

## Synthetic Sulfide Minerals (III)

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### 1. Introduction

In order to elucidate the genetic conditions of metallic ore deposits, it is necessary to determine the phase equilibrium relations between ore forming minerals. In this study, first of all, the synthesis of minerals of stoichiometric composition is required. In the last few years the present authors have been studying on the phase relations between several sulfide minerals. The results of synthetic preparation of these sulfide minerals were reported in the previous papers<sup>1)2)</sup>. In this present paper, methods of synthesis and properties of three synthesized sulfide minerals, such as monoclinic pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ), chalcostibite ( $\text{CuBiS}_2$ ), and horobetsuite ( $\text{BiSbS}_3$ ), will be described.

The synthesis of two minerals except monoclinic pyrrhotite was mostly carried out in an evacuated rigid glass tube by means of solid state reactions between simple sulfides, such as chalcocite ( $\text{Cu}_2\text{S}$ ), bismuthinite ( $\text{Bi}_2\text{S}_3$ ), and stibnite ( $\text{Sb}_2\text{S}_3$ ). Only monoclinic pyrrhotite was mainly synthesized from troilite ( $\text{FeS}$ ) under hydrothermal conditions. These simple sulfides were prepared beforehand from metallic elements and sulfur. Purity of the metals used as primary starting materials for the synthesis is 99.99% in electrolytic copper, 99.9% in electrolytic iron, and more than 99.9% in both of bismuth and antimony. Crystalline sulfur refined to 99.9% as guaranteed reagent was utilized.

The synthetic products were identified by means of microscopic observation under reflected light and X-ray powder diffraction, and their thermal behaviors were examined by the differential thermal analysis. X-ray studies were carried out by X-ray diffractometer, Geigerflex. Mn-filtered  $\text{FeK}_\alpha$  radiation was employed for only monoclinic pyrrhotite and Ni-filtered  $\text{CuK}_\alpha$  radiation for the other two minerals. The differential thermal analysis was all carried out in the evacuated silica glass tube and in the synthetic experiments nine vertical electric furnaces wound by Kanthal wire were used.

### 2. $\text{Fe}_{1-x}\text{S}$ (Monoclinic pyrrhotite)

As mineral phases belonging to pyrrhotite group troilite, hexagonal pyrrhotite, and monoclinic pyrrhotite have been widely known. According to Grønvold and Haraldsen<sup>3)</sup>, troilite with a B-8 (NiAs)-like superstructure has a stoichiometric composition of  $\text{FeS}$  and hexagonal pyrrhotite with the B-8 (NiAs) structure has a composition ranging between  $\text{Fe}_{0.935}\text{S}$  and  $\text{Fe}_{0.900}\text{S}$  (48.31 to 47.39 atomic per cent Fe) below  $325^\circ\text{C}$ . But the latter is stable in all composition ranges of  $\text{FeS}$  to  $\text{Fe}_{0.847}\text{S}$  (50.00 to 45.87 atomic per cent Fe) above  $325^\circ\text{C}$ . On the other hand, monoclinic pyrrhotite with low symmetric structure is stable only below  $325^\circ\text{C}$  and has a composition close to that of  $\text{Fe}_{0.877}\text{S}$  (46.73 atomic per cent Fe). Besides, many other investigators, such as Hägg and Sucksdorff<sup>4)</sup> or Carpenter and Desborough<sup>5)</sup> have studied on the stability regions of these three phases and on the phase relations between them, but results have not been established yet. The present authors have been also studying on these subjects, and tried to synthesize them.

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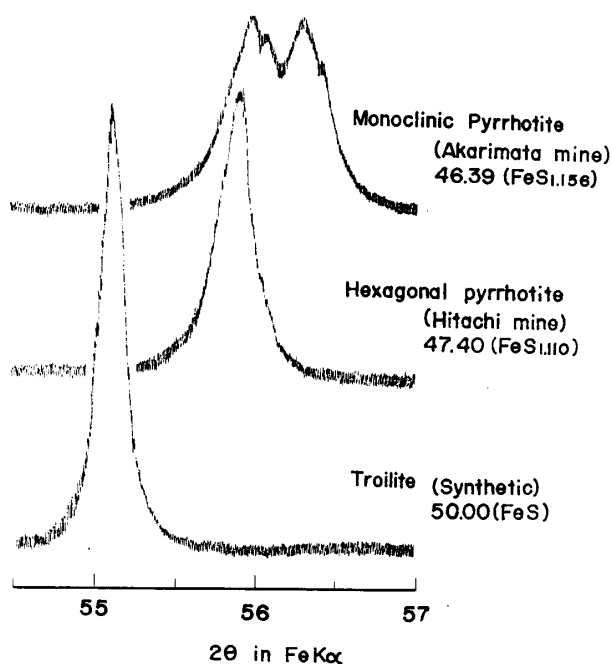


Fig. 1. A variation of X-ray diffraction peak between monoclinic and hexagonal pyrrhotites and troilite.

Since troilite and hexagonal pyrrhotite were described in the previous paper<sup>1)</sup>, only monoclinic pyrrhotite is described here. Monoclinic pyrrhotite is found commonly from many copper and iron sulfide deposits. It is distinguished from troilite and hexagonal pyrrhotite by the characteristic split of diffraction peak found between 55° and 57° of  $2\theta$  by Mn-filtered  $\text{FeK}\alpha$ , while the other two show the diffraction of single peak for (102) in this region of  $2\theta$  as shown in Fig. 1.

Monoclinic pyrrhotite was synthesized by two ways; one was a dry method and the other a wet method.

By the first method, it was formed by annealing hexagonal pyrrhotite which is richer in sulfur than  $\text{Fe}_{0.885}\text{S}$  (46.95 atomic per cent Fe) at temperature below 325°C, the high (hexagonal form)-low (monoclinic form) inversion point. The annealing was performed mostly at 300°C

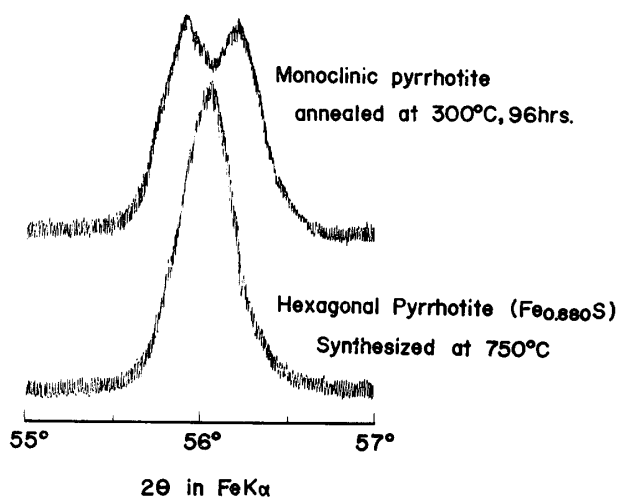


Fig. 2. A result of annealing experiment of pyrrhotite.

for 48 hours or 96 hours. Under this condition the transformation of several hexagonal pyrrhotites with a composition ranging between  $\text{Fe}_{0.885}\text{S}$  and  $\text{Fe}_{0.855}\text{S}$  (46.95 to 46.08 atomic per cent Fe) into monoclinic form was successful. One example of the results is shown in Fig. 2. When kept at  $300^\circ\text{C}$  for 96 hours, the synthetic hexagonal pyrrhotite with composition of  $\text{Fe}_{0.880}\text{S}$  (46.82 atomic per cent Fe) showing a single peak at  $56.05^\circ$  changed into monoclinic form representing double peaks at  $55.92^\circ$  and  $56.19^\circ$  in  $2\theta$  ( $\text{FeK}\alpha$ ).

By the second method, it was synthesized by the reaction between synthetic iron sulfide, troilite ( $\text{FeS}$ ), and an aqueous solution of several sulfide in a sealed Hario glass tube. As the sulfur sources, 39.39%, 20.00%, 13.04%, and 4.76% aqueous solution of sodium sulfide ( $\text{Na}_2\text{S}$ ) and about 7% aqueous solution of ammonium sulfide,  $((\text{NH}_4)_2\text{S})$  were employed. After the introduction into the Hario glass tube about 200 mg of troilite ( $\text{FeS}$ ) which was ground under 200 mesh and 3 cc of the desired aqueous solution, the tube was carefully sealed not to make difference in wall thickness. The sealed glass tube, about 100 mm in length, 10 mm in the inside diameter, 1 mm in wall thickness and about  $8\text{ cm}^3$  in the inside capacity was put into a sheath of tin plate and was hung into the furnace. Then, temperature was elevated very slowly and carefully from room temperature up to  $200^\circ\text{C}$  for 6 hours, because it was supposed that the vapor pressure inside of the tube might become considerable high at temperature close to  $200^\circ\text{C}$ . Synthetic experiments were performed at  $130^\circ\text{C}$ ,  $150^\circ\text{C}$ ,  $180^\circ\text{C}$ ,  $200^\circ\text{C}$  and  $225^\circ\text{C}$ , and the estimated vapor pressures were about 25 atm. at  $225^\circ\text{C}$ , 15 atm. at  $200^\circ\text{C}$  and 10 atm at

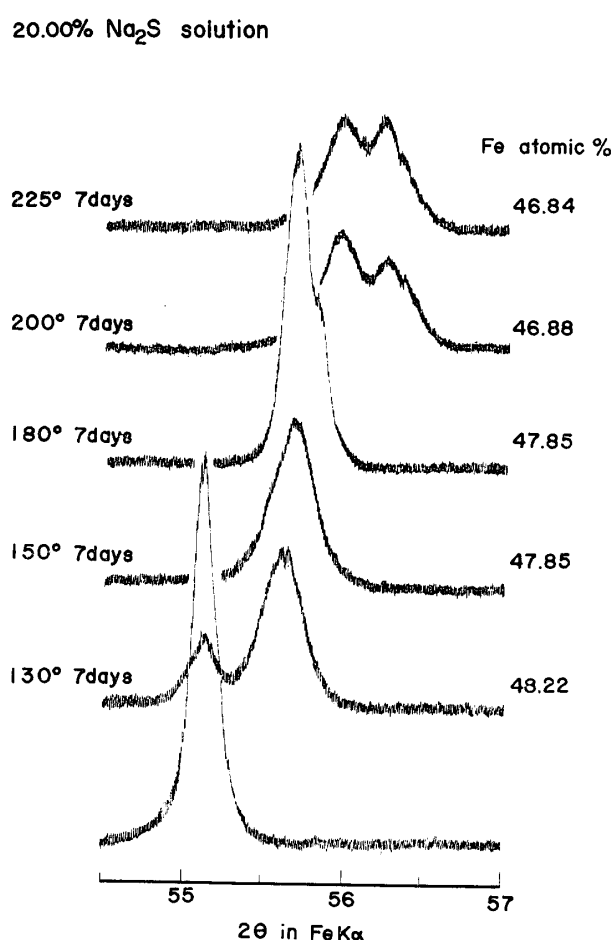


Fig. 3. Results of hydrothermal synthetic experiments of monoclinic pyrrhotite in  $\text{Na}_2\text{S}$  20.00% solution.

180°C, respectively.

Some results of the synthesis by wet method are given in Fig. 3. Other results were nearly same as these ones. When heated, at first troilite (FeS) directly changed into hexagonal pyrrhotite with a composition close to that of  $\text{Fe}_{0.92}\text{S}$  (about 47.90 atomic per cent Fe), while the latter continuously changed its composition towards that enriched in sulfur, finally becoming monoclinic pyrrhotite by reacting with sulfur in the aqueous solution. In general the reactions proceed satisfactorily with rising temperature, or with the increase of concentration of the aqueous solutions. Monoclinic pyrrhotite was produced by this method under the following conditions; at the temperature above 200°C for 7 days in 20.00% and 39.39% aqueous solution of sodium sulfide, and at 225°C for 4 days in 7% aqueous solution of ammonium monosulfide. Recently, Moh<sup>6)</sup> described that monoclinic pyrrhotite was formed by the treatment of stoichiometric FeS with ammonium disulfide at 130°C for 4 days.

Monoclinic pyrrhotite synthesized by the former method, is megascopically an aggregate of fine granules of grayish bronze yellow in color and that by the latter method a sintered lump of grayish color. Under the microscope, it has weak reflective pleochroism changing from yellowish cream to pinkish cream in color and shows under the crossed nicols strong anisotropism changing its interference color from reddish brown through purple to bluish gray. When etched by  $\text{HNO}_3$  (1:1), it changes color into brown with effervescence. By KOH (sat.) and  $\text{HgCl}_2$

Table 1. The data of X-ray powder diffraction for synthetic and natural pyrrhotites

1		2		3	
d Å	I	d Å	I	d Å	I
5.84	10	{5.78	15	{5.81	20
5.78	10	{5.73	30	{5.75	20
5.28	10	5.27	?	5.29	15
4.71	7	—	—	4.72	15
4.27	20*	—	—	—	—
4.08	18	4.08	10	—	—
4.00	10*	—	—	—	—
3.69	5	—	—	3.65	5
3.35	100*	—	—	—	—
—	—	—	—	3.14	15
—	—	—	—	3.049	15
2.982	40	2.982	80	2.982	100
—	—	2.854	30	2.860	20
{2.646	50	{2.649	100	{2.649	85
{2.638	45	{2.637	85	{2.637	80
2.279B	10*	—	—	—	—
{2.066	55	{2.067	90	{2.066	90
{2.060	45	{2.057	90	{2.058	80
1.801	5*	—	—	—	—
—	—	1.721	60	—	—
1.720	30	1.717	45	1.720	80
—	—	1.712	20	—	—
—	—	1.601B	15	1.599B	5
1.560	8	1.558	15	—	—
1.444	8	1.443	10	1.441	10
1.426	8	1.426	50	1.426	30
1.376B	5	1.366	15	—	—
1.324	8	—	—	1.323	10
1.320	8	1.320B	20	1.316	15
1.287	5	—	—	—	—

1: Monoclinic pyrrhotite synthesized in 20%  $\text{Na}_2\text{S}$  solution (200°, 7days).

2: Monoclinic pyrrhotite produced by annealing of hexagonal pyrrhotite (300°, 2days).

3: Monoclinic pyrrhotite in natural occurrence (Ashio mine).

\*: These diffractions do not belong to pyrrhotite.

Table 2. A collation of the X-ray powder data for monoclinic pyrrhotite synthesized in Na<sub>2</sub>S solution with Carpenter's data

1			2		
d(obs.) Å	I	hkl	d(calc.) Å	d Å	I
5.74	mw*	{111 111	5.76 5.75	{5.78 5.76	12 10
5.27	w*	{112 112	5.28 5.27	5.27	10
4.71	w*	{113 113	4.69 4.68	4.70	10
4.43	vvw*	{211 211	4.42 4.41	—	
3.61	w*	{106 115 115 106	3.62 3.62 3.61 3.61	{3.63 3.62 3.60	8 8 10
3.43	w	020, 310	3.44	3.47	10
3.22	vw*	{206 116 116 206	3.21 3.21 3.20 3.19	{3.22 3.20	15 12
3.13	m*	{313 023 313	3.14 3.13 3.12	{3.15 3.13	5 5
2.975	s	400, 220	2.976	2.977	72
2.849	vw	008	2.847	—	
2.634	vs*	{404 224 224 404	2.645 2.641 2.634 2.630	{2.645 2.639 2.634	78 60 55
2.547	vw*	{316 026 316	2.555 2.548 2.540	2.550*	8
2.374	vvw	019	2.375	—	
2.205	vw*	{422 132 132 422	2.209 2.207 2.206 2.205	—	
2.159	vw*	{133 133	2.158 2.156	—	
2.057	vvs*	{408 228 228 408	2.065 2.061 2.054 2.050	{2.065 2.062 2.056 2.049	100 100 78 30
1.982	vvw*	{331 331	1.977 1.976	—	
1.766	w*	{428 428	1.770 1.761	—	
1.718	s	040, 620	1.718	1.719	56
1.633	w*	{242 242	1.634 1.633	{1.635 1.631	5 5
1.488	vw	800, 440	1.488	—	
1.439	w*	{804 444 444 804	1.442 1.441 1.438 1.437	{1.443 1.439	10 10
1.425	w	0. 0. 16	1.424	1.426	10
1.323	mw*	{808 448	1.323 1.321	{1.324 1.321	15 15
1.315	mw*	{448 808	1.317 1.315	1.315	12
1.288	vw*	{4. 0. 16 2. 2. 16	1.288 1.286	{1.289 1.286	7 7
1.281	vw*	{2. 2. 16 4. 0. 16	1.283 1.281	—	

1: X-ray powder data for natural monoclinic pyrrhotite by Carpenter & Desborough.<sup>5)</sup>

2: X-ray powder data for monoclinic pyrrhotite synthesized in 20% Na<sub>2</sub>S solution.

\* broad peak

(20%), it is slightly stained into brown in color but it is negative to KCN (20%),  $\text{FeCl}_3$  (20%) and HCl (1:1). These optical properties and etching reactions are in good accordance with those of natural pyrrhotite described by Short<sup>7)</sup>, Uytenbogaardt<sup>8)</sup>, Farnham<sup>9)</sup> and Ramdohr<sup>10)</sup>.

The X-ray powder data of monoclinic pyrrhotites synthesized by the two methods mentioned above are given in Table I comparing with those of natural monoclinic pyrrhotite from Ashio Mine. They are in good agreement with each other. Most recently, Carpenter and Desborough<sup>5)</sup> described that all natural pyrrhotite examined by them belonged to super-structure type and 20 specimens of monoclinic pyrrhotite from 18 localities had also super-lattice. In order to compare with their data, more detailed value of X-ray powder diffraction was measured at scanning speed of  $0.25^\circ/\text{min}$ . which is shown in Table 2. The agreement of both data suggested that monoclinic pyrrhotite synthesized in this study has also super-lattice.

The differential thermal analysis curve of synthetic monoclinic pyrrhotite is shown in Fig. 4 together with those of natural monoclinic and hexagonal pyrrhotites and synthetic troilite. Only a sharp endothermic peak with head at about  $320^\circ\text{C}$  representing the latent heat of transformation from low-monoclinic form to high-hexagonal form is observed. It resembles closely to that of natural monoclinic pyrrhotite, but it looks different from those of other two.

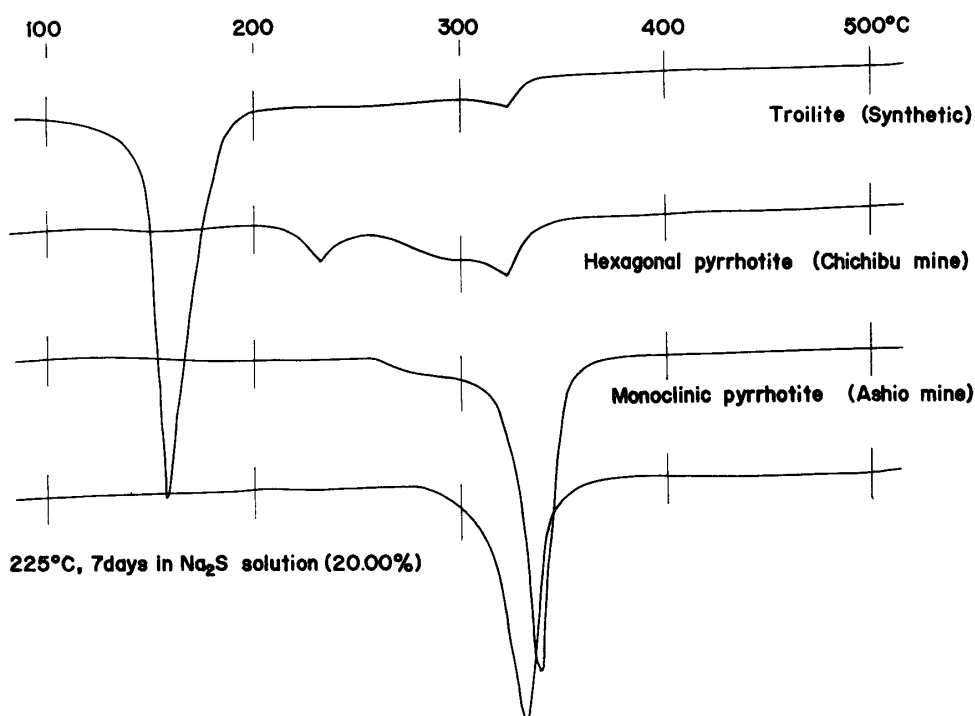


Fig. 4. Differential thermal curves for monoclinic pyrrhotite synthesized by wet method as compared with natural pyrrhotites and synthetic troilite.

### 3. $\text{CuSbS}_2$ (Chalcostibite)

Chalcostibite was known for long time as cupro-antimony sulfide minerals and was already produced artificially by Gaudin and Dicke<sup>11)</sup> from copper-antimony sulfide melt.

It was synthesized by two methods, one was reaction between cuprous sulfide ( $\text{Cu}_2\text{S}$ ) and antimony sulfide ( $\text{Sb}_2\text{S}_3$ ) in solid state, the other was direct production from copper metal, antimony metal, and crystalline sulfur.

In the former method, cuprous sulfide and antimony sulfide which were prepared from copper, antimony and sulfur by the same method as described in the previous paper<sup>1)</sup> were accurately weighed with the molecular ratio of one to one, and were mixed thoroughly under acetone in an agate mortar. After the mixture was sealed in the evacuated Hario glass tube it was heated in the electric furnace at 500°C for 120 hours or 168 hours. Generally a homogeneous cupro-antimony sulfide was produced by the first heating.

In the latter method, charges weighed exactly in proportion to one copper and one antimony to two sulfur in molecular ratio were sealed in the silica glass tube under reduced pressure at  $10^{-3}$  mm Hg. The sealed glass tube was put into the furnace. Temperature of the furnace was elevated very slowly from room temperature up to 750°C for about 36 hours and then was kept at 750°C for 24 hours. After it was kept at this temperature at which the content was entirely melted, it was annealed in the furnace by cutting off the electric source of the furnace.

Product synthesized by the former method, megascopically, is an aggregate of fine grains, grayish in color with metallic luster and that by the latter method is a sponge like lump with lead-gray color. However, both products have perfectly the same properties in optical, thermal and X-ray studies, and are identical with chalcostibite. Under the microscope, it has very distinct pleochroism changing from creamy white to purplish gray in reflection color and shows a very strong anisotropism. Its interference color changes from dark purplish gray through brownish gray to creamy gray under the crossed nicols. In the etching reaction, it stains to

Table 3. X-ray powder data for synthetic chalcostibite.

1		2		
d Å	I	d Å	I	hkl
7.31	89	7.38	2	020
4.65	13	4.67	1	120
3.63	71	3.65	1	011, 040
3.145	100	3.13	10	{111
3.115	82			{140
3.02	64	3.00	9	{200
3.00	93			{031
2.955	19	—	—	—
2.788	7	2.79	1/2	220
2.618	7	—	—	—
2.561	11	2.56	1	230
2.417	9	—	—	—
2.309	62	2.31	4	240, 051
2.248	34	2.24	2	160, 221
2.123	27	2.12	3	231
1.901	28	1.895	3	003
1.831	30	1.831	4	022, 251
1.821	64	1.817	1/2	071, 080
1.764	41	1.762	5	{311
1.761	48			{340
1.744	16	1.743	1/2	171
1.689	9	1.687	1	261
1.624	18	1.621	2	142
1.608	15	1.603	1	202
1.598	7	—	—	—
1.554	11	1.554	1	{190, 271
1.450	9	—	—	{280
1.441	19	1.441	3	{370, 191
1.357	5	1.372	1/2	{430, 281
1.349	7	1.344	1	421, 312
				—

1: Synthetic chalcostibite,  $\text{CuSbS}_2$ .

2: Natural chalcostibite, (by Berry & Thompson<sup>12)</sup>).

brown in color by  $\text{HNO}_3$  (1:1), is etched to bring out scratches by KCN (20%), and is tarnished slightly by  $\text{HgCl}_2$  (20%). However, it is negative to HCl (1:1), KOH (sat.) and  $\text{FeCl}_3$  (20%). These optical properties are in nearly accordance with those of natural chalcostibite described by Uytendogaardt<sup>8)</sup>, Farnham<sup>9)</sup> etc.

The data of X-ray powder diffraction for synthesized chalcostibite are shown in Table 3, compared with those of natural chalcostibite described by Berry and Thompson<sup>12)</sup>. They are in good agreement with each other.

As shown in Fig. 5, the differential thermal analysis curve has only one very distinct endothermic peak beginning at about 550°C. It seems to represent the latent heat of congruent melting. From this curve, it is considered that chalcostibite does not undergo transformation up to its melting point.

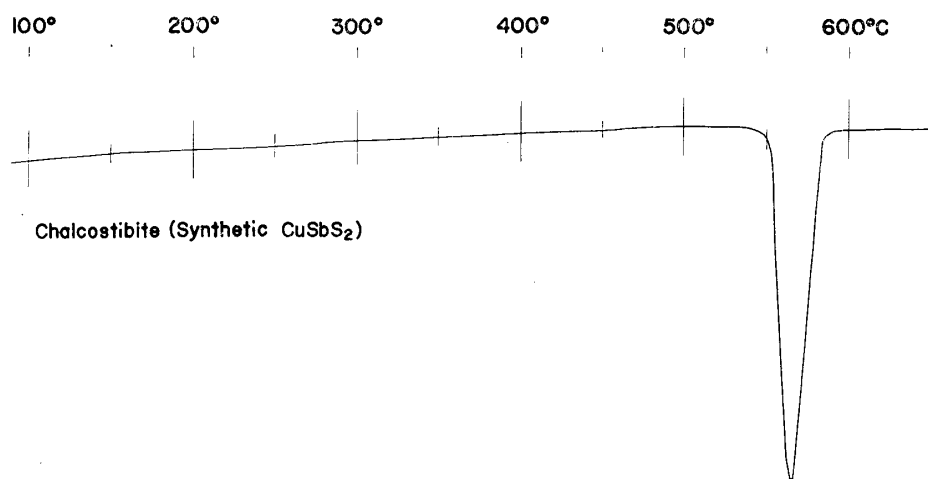


Fig. 5. The differential thermal curve for synthetic chalcostibite.

#### 4. $\text{BiSbS}_3$ (Horobetsuite)

Horobetsuite was newly found by K. Hayase<sup>13)</sup> from Horobetsu Mine, Hokkaido in 1955. It belongs chemically to bismuthinite ( $\text{Bi}_2\text{S}_3$ )–stibnite ( $\text{Sb}_2\text{S}_3$ ) system and is a mixed crystal of nearly an equal amount of bismuthinite and stibnite in molecular ratio. Hayase proposed the name “Horobetsuite” to designate the mineral belonging to this system with molecular ratio of  $\text{Sb}_2\text{S}_3$  to  $\text{Bi}_2\text{S}_3$  between 7:3 and 3:7. However, the conclusion whether a new mineral name “Horobetsuite” is reasonable or not should be necessary to be detained until the existence of perfect solid solution in them is ascertained. The present authors have been studying to establish the phase relations between  $\text{Bi}_2\text{S}_3$  and  $\text{Sb}_2\text{S}_3$ .  $\text{BiSbS}_3$  was synthesized during this study.

$\text{BiSbS}_3$  was produced by solid reaction between bismuth sulfide ( $\text{Bi}_2\text{S}_3$ ) and antimony sulfide ( $\text{Sb}_2\text{S}_3$ ) which were prepared beforehand. Both simple sulfides were exactly weighed in the proportion of fifty to fifty and were mixed sufficiently under acetone in the agate motor. Then, the mixture sealed in the evacuated Hario glass tube was put into the electric furnace and heated at 500°C for 120 hours. The charge usually became completely homogeneous by the single heating.

Megascopically, synthesized  $\text{BiSbS}_3$  is lead-gray in color and an aggregate of fine granules, but once melted, it appears to be fibrous or an aggregate of needle-like crystals. In polished section, it is homogeneous, white with purplish tint in color, changing slightly to brownish by reflection



Table 4. X-ray powder data for synthetic horobetsuite.

1		2		
d Å	I	d Å	I	hkl
5.68	52	5.63	36	200
5.08	34	5.05	26	120
3.99	30	3.97	25	220
3.71	9	—	—	—
3.59	100	3.56	100	310
3.55	42	—	—	—
3.52	11	—	—	—
3.23	9	—	—	—
3.13	20	3.11	25	320
3.09	34	3.08	29	211
2.797	30	2.78	23	221
2.711	11	2.70	9	410
2.630	7	2.63	5	311
2.529	45	2.51	49	420
2.515	10	—	—	—
2.449	9	2.44	7	321
2.295	14	2.29	15	401
2.253	17	2.24	23	141
2.235	7	—	—	—
2.116	7	—	—	—
2.101	14	2.09	18	520
2.087	6	—	—	—
1.991	7	1.98	6	?
1.951	24	1.94	27	002, 431
1.930	13	1.92	15	?
1.887	19	1.88	24	112
1.865	6	1.86	6	?
1.849	6	1.84	6	022
1.775	4	1.78	4	212
1.758	6	—	—	—
1.737	9	1.73	10	222
1.715	9	1.71	7	312

1: Synthetic BiSbS<sub>3</sub>.2: Natural horobetsuite from Horobetsu Mine (by Hayase<sup>13</sup>).

pleochroism, and shows distinct anisotropism changing its interference color from pale creamy through brownish to bluish gray. By HNO<sub>3</sub> (1:1), it stains to brownish black, and it stains also slightly by KOH (sat.). However, it is negative to HCl (1:1), KCN (20%), FeCl<sub>3</sub> (20%) and HgCl<sub>2</sub> (20%).

The data of X-ray powder diffraction for synthesized BiSbS<sub>3</sub> are given in Table 4 compared

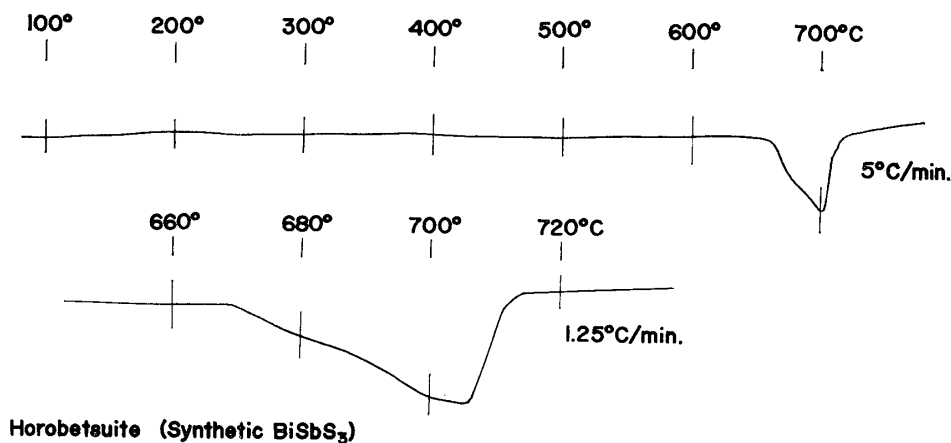


Fig. 6. The differential thermal curves for synthetic horobetsuite.

with those of afore-said natural horobetsuite of type locality found by Hayase.<sup>13)</sup> These properties of optics and X-ray diffraction of synthetic BiSbS<sub>3</sub> agree approximately with those of natural horobetsuite.

The differential thermal analysis was also examined with synthesized BiSbS<sub>3</sub>. The two curves given by the analysis are shown in Fig. 6, one of which was obtained in a heating rate of 5°C per minute, and the other, at 1.25°C per minute. These wide-spread endothermic peak beginning at about 670°C with end point at 706°C suggests that this phase is solid solution. Namely, this endothermic peak shows the characteristic of the reaction occurring continuously with rising temperature from the beginning to the end. It is considered that the beginning point of the peak corresponds to solidus temperature and the end point, to liquidus temperature of BiSbS<sub>3</sub>.

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