite), Cu<sub>3</sub>Bi<sub>5</sub>S<sub>9</sub> (synthetic phase), CuBi<sub>3</sub>S<sub>5</sub> (new synthesized phase), Cu<sub>3</sub>AsS<sub>4</sub> (enargite) and Cu<sub>3</sub>SbS<sub>4</sub> (stibnite).

### 2. Method of Synthesis of Minerals

The synthesis of sulfide minerals described in this paper was carried out within rigid silica glass or Hario glass tubes,\*\* 5 or 8 mm in inside diameter, by means of mostly solid state reactions between simple sulfides prepared previously from metallic elements and sulfur.

As primary starting materials for synthesis, copper, iron, bismuth, antimony, arsenic metals and crystalline sulfur were used. The purity of the metals is 99.999% in electrolytic copper, 99.9% in electrolytic iron and better than 99.9% in both bismuth and antimony. Besides, metallic arsenic prepared as medical reagent of 99.98% purity by Kishida Chemical Co. and crystalline sulfur refined as guaranteed reagent by Kanto Chemical Co. were utilized. Prior to experiment, copper and iron were particularly reduced in hydrogen atmosphere at about 950°C for 2 hours, because they are covered usually by thin film of their oxides.

Charges, prepared by mixing of the requisite amounts of two or three synthesized simple sulfides or sometimes metallic elements and sulfur were introduced into a glass tube which had been closed at one end. The tube was evacuated under 10<sup>-3</sup> mm Hg by rotary vacuum pump and sealed with care not to heat the contents. Then, it was heated at desired temperature for various hours in the vertical Kanthal wire wound electric furnaces which were controlled their temperature with ±2°C in accuracy by potentiometric auto-regulators. After heating, the charges were sometimes quenched in water and other times cooled in air or more slowly in the furnaces.

Synthesized products were identified by means of microscopic observation, X-ray powder diffraction and differential thermal analysis (D.T.A.) as mentioned in the former paper<sup>1)</sup> by the present authors. In this case, however, only for CuFeS<sub>2</sub> (chalcopyrite) and Cu<sub>5</sub>FeS<sub>4</sub> (bornite),

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\*\* Hario glass tube, corresponding to Corning's Pyrex glass in quality, is made by Shibata Chemical Apparatus Co.

FeK $\alpha$  radiation was employed in X-ray diffraction and D.T.A. performed in nitrogen atmosphere, but for the others, CuK $\alpha$  radiation was used and D.T.A. performed in the evacuated sealed silica glass tubes.

### 3. CuFeS $_2$ (Chalcopyrite)

CuFeS $_2$  was synthesized easily by reaction between cupric sulfide (CuS) and ferrous sulfide (FeS) in powder under 200 meshes. Both simple sulfides were prepared by the methods as mentioned in the last report<sup>1)</sup>, and they were accurately weighed in the molecular ratio of one to one. After thorough mixing under acetone in an agate motor, the mixtures were sealed in a Hario glass tube under vacuum of 10<sup>-3</sup> mm Hg formed by rotary vacuum pump, and then put in an electric furnace kept at 400°C or 450°C for 48 hours. The product was ground and thoroughly mixed again under acetone. It was again sealed in the glass tube under vacuum and was maintained at 450°C for 48 hours. After re-heating, it was rapidly cooled in water.

CuFeS $_2$  synthesized by means as mentioned above was completely identical with chalcopyrite in various properties as follows.

Synthetic chalcopyrite is usually aggregates of fine granules, brass yellow in colour. Under the microscope, it is yellow in reflecting colour, and shows weak anisotropism under the crossed nicols. When etched with HNO $_3$  (1 : 1), it is stained by fume. However, it is negative to HCl (1 : 1), KOH (sat.), KCN (20%), FeCl $_3$  (20%) or HgCl $_2$  (20%). These optical properties and etching reactions are in good accordance with those of natural chalcopyrite described by Short<sup>2)</sup>, Ramdohr<sup>3)</sup>, Uytendogaardt<sup>4)</sup> and Farnham<sup>5)</sup>.

The data of X-ray diffraction of synthetic chalcopyrite are shown in Table 1 as compared with those of natural chalcopyrite determined by Berry and Thompson<sup>6)</sup>.

Table 1. The data of X-ray powder diffraction for synthetic CuFeS $_2$

1		2		3		
d (Å)	I	d (Å)	I	d (Å)	I	hkl
3.04	100	3.04	100	3.03	10	112
2.646	5	2.646	6	2.63	1/2	020
2.608	2	2.611	1			004
1.871	17	1.871	15	1.865	4	220
1.858	34	1.858	25	1.854	8	024
1.593	18	1.593	15	1.591	6	132
1.576	10	1.576	5	1.573	2	116, 033
—	—	—	—	1.518	1/2	224
1.322	5	1.322	1	1.323	1	040
1.303	3	—	—	1.303	1/2	008
1.213	5	1.212	2	1.214	1	332
1.205	8	1.205	4	1.205	3	136, 143
1.077	10	1.077	6	1.077	6	244
1.069	5	—	—	1.069	3	228

1 : Chalcopyrite (synthetic). 2 : Chalcopyrite (Manzo mine).  
3 : X-ray powder data for chalcopyrite by Berry and Thompson<sup>6)</sup>.

Also, the differential thermal analysis was examined on synthetic chalcopyrite in nitrogen atmosphere by the method described by one of the present authors and his co-workers in the

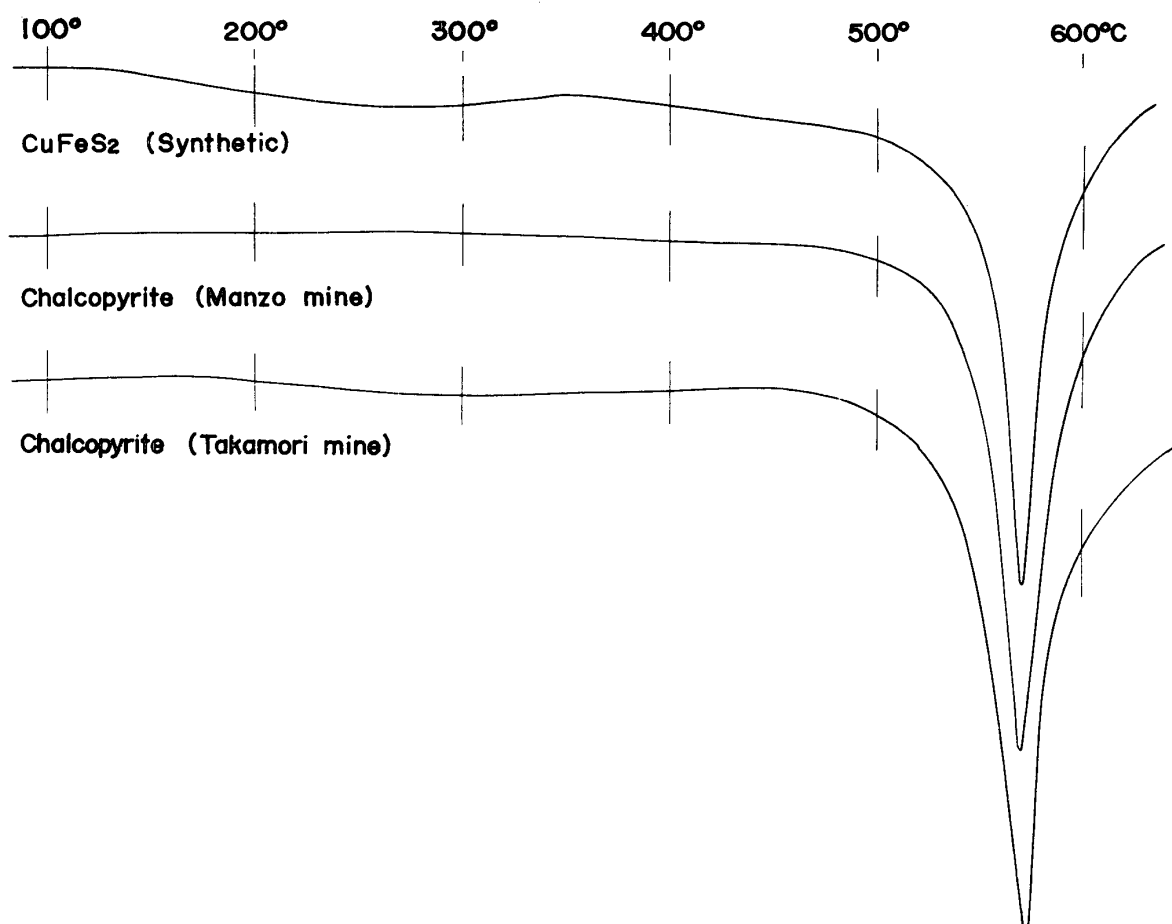


Fig. 1. Differential thermal curves for synthetic  $\text{CuFeS}_2$  and natural chalcopyrites.

previous paper<sup>7)</sup>. The result is shown in Fig. 1 in comparison with those of natural chalcopyrite. They have a distinct endothermic peak at about  $570^\circ\text{C}$  which represents the latent heat of transformation from  $\alpha$ -form of tetragonal lattice to  $\gamma$ -form of cubic face centred lattice, studied by Hiller and Probsthain.<sup>8, 9)</sup>

These properties of synthetic chalcopyrite coincide with those of natural chalcopyrite.

#### 4. $\text{Cu}_5\text{FeS}_4$ (Bornite)

Bornite was produced by solid reaction between cuprous sulfide ( $\text{Cu}_2\text{S}$ ) and synthetic chalcopyrite ( $\text{CuFeS}_2$ ), mixed in proportion to four to one in molecular ratio, by heating. The synthetic method of bornite is almost the same as that of chalcopyrite. Namely, cuprous sulfide and synthetic chalcopyrite thoroughly mixed with each other were heated at  $550^\circ\text{C}$  or  $600^\circ\text{C}$  for 24 hours in sealed silica tube, after heating from room temperature to  $550^\circ\text{C}$  or  $600^\circ\text{C}$  for 6 hours. Then the specimen was completely ground under acetone and then sealed again in silica tube under vacuum. It was heated at  $550^\circ\text{C}$  or  $600^\circ\text{C}$  for 120 hours, and then it was instantly quenched in water or was slowly cooled in the furnace.

The product is megascopically yellowish brown in colour, but it promptly changes its colour into reddish or bluish brown to purple by oxidation in air. Under the microscope with illuminator, it is reddish brown in colour and shows isotropism under crossed nicols. Its hardness is low. When etched by  $\text{HNO}_3$  (1 : 1), it is stained to change its colour with effervescence and gives many fine cracks. However, it is negative to  $\text{HCl}$  (1 : 1),  $\text{KOH}$  (sat.),  $\text{KCN}$  (20%),  $\text{FeCl}_3$

Table 2. The data of X-ray powder diffraction for synthetic  $\text{Cu}_5\text{FeS}_4$ 

1		2		3	
d (Å)	I	d (Å)	I	d (Å)	I
4.07	8	4.07	4	4.08	1
—		—		3.64	1/2
—		—		3.48	1/2
3.31	25	3.27	29	3.31	4
3.27	8	—		—	
3.17	40	3.15	49	3.18	6
3.04	5	—		3.01	1/2
2.913	2	—		—	
2.811	15	2.805	20	2.80	2
2.745	25	2.739	36	2.74	5
2.638	2	—		2.63	1/2
2.517	18	2.515	26	2.50	4
2.501	18	—		2.13	2
2.145	3	—		2.11	1/2
2.112	6	2.113	5	—	
1.958	6	—		1.937	10
1.936	100	1.937	100	—	
1.854	5	1.848	4	—	
1.670	2	1.669	5	—	
1.653	12	1.650	12	1.652	3
1.583	3	1.580	4	1.584	1
1.533	3	1.537	5	1.534	1
1.472	2	1.433	7	1.474	1/2
1.427	5	1.427	4	1.427	2
1.370	3	1.370	2	1.370	2
1.264	2	—		—	
1.119	7	1.119	10	1.119	5

1 : Synthetic  $\text{Cu}_5\text{FeS}_4$ .    2 : Bornite from Jinmu mine.

3 : X-ray powder data for bornite by Berry and Thompson<sup>6)</sup>.

(20%) and  $\text{HgCl}_2$  (20%). These optical properties and etching reactions are in good accordance with those of natural bornite described by Short<sup>2)</sup>, Ramdohr<sup>3)</sup> and Uytendogaardt<sup>4)</sup> etc.

In order to form low temperature form of synthetic bornite, the product was kept at 180°C for 50 hours. The result of X-ray diffraction is given in Table 2, as compared with the data of natural bornite and those by Berry and Thompson<sup>6)</sup>. Close agreement is noticed between them.

The differential thermal curves of synthetic and natural bornites are shown in Fig. 2. They are almost similar and indicate an endothermic peak with two steps, corresponding to 200°C and 270°C respectively. It is considered to represent the high-low inversion of bornite polymorphism, studied by Frueh<sup>10)</sup> or Morimoto and Kullerud<sup>11)</sup>.

Sugaki has examined the relation of solid solution of  $\text{Cu}_5\text{FeS}_4$ - $\text{CuFeS}_2$ - $x$ . According to his results, chalcopyrite is soluble in bornite in solid state up to about 40 mol percent at 540°C. The length of unit-cell edge of the bornite solid solutions is given in Table 3. As shown in Fig. 3, a nearly linear relation is observed between the length and their compositions.

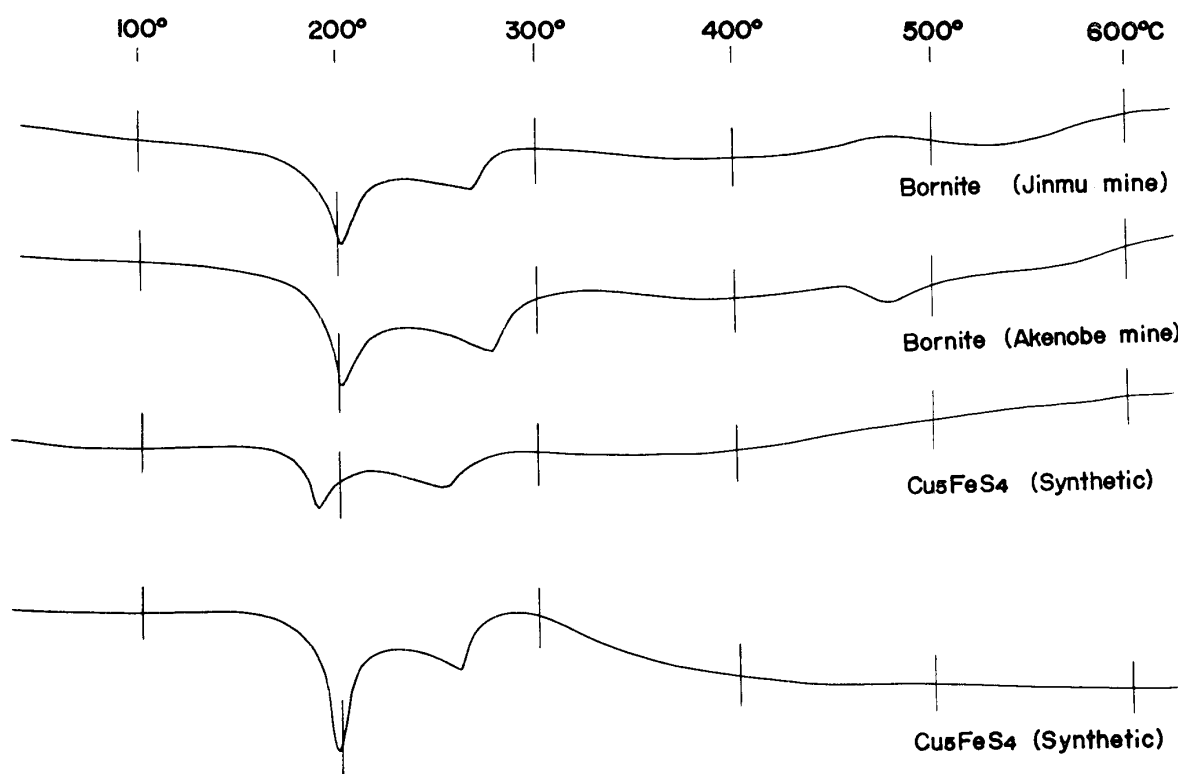


Fig. 2. Differential thermal curves for synthetic Cu<sub>5</sub>FeS<sub>4</sub> as compared with bornites from the Jinmu and Akenobe mines.

Table 3. Unit-cell edges of Cu<sub>5</sub>FeS<sub>4</sub>-CuFeS<sub>2-x</sub> solid solution

Cu <sub>5</sub> FeS <sub>4</sub> content		Unit-cell edges
wt. %	mol %	a <sub>0</sub> (Å)
100.0	100.0	10.946
97.5	93.4	10.929
95.0	87.4	10.914
90.0	76.5	10.891
85.0	67.5	10.867
80.0	59.4	10.847

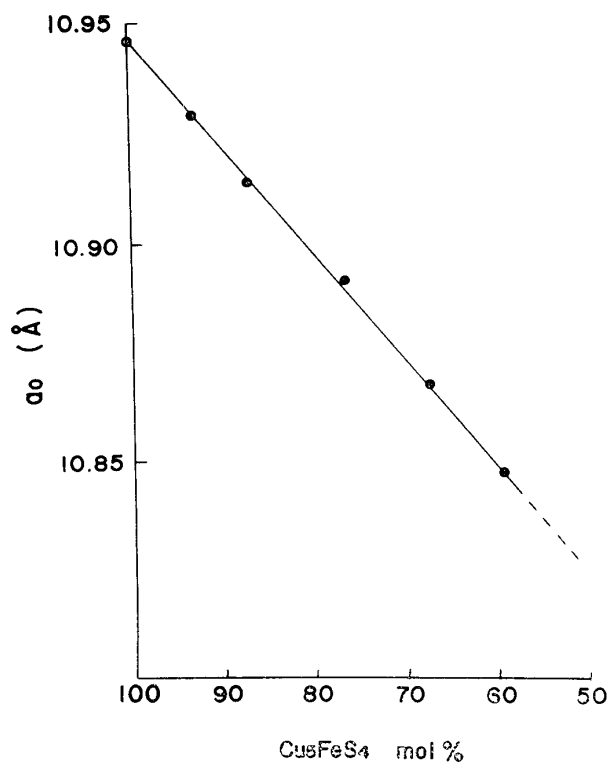


Fig. 3. Composition of synthetic Cu<sub>5</sub>FeS<sub>4</sub>-CuFeS<sub>2-x</sub> solid solutions versus lattice constant relationship.

## 5. $\text{Cu}_3\text{BiS}_3$ (Wittichenite)

Wittichenite was synthesized by two methods, one is reaction between cuprous sulfide ( $\text{Cu}_2\text{S}$ ) and bismuth sulfide ( $\text{Bi}_2\text{S}_3$ ) in solid phase, the other is direct production from copper metal, bismuth metal and sulfur.

In the former method, cuprous sulfide ( $\text{Cu}_2\text{S}$ ) and bismuth sulfide ( $\text{Bi}_2\text{S}_3$ ) used as a starting materials were formed at first from copper, bismuth and sulfur by the method described in the last report<sup>1)</sup>. They were exactly weighed in the molecular ratio of three cuprous sulfide to one bismuth sulfide, and were mixed thoroughly under acetone in agate mortar. After sealing in the evacuated Hario glass tube, they were heated in the electric furnace at  $500^\circ\text{C}$  for 48 hours or 72 hours.

In the later method, charges weighed exactly in proportion of three copper, one bismuth to three sulfur in molecular ratio were sealed in the Hario glass tube under vacuum in  $10^{-3}$  mm Hg. The sealed glass tube was put in the furnace and kept at  $300^\circ\text{C}$  for about 12 hours, continuously at  $500^\circ\text{C}$  for 48 hours. When the reaction was incomplete and sulfur remained in the upper part of the sealed tube, the tube was kept upside down in furnace for longer period. After the sulfur was entirely disappeared by reaction with metals, the content was taken out and ground in an agate mortar to mix uniformly under acetone. Then it was again sealed in the evacuated glass tube and heated at  $500^\circ\text{C}$  for more than 48 hours. After heating, it was instantly quenched in water or cooled in air.

Both products synthesized by the above mentioned two ways have perfectly same properties, and are identical with wittichenite.

Synthetic wittichenite is usually somewhat sintered and megascopically dark gray in colour. Under the reflection microscope, it is grayish white with a little purplish tint in colour and shows moderately anisotropism under crossed nicols. When etched with  $\text{HNO}_3$  (1 : 1), it stains to brownish colour with effervescence, with KCN (20%), makes bluish iridescence and with KOH (sat.), it is slowly stained slightly. However, it is negative to HCl (1 : 1),  $\text{FeCl}_3$  (20%) and  $\text{HgCl}_2$  (20%). These optical properties are in good accordance with those of natural wittichenite described by Short<sup>2)</sup> and Uytendogaardt<sup>4)</sup> etc.

The X-ray powder data of synthetic wittichenite, as shown in Table 4, agree with those of natural wittichenite and the data by Nuffield<sup>12)</sup>.

The differential thermal analysis curve of synthetic wittichenite given from the examination in vacuum is shown in Fig. 4. It has large and small endothermic peaks which have an end point at about  $530^\circ\text{C}$  and  $550^\circ\text{C}$  respectively. It is considered that the former corresponds to the incongruent melting of wittichenite and the later indicates the completion of its melting.

## 6. $\text{CuBiS}_2$ (Cuprobismuthite or Emplectite)

$\text{CuBiS}_2$  is one of homogeneous phase in the system of  $\text{Cu}_2\text{S}$ – $\text{Bi}_2\text{S}_3$ . However, it is stable only below about  $475^\circ\text{C}$ , because two phases,  $\text{Cu}_3\text{BiS}_3$  and  $\text{Cu}_3\text{Bi}_5\text{S}_9$ , become stable above  $475^\circ\text{C}$ .

$\text{CuBiS}_2$  was synthesized by reaction between cuprous sulfide ( $\text{Cu}_2\text{S}$ ) and bismuth sulfide ( $\text{Bi}_2\text{S}_3$ ) which were prepared beforehand from copper, bismuth and sulfur in the same methods as described<sup>1)</sup> formerly. Both sulfides were accurately weighed in the proportion of fifty to fifty and mixed sufficiently under acetone. Then the mixture sealed in the evacuated Hario glass tube was put in the electric furnace. After heating it at  $500^\circ\text{C}$  for 2 days, it was annealed at temperature between  $300^\circ\text{C}$  and  $450^\circ\text{C}$  for 7 days or 10 days in which  $\text{CuBiS}_2$  was a

Table 4. The data of X-ray powder diffraction for synthetic  $\text{Cu}_3\text{BiS}_3$ 

1		2		3		
d (Å)	I	d (Å)	I	d (Å)	I	hkl
5.66	20	5.64	30	5.68	1	011
5.22	20	5.20	30	5.22	1	020
4.55	55	4.55	55	4.55	4	111
3.85	45	3.85	45	3.83	3	200
3.62	15	3.61	30	3.62	1	121, 210
3.35	20	3.35	60	3.34	1	002, 201
3.18	50	3.18	60	3.19	3	012, 211
3.08	80	3.08	130*	3.08	8	220, 102, 031
2.95	35	2.96	45	2.96	1	112
2.861	100	2.860	100	2.85	10	131
2.814	25	2.811	30	2.81	1/2	022
2.648	50	2.650	70*	2.66	4	122
2.604	15	2.605	30			
2.578	25	2.574	35	2.58	2	040, 230
2.492	5	2.497	20	2.49	1/2	310
2.401	20	2.400	25	2.39	3	032, 231, 301
2.338	10	2.356	25	2.34	1/2	311
2.301	7					
2.275	2			2.28	1/2	141, 320, 132
2.181	10	2.189	20	2.17	2	013, 321
2.104	5			2.10	1/2	113
2.051	15	2.048	70	2.05	2	330, 023, 042
2.038	10	2.029	35			241
1.997	25					312, 150
1.987	15	1.984	30	1.989	2	123
1.926	10	1.927	25	1.910	1/2	151
1.886	20	1.871	100*	1.895	3	322
1.824	30	1.826	45			
1.812	10			1.821	3	113, 250
1.765	25	1.761	40	1.762	3	052

1 :  $\text{Cu}_3\text{BiS}_3$  (synthetic) 2 : Wittichenite (Obari mine) 3 : Data for wittichenite by Nuffield<sup>(2)</sup>

\* Diffraction lines of associated chalcopyrite fall on these lines.

stable single phase. If it was heated at first at 300°C or 400°C, longer period will be required.

The product is usually a mass of powder gray in colour. In polished section, only mono phase grayish white in colour is observed, which is very similar to that of wittichenite, and shows considerable anisotropism changing in interference colour from grayish yellow to bluish gray. Although it is slightly stained by etching with  $\text{HNO}_3$  (1 : 1), it is negative to  $\text{HCl}$  (1 : 1),  $\text{KOH}$  (sat.),  $\text{KCN}$  (20%),  $\text{FeCl}_3$  (20%) and  $\text{HgCl}_2$  (20%). These optical properties do not agree perfectly with those of emplectite or cuprobismuthite described by Short<sup>(2)</sup>, Ramdohr<sup>(3)</sup>, Uytendogaardt<sup>(4)</sup> and Farnham<sup>(5)</sup>, but they are closer to the properties of emplectite. Namely, the authors except Farnham have a doubt of the validity of cuprobismuthite as mineral species.

The X-ray powder data of synthetic  $\text{CuBiS}_2$  are shown in Table 5 as compared with those of natural emplectite and cuprobismuthite by Berry and Thompson<sup>(6)</sup>. Chemical composition of

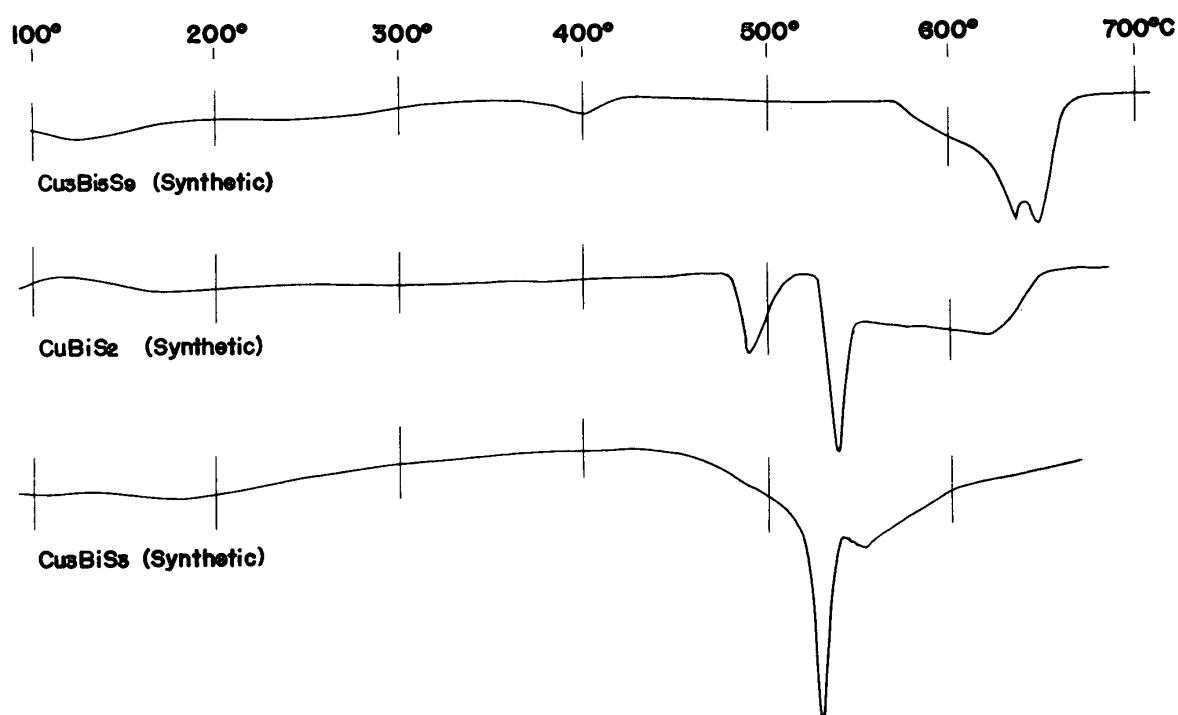


Fig. 4. Differential thermal curves for synthetic  $\text{Cu}_3\text{Bi}_5\text{S}_9$ ,  $\text{CuBiS}_2$  and  $\text{Cu}_3\text{BiS}_3$ .

$\text{CuBiS}_2$  is applied generally to emplectite occurring commonly in nature, but it is also given to cuprobismuthite by Nuffield<sup>13)</sup>. So, it is hard to say which mineral corresponds to  $\text{CuBiS}_2$  synthesized now. However, according to X-ray powder diffraction data, as shown in Table 5, it corresponds to rather cuprobismuthite than emplectite. But it is required further examinations to solve this problem.

Also, the differential thermal analysis was examined on synthetic  $\text{CuBiS}_2$  in vacuum. The curve shown in Fig. 4 has two distinct endothermic peaks beginning at about  $480^\circ\text{C}$  and  $525^\circ\text{C}$  with pointed ends at  $490^\circ\text{C}$  and  $535^\circ\text{C}$  respectively. The former represents the decomposition of  $\text{CuBiS}_2$  into  $\text{Cu}_3\text{BiS}_3$  (wittichenite) and  $\text{Cu}_3\text{Bi}_5\text{S}_9$ , and the later, their eutectic melting. In addition to these two peaks, more extensive endothermic reaction which ends at about  $620^\circ\text{C}$  is recognized. It is thought that this endothermic phenomenon corresponds to the liquidation with changing its composition and the end point indicates the completion of melting.

## 7. $\text{Cu}_3\text{Bi}_5\text{S}_9$ (Synthetic Phase)

In nature, no occurrence of the mineral which has a chemical composition of  $\text{Cu}_3\text{Bi}_5\text{S}_9$  has been reported. However, it was recognized as a stable crystalline phase by Nuffield<sup>12)</sup> during his study on cupro-bismuth sulfide minerals such as wittichenite, klapprothite or emplectite. The present authors have also ascertained that it is really a stable phase in the system  $\text{Cu}_2\text{S}-\text{Bi}_2\text{S}_3$ \*.

$\text{Cu}_3\text{Bi}_5\text{S}_9$  was also synthesized from cuprous sulfide ( $\text{Cu}_2\text{S}$ ) and bismuth sulfide ( $\text{Bi}_2\text{S}_3$ ) in the same way as  $\text{CuBiS}_2$ . The mixture in the accurate molecular ratio of three cuprous sulfide to five bismuth sulfide was carefully ground together under acetone in an agate mortar and immediately sealed in the evacuated Hario glass tube. Then, it was heated for 72 to 120 hours at  $500^\circ\text{C}$ . The charge became usually completely homogeneous by only single heating.

\* The phase relations of  $\text{Cu}_2\text{S}-\text{Bi}_2\text{S}_3$  system will be published in the near future.



Table 5. The data of X-ray powder diffraction for synthetic  $\text{CuBiS}_2$ 

1		2		3	
d (Å)	I	d (Å)	I	d (Å)	I
5.01	25			4.72	20
4.37	20				
4.31	25	4.31	30	—	—
3.71	50	—	—	—	—
3.63	85	3.65 B	40	3.65	5
3.47	40	3.47	10	—	—
3.22	80	3.23	40	3.23	90
—	—	—	—	3.13	70
3.10	100	3.10	100	3.05	100
3.00	30	—	—	—	—
2.94	10			—	—
2.92	25	2.96 B	5	—	—
2.866	40	2.86 B	10	2.83	5
2.731	40	2.73	60	2.73	5
2.675	5	—	—	—	—
2.589	12	2.58	10	—	—
2.528	10	—	—	—	—
2.492	12	2.49	5	—	—
2.443	5	—	—	2.42	5
2.344	5	—	—	2.34	50
2.307	20	2.30	5	—	—
2.214	5	—	—	2.25	10
2.178	50	2.17	20	2.17	40
2.151	5	—	—	—	—
2.132	15	—	—	—	—
2.113	12	—	—	—	—
2.092	25	2.09	20	—	—
1.997	20	2.00	5	—	—
1.959	20	1.961	30	1.965	20

1 : Synthetic  $\text{CuBiS}_2$  (at  $400^\circ\text{C}$ )    2 : Data for cuprobismuthite by Berry and Thompson<sup>(6)</sup>

3 : Data for emplectite by Berry and Thompson<sup>(6)</sup>

Synthesized  $\text{Cu}_3\text{Bi}_5\text{S}_9$  is generally in powder, dark silver gray in colour. Under the microscope, it is also grayish white, more or less lighter than that of wittichenite, in colour and shows weak reflective pleochroism and very strong anisotropism varying in interference colour from yellowish gray through brownish gray to grayish purple. In the etching reactions, it stains quickly with effervescence and changes its colour into brown by  $\text{HNO}_3$  (1 : 1), but it is negative to  $\text{HCl}$  (1 : 1),  $\text{KOH}$  (sat.),  $\text{KCN}$  (20%),  $\text{FeCl}_3$  (20%) and  $\text{HgCl}_2$  (20%).

The data of X-ray powder diffraction of synthetic  $\text{Cu}_3\text{Bi}_5\text{S}_9$  are given in Table 6.

Differential thermal analysis curve obtained for  $\text{Cu}_3\text{Bi}_5\text{S}_9$  in vacuum is shown in Fig. 4. It shows an extensive endothermic reaction having two pointed ends at about  $635^\circ\text{C}$  and  $650^\circ\text{C}$ , corresponding to the incongruent melting of  $\text{Cu}_3\text{Bi}_5\text{S}_9$  to  $\text{CuBi}_3\text{S}_5$  and liquid and to the completion of melting respectively.

Table 6. The data of X-ray powder diffraction for synthetic  $\text{Cu}_3\text{Bi}_5\text{S}_9$  and  $\text{CuBi}_3\text{S}_5$ 

1		2	
d (Å)	I	d (Å)	I
5.61	15	5.81	4
4.48	15	4.70	20
4.26	5	3.65	40
3.84	5	3.51	100
3.64	15	3.31	25
3.61	55	3.18	15
3.47	95	3.09	10
3.44	80	2.97	40
3.30	30	2.835	55
3.25	6	2.788	5
3.18	13	2.663	5
2.95	55	2.542	10
2.91	10	2.410	5
2.844	25	2.344	5
2.822	100	2.295	25
2.660	13	2.122	30
2.571	5	2.058	10
2.501	10	2.018	30
2.380	5	2.004	15
2.262	35	1.993	15
2.178	7	1.975	10
2.109	20	1.920	20
2.094	20	1.854	10
2.071	12	1.820	5
2.003	45	1.763	8
1.987	20	1.750	20
1.901	10		
1.892	20		
1.862	5		
1.831	5		

1 : Synthetic  $\text{Cu}_3\text{Bi}_5\text{S}_9$     2 : Synthetic  $\text{CuBi}_3\text{S}_5$ 

### 8. $\text{CuBi}_3\text{S}_5$ (Synthetic New Phase)

$\text{CuBi}_3\text{S}_5$  was found as one of the homogeneous crystalline phase in the system  $\text{Cu}_2\text{S}-\text{Bi}_2\text{S}_3$  during the investigation of phase equilibrium relations of this system by the present authors. No one has reported on this phase, and  $\text{Cu}_2\text{Bi}_4\text{S}_7$  ( $\text{Cu}_2\text{S} \cdot 2\text{Bi}_2\text{S}_3$ ) which has been described as "Phase A" by Gaudin and Dicke<sup>14)</sup> and as "Dognacskite" in Dana's System of Mineralogy<sup>15)</sup> has the composition nearest to this phase among the data thus far published.

The synthetic method of  $\text{CuBi}_3\text{S}_5$  was entirely the same as that of  $\text{Cu}_3\text{Bi}_5\text{S}_9$  except a mixing ratio of the charge. The charge was prepared by mixing uniformly one cuprous sulfide ( $\text{Cu}_2\text{S}$ ) to three bismuth sulfide ( $\text{Bi}_2\text{S}_3$ ) in the molecular ratio.

In polished sections, synthesized  $\text{CuBi}_3\text{S}_5$  appears heterogeneous at first because of its reflective pleochroism, but careful observation shows that it is homogeneous. It varies from light

grayish white to grayish white with purplish tint in colour under the reflection light and has distinct anisotropism from cream yellowish colour through brownish gray to dark purplish gray under crossed nicols. When etched with  $\text{HNO}_3$  (1 : 1), it fumes and tarnishes quickly to change its colour into brownish black. However, it is negative to  $\text{HCl}$  (1 : 1),  $\text{KOH}$  (sat.),  $\text{KCN}$  (20%),  $\text{FeCl}_3$  (20%) or  $\text{HgCl}_2$  (20%).

The X-ray powder diffraction data are shown in Table 6.

The differential thermal analysis for synthesized phase,  $\text{CuBi}_3\text{S}_5$ , gives the curves as shown in Fig. 5, one of which was obtained in a heating rate of  $5^\circ\text{C}$  per minute, and the other, of  $1.25^\circ\text{C}$  per minute between  $600^\circ\text{C}$  and  $720^\circ\text{C}$ . The latter curve, which is similar to the second endothermic curve of  $\text{CuBiS}_2$  in shape, has a very distinct endothermic peak beginning at about  $650^\circ\text{C}$  and widespread small endothermic peak ending at about  $700^\circ\text{C}$ . They represent respectively the incongruent melting of  $\text{CuBi}_3\text{S}_5$  to  $\text{Bi}_2\text{S}_3$  and liquid and the melting with continuous changing its chemical composition. The end of endothermic reactions indicates the completion of melting.

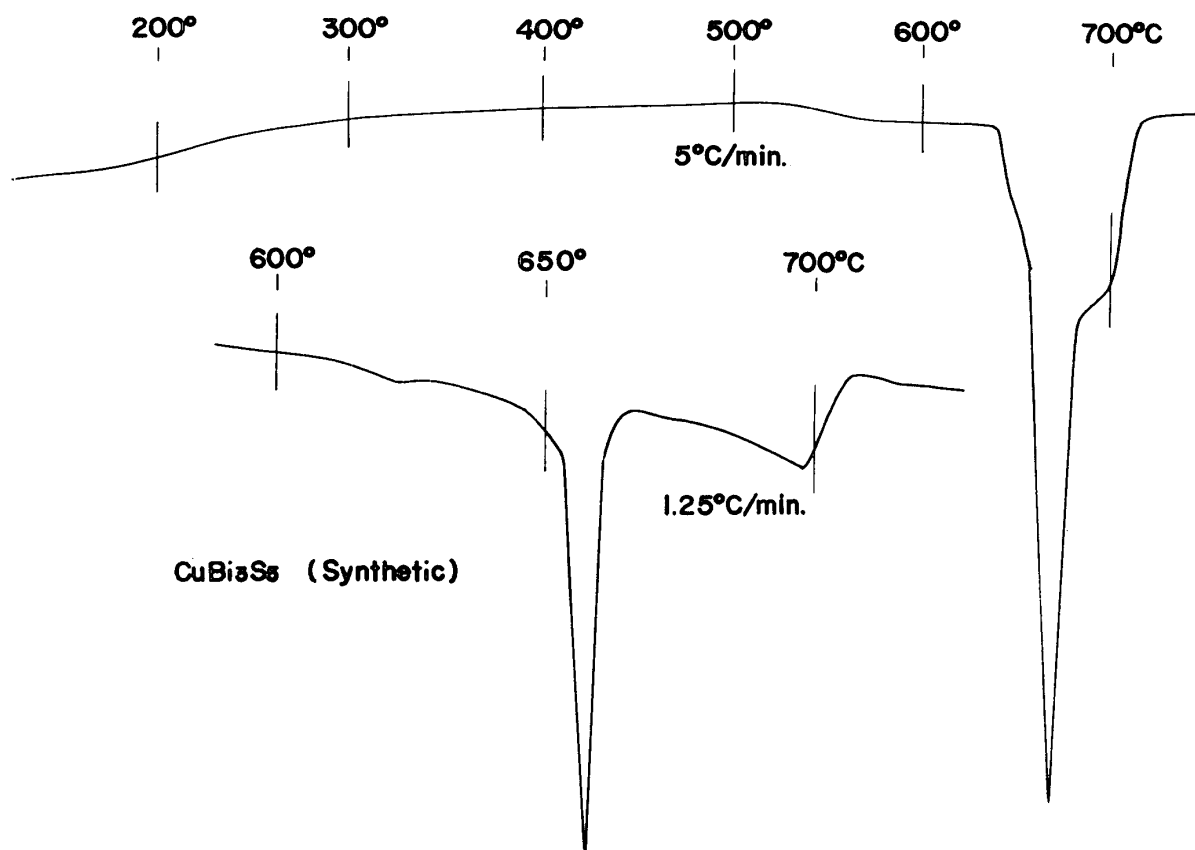


Fig. 5. Differential thermal curves for  $\text{CuBi}_3\text{S}_5$  synthesized.

### 9. $\text{Cu}_3\text{AsS}_4$ (Enargite)

Enargite was synthesized by three ways as follows. The first is the method by reaction between solid copper, liquid arsenic and sulfur vapour at temperatures lower than the melting point of enargite, the second, by annealing of  $\text{Cu}_3\text{AsS}_4$  melt, and the third, by solid reaction between cupric sulfide ( $\text{CuS}$ ) and arsenic sulfide ( $\text{AsS}$ ). It is rather difficult to produce a entirely pure enargite by the former two ways as compared with that by the last way.

In the first method, metallic copper, arsenic and crystalline sulfur weighed exactly in stoichi-

ometric proportions to form  $\text{Cu}_3\text{AsS}_4$  were sealed together in the evacuated Hario glass tube and then the sealed tube was kept in the electric furnace at  $500^\circ\text{C}$  or  $550^\circ\text{C}$  for long period of one or two weeks after heating from room temperature up to  $500^\circ\text{C}$  for about 24 hours. Then, it was cooled slowly in the furnace from  $500^\circ\text{C}$  down to room temperature for about 48 hours. It was difficult to completely expend sulfur as the reaction was very sluggish. When sulfur was entirely consumed, the content was taken out and ground into powder to mingle as uniformly as possible under acetone. Then, it was again sealed and re-heated at  $500^\circ\text{C}$  for 48 hours.

In the second method, the requisite amount of copper, arsenic and sulfur were sealed together in the evacuated silica glass tube, and put in the furnace. Temperature was elevated very slowly from room temperature up to about  $700^\circ\text{C}$  for 72 hours, especially slowly with caution in the vicinity of melting, because vapour pressure inside of the tube was thought to be considerably high. After melting and keeping for several hours more, it was annealed very slowly from  $700^\circ\text{C}$  to room temperature for about one week to absorb sulfur vapour filled in the glass tube.

In the third method, cupric sulfide and arsenic sulfide accurately weighed in proportion to three to one were mixed thoroughly and then heated in the sealed, evacuated Hario glass tube at  $500^\circ\text{C}$  for 48 hours or 72 hours.

Among these three ways, the last one is the most easy to synthesize enargite.

Only the product formed from the melt is quite similar to natural enargite in appearance, that is, aggregate of prismatic crystals with well-cleavages developed. In polished sections, it is homogeneous, prismatic in shape, grayish white with pinkish tint in colour, varying slightly by reflective pleochroism and shows very strong anisotropism under the crossed nicols. Its interference colour varies from reddish through yellowish to bluish gray. By KCN (20%), it is etched distinctly to bring out a parallel prismatic structures with colour change into brown, and

Table 7. The data of X-ray powder diffraction for synthetic  $\text{Cu}_3\text{AsS}_4$

1		2		3		
d (Å)	I	d (Å)	I	d (Å)	I	hkl
4.88	5	4.87	5	4.87	1/2	110
3.22	100	3.22	100	3.22	10	120, 200
3.08	20	3.09	20	3.08	4	002
2.99	5	—	—	2.97	1/2	210
2.857	35	2.857	40	2.87	8	121, 201
2.226	13	2.226	10	2.22	3	122, 202
—	—	1.918	2	1.910	1/2	222
1.857	75	1.857	50	1.859	9	040, 320
1.731	20	1.731	18	1.731	6	123, 203
—	—	1.618	2	—	—	—
1.608	5	1.610	4	1.608	4	240, 400
—	—	1.607	8	—	—	—
1.592	15	1.591	10	1.590	5	042, 322
1.589	15	1.589	10	—	—	—
1.559	4	1.558	4	1.556	4	241, 401
1.555	5	1.556	5	—	—	—

1 : Synthetic  $\text{Cu}_3\text{AsS}_4$     2 : Enargite (Kinkaseki mine)

3 : Data for enargite by Berry and Thompson<sup>6)</sup>

it shows clear grain boundary by  $\text{FeCl}_3$  (20%). It is negative to  $\text{HCl}$  (1 : 1),  $\text{KOH}$  (sat.),  $\text{HNO}_3$  (1 : 1) and  $\text{HgCl}_2$  (20%). These optical properties of synthetic  $\text{Cu}_3\text{AsS}_4$  is in good accordance with those of natural enargite described by Short<sup>2)</sup>, Ramdohr<sup>3)</sup>, Uytenbogaardt<sup>4)</sup> and Farnham<sup>5)</sup>.

The data of X-ray powder diffraction of synthetic enargite are given in Table 7, compared with those of natural enargite from Kinkaseki mine and the data by Berry and Thompson<sup>6)</sup>. They show good agreement to each other.

In Fig. 6 are shown the differential thermal analysis curves of synthetic and natural enargite. Only a sharp endothermic peak beginning at  $670^\circ\text{C}$  with head at about  $700^\circ\text{C}$  is observed. Since this peak represents the congruent melting of enargite, this curve shows no endothermic phenomenon such as a phase inversion before melting. Natural enargite shows a very similar result as shown in Fig. 6.

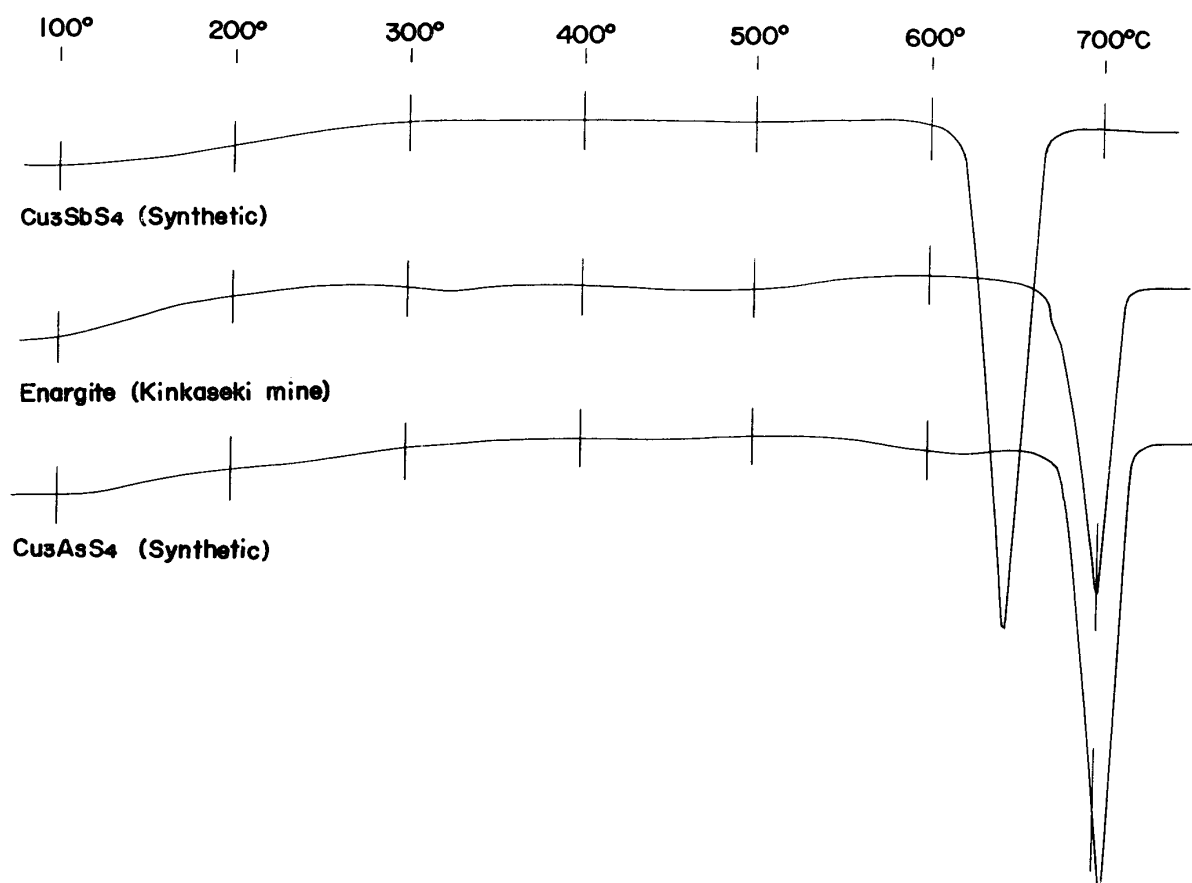


Fig. 6. Differential thermal curves for synthetic  $\text{Cu}_3\text{SbS}_4$  and  $\text{Cu}_3\text{AsS}_4$  in comparison with the curve for enargite from the Kinkaseki mine, Formosa.

## 10. $\text{Cu}_3\text{SbS}_4$ (Famatinite)

The synthesis of famatinite can be done most easily by the first method among the three ways as mentioned on enargite, because of difficulty of synthesis of antimony sulfide ( $\text{Sb}_2\text{S}_3$ ) as described in the last paper<sup>1)</sup>.

Copper, antimony and sulfur weighed exactly in molecular ratio of three to one to four were sealed together in the evacuated Hario glass tube and heated firstly at  $300^\circ\text{C}$  for several hours, then at  $400^\circ\text{C}$  for 24 hours continuously at  $500^\circ\text{C}$  for 72 hours or 120 hours. Sulfur disap-

peared more quickly during the synthesis of famatinite than during that of enargite. To make the mixture more homogeneous, it was ground and mixed thoroughly and then re-heated at 500°C for more 48 hours.

If antimony sulfide was prepared previously, however, synthesis by reaction between simple sulfides is the most easy way. Mixture of four cupric sulfide (CuS), one cuprous sulfide (Cu<sub>2</sub>S) and one antimony sulfide (Sb<sub>2</sub>S<sub>3</sub>) in molecular ratio was thoroughly mixed under acetone and sealed in an evacuated glass tube. It was heated at 500°C for 48 hours and then was cooled in air.

Under the microscope, it is pinkish gray in colour with weak reflective pleochroism and shows strong anisotropism varying from dark bluish gray to orange brown. Also, it is usually shown polysynthetic twinning. When etched with HNO<sub>3</sub> it shows iridescence with fume, and with KCN (20%) tarnish slowly to darker gray. These optical properties are in good agreement with those of natural famatinite described by the authors<sup>2)-5)</sup>.

The X-ray powder data of synthetic famatinite are shown in Table 8, as compared with those of natural famatinite by Berry and Thompson<sup>6)</sup>. As natural famatinite contains some arsenic substituting for antimony, the X-ray diffraction angles (2θ) shift towards high angle from those of stoichiometric Cu<sub>3</sub>SbS<sub>4</sub>.

Table 8. The data of X-ray powder diffraction for Cu<sub>3</sub>SbS<sub>4</sub>

1		2	
d (Å)	I	d (Å)	I
5.40	4	—	—
4.84	10	4.77	2
3.82	4	—	—
3.11	100	3.08	10
2.99	7	2.96	1/2
2.694	14	2.67	3
2.410	3	—	—
2.353	4	2.33	1/2
2.199	2	2.18	1/2
2.001	4	1.973	1/2
1.905	50	1.888	7
1.797	2	—	—
1.704	1	—	—
1.623	30	1.610	5
1.604	2	—	—
1.553	5	1.542	1

1 : Synthetic Cu<sub>3</sub>SbS<sub>4</sub>    2 : Data for famatinite by Berry and Thompson<sup>6)</sup> (Famatina mine)

As shown in Fig. 6, the differential thermal analysis curve has a large endothermic peak at about 640°C representing the latent heat of congruent melting. From this, it is considered that famatinite has also no transformation up to its melting point.

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