# Synthetic Sulfide Minerals (IV)

Asahiko SUGAKI*, Hiromi SHIMA* and Arashi KITAKAZE*

(Received December 7, 1972)

## Introduction

In order to make clear the genetic condition under which sulfide minerals in ore deposits have formed in some geological circumstances, an investigation on the phase equilibrium of several sulfide systems has been carried out by the present authors. During the experiments on the systems of Cu–Bi–S, Cu–Sb–S, Fe–Bi–S and Cu–Fe–Bi–S, new phases such as $Cu_8Bi_8S_{19}$, $Cu_3SbS_3$, $FeBi_4S_7$ and $Cu_{8.4}Fe_{1.2}Bi_{10.8}S_{22}$ which have not been found yet in nature were synthesized. Also during the study on the join $Cu_2S$–$Bi_2S_3$ in the system Cu–Bi–S[1], emplectite was formed at temperature as low as 250°C although its synthesis has been difficult up to the present because it is a low temperature phase. Four synthetic new phases as above and synthetic emplectite, and their synthetic methods, optical properties, X–ray powder and crystal data, and DTA curves etc. will be described as below in this paper. The synthetic method of several sulfides was already described in detail in the previous papers[2),3),4)] by the present authors. Synthesis of those new phases and emplectite mentioned above was also done with mostly the same method. Thus, the method will be described only briefly in this paper.

## $Cu_8Bi_8S_{19}$ (New Phase)

During a study on the phase equilibrium in the system Cu–Bi–S[1], a new phase $Cu_8Bi_8S_{19}$ was found. This phase is stable at temperatures below 498° $\pm$5°C, and assembles with covellite, bismuthinite, wittichenite, cuprobismutite, phase $CuBi_3S_5$ and liquid in an equilibrium state at 400°C. However the appearance of the phase $Cu_8Bi_8S_{19}$ in nature is unknown yet.

The synthesis of the phase was done by the dry method in an evacuated Hario glass tube in the same way as that of simple sulfides described formerly[2)]. Namely, as starting materials for synthesis electrolytic copper of which purity is 99.99% in a chip-shaped form about 5 mm in size, granule of metallic bismuth, 99.9% in purity, and crystal fragment of sulfur refined to 99.9% as guarantee reagent were employed, and these charges weighed exactly by chemical balance in proportion to 8 copper, 8 bismuth and 19 sulfur in the atomic ratio were sealed in the Hario glass tube, 8 mm in inside diameter, under vacuum in

* Department of Mining and Mineral Engineering

$10^{-3}$ mm Hg by rotary vacuum pump. The sealed glass tube was put into an electric furnace and heated at 400°C for 2 days after being kept at 300°C for 24 hours, then at 460°C for 4 days to 7 days. By heating, the starting materials were entirely consumed and changed into sulfides. The sealed glass tube was cooled in air after heating. The product was taken out from the tube, and ground into powder in an agate motor under aceton to prevent oxidation and mixed completely. Then it was again sealed in the evacuated glass tube and kept for 10 days to 15 days in the furnace maintained at 460°C. The product obtained by reheating was mostly a homogeneous phase, which is massive aggregate of grains colored lead-gray with metallic luster. The needle like crystals, as shown in Fig. 1, of $Cu_8Bi_8S_{19}$ were sometimes grown from the surface of the sintered aggregate mass.

The phase $Cu_8Bi_8S_{19}$ was also synthesized at temperature as low as 300°C by reaction between cuprous sulfide ($Cu_2S$), cupric sulfide (CuS) and bismuth sulfide ($Bi_2S_3$) which were prepared beforehand from copper, bismuth and sulfur in the same method as described in the previous paper[2]. These sulfides were accurately weighed in molecular ratio of one $Cu_2S$, six CuS and four $Bi_2S_3$, and sufficiently mixed each other under aceton. Then the mixture sealed in the evacuated Hario glass tube was put into the electric furnace. To form a homogeneous phase by mutual solid reaction between the sulfides in the mixture at such low temperature as 300°C, heating for a long period several times, and grinding and mixing uniformly after each heating were necessary. Namely, the mixture was thrice heated at 300°C for 15 days, at 300°C for 34 days, and at 300°C for 51 days. After the first and the second heatings, the product was ground into power under aceton and mixed completely. It was rapidly cooled in water after the third heating. By heating three times the product became usually a homogeneous phase when its polished surface is observed under microscope. It is formed as slightly sintered aggregate of fine grains, several microns to 100 microns in size.

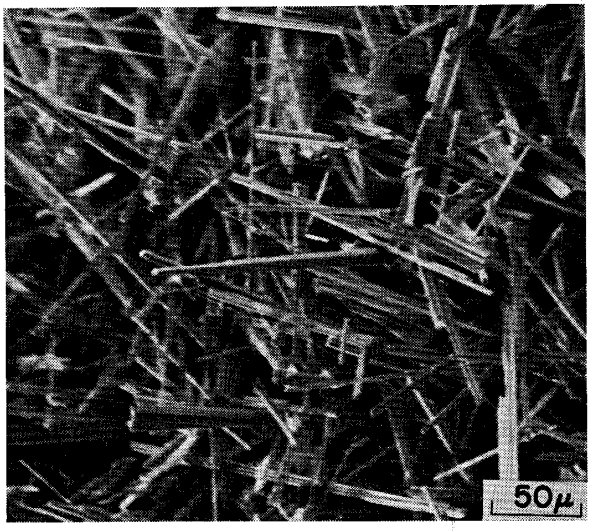


Fig. 1. Scanning electron micrograph of acicular crystals of compound $Cu_8Bi_8S_{19}$ synthesized at 460°C.

Under the microscope with illuminator, the phase $Cu_8Bi_8S_{19}$ has weak pleochroism changing its color from brownish white to pale brownish white in air, and also shows strong anisotropic property changing its interference color from dark bluish gray through dark brown to yellow brown under crossed nicols. Its reflecting color is very similar to synthetic wittichenite and cuprobismutite, but slightly deeper brownish tint than theirs. Also, in comparison

Table 1. The data of X-ray powder diffraction for synthetic $Cu_8Bi_8S_{19}$

| d (meas.) | I | hkl | d (calc.)* | d (meas.) | I | hkl | d (calc.)* |
|---|---|---|---|---|---|---|---|
| 6.549 | 15 | 140 | 6.591 | 2.724 | 24 | 181 | 2.733 |
| 5.810 | 10 | 200 | 5.795 | | | 440 | 2.725 |
| 5.717 | 10 | 210 | 5.703 | 2.680 | 8 | 0, 12, 0 | 2.671 |
| 5.556 | 28 | 150 | 5.609 | 2.650 | 9 | 271 | 2.657 |
| 5.324 | 4 | 060 | 5.342 | 2.612 | 16 | 341 | 2.611 |
| 4.688 | 8 | 240 | 4.696 | 2.603 | 10 | 2, 11, 0 | 2.603 |
| 3.945 | 6 | 080 | 4.006 | | | 1, 12, 0 | 2.603 |
| 3.849 | 18 | 310 | 3.836 | 2.574 | 10 | 191 | 2.578 |
| 3.760 | 42 | 180 | 3.786 | 2.534 | 17 | 351 | 2.536 |
| | | 320 | 3.756 | 2.466 | 44 | 0, 10, 1 | 2.489 |
| 3.742 | 43 | 101 | 3.738 | | | 361 | 2.453 |
| | | 111 | 3.713 | 2.449 | 34 | 1, 10, 1 | 2.433 |
| 3.641 | 26 | 121 | 3.640 | | | 2, 12, 0 | 2.426 |
| 3.562 | 60 | 270 | 3.592 | 2.393 | 4 | 1, 13, 0 | 2.411 |
| 3.534 | 25 | 041 | 3.542 | 2.309 | 20 | 0, 14, 0 | 2.289 |
| | | 131 | 3.528 | 2.253 | 6 | 2, 13, 0 | 2.269 |
| 3.478 | 34 | 340 | 3.480 | 2.228 | 6 | 2, 12, 1 | 2.212 |
| 3.382 | 12 | 141 | 3.387 | 2.176 | 20 | 1, 12, 1 | 2.173 |
| 3.303 | 12 | 350 | 3.309 | 2.154 | 20 | 4, 6, 1 | 2.140 |
| 3.253 | 48 | 211 | 3.247 | 2.138 | 6 | 2, 14, 0 | 2.129 |
| | | 151 | 3.229 | 2.101 | 6 | 1, 15, 0 | 2.101 |
| 3.203 | 24 | 0, 10, 0 | 3.205 | 2.079 | 46 | 3, 10, 1 | 2.092 |
| | | 221 | 3.198 | | | 471 | 2.081 |
| 3.160 | 100 | 061 | 3.175 | 2.048 | 8 | 481 | 2.018 |
| | | 360 | 3.130 | 1.998 | 18 | 0, 16, 0 | 2.003 |
| 3.121 | 58 | 231 | 3.121 | 1.974 | 60 | | |
| | | 1, 10, 0 | 3.089 | 1.943 | 18 | | |
| 3.048 | 24 | 161 | 3.063 | 1.931 | 22 | | |
| 3.003 | 10 | 290 | 3.034 | 1.905 | 10 | | |
| 2.903 | 70 | 251 | 2.908 | 1.878 | 70 | | |
| 2.859 | 8 | 400 | 2.897 | 1.831 | 18 | | |
| | | 410 | 2.886 | 1.807 | 14 | | |
| | | 1, 11, 0 | 2.826 | 1.765 | 20 | | |
| 2.788 | 100 | 081 | 2.812 | 1.748 | 18 | | |
| | | 2, 10, 0 | 2.805 | 1.742 | 18 | | |
| | | 261 | 2.785 | | | | |
| 2.767 | 50 | 301 | 2.672 | | | | |

* Indices were determined by the crystal data, orthorhombic, a=11.59 Å, b=32.05Å, c=3.95 Å, obtained on the oscillation and Weissenberg photographs for the single crystal.

with bismuthinite it is slightly darker. When etched by $HNO_3$ (1: 1), it immediately changes its color into black. By fume of HCl (1: 1) it is tarnished. However it is negative to KOH (sat.), KCN (20%), $FeCl_3$ (20%) and $HgCl_2$ (20%). It is obviously distinguished from bismuthinite by difference of reaction with KOH (sat.).

The data of X-ray powder diffraction for synthetic $Cu_8Bi_8S_{19}$ are given in Table 1. By the measurement on oscillation and Weissenberg photographs for a single crystal of $Cu_8Bi_8S_{19}$, its cell dimension was determined as follows: orthorhombic, a=11.59Å, b=32.05Å, c=3.95Å, and a space group was Pbnb. The density of $Cu_8Bi_8S_{19}$ measured in solution of carbon tetrachloride by Barman density balance was 6.38 g/cm$^3$. On the other hand it was calculated by the crystal data and the chemical composition, and a value 6.31 g/cm$^3$ was obtained as Z=2. Both values are in good accord. Also the crystal structure of the phase was recently determined by Ozawa and Takeuchi[5] on its short prismatic crystals produced by the present authors.

Also, the differential thermal analysis was examined on the synthetic $Cu_8Bi_8S_{19}$ by the evacuated silica tube method[6]. The DTA curve shown in Fig. 2 has a very distinct endothermic peak beginning at 498°C with pointed end at 515°C, and a widespreaded small endothermic peak ending at 575°C continued from the former endothermic reaction. The peaks are considered to represent respectively the incongruent melting of $Cu_8Bi_8S_{19}$ to phase $Cu_3Bi_5S_9$ and liquids, and the melting with continuously changing chemical composition of the melt along liquidus.

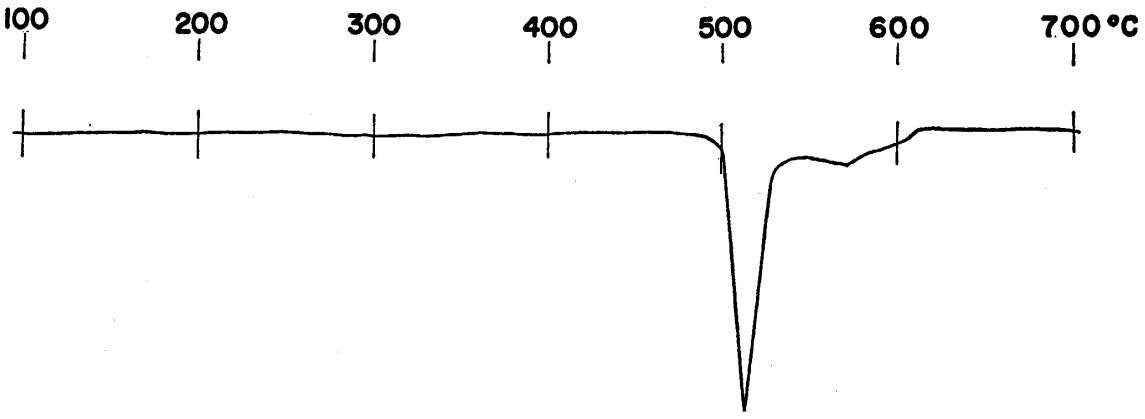


Fig. 2. Differential thermal curve for synthetic $Cu_8Bi_8S_{19}$.

## $CuBiS_2$ (Emplectite)

Emplectite $CuBiS_2$ was synthesized by a reaction between cuprous sulfide ($Cu_2S$) and bismuth sulfide ($Bi_2S_3$) at temperature as low as 250°C. Both sulfides were prepared by the method as mentioned in the previous paper[3], and they were accurately weighed in the molecular ratio of one to one. After

grinding and mixing under aceton in an agate motor, the mixture was pressed in the stainless steel cylinder, 5 mm in inside diameter, by the piston-type squeezer under pressure of approximate 1000 Kg/cm$^2$ and as a result a harden cylindrical rod, 6 mm in length, of the mixture was formed. The rod was sealed in the Hario glass tube under vacuum of $10^{-3}$mm Hg, and then put into an electric furnace kept at 250°C for 26 days. After heating it was cooled in air. By the treatment mentioned above the mixture almost became a homogeneous phase microscopically. But when the reaction was insufficient

Table 2. The data of X-ray powder diffraction for synthetic $CuBiS_2$

| (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 | 2.216 | 100 | 111 |
| 3.13 | 86 | 3.119 | 77 | 104 |
| 3.07 | 78 | 3.065 | 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 $CuBiS_2$ (emplectite)

(2) Natural emplectite (Tannenbaum, Saxsony)[11]

very slight amount of materials of the join $Cu_2S$–$Bi_2S_3$ such as chalcocite, bismuthinite and wittichenite etc. were found as small grains in the host homogeneous phase.

The synthesized phase is a sintered aggregate of fine grains and megascopically lead-gray in color with submetallic luster. In polished section, it is grayish white in color which is similar to that of wittichenite, but slightly lighter. Its reflecting pleochroism is scarecely observed. It shows strong anisotropism changing interference color from grayish yellow to bluish gray, more distinct than that of wittichenite. When etched by $HNO_3$ (1 : 1), it slightly stains slowly. By HCl (1 : 1), it is negative or sometimes stained to yellow. However, it is negative to KOH (sat.), KCN (20%), $FeCl_3$ (20%) and $HgCl_2$ (20%). These optical and etching data do not agree perfectly with those of emplectite described by Short[7], Ramdohr[8], Uytenbogaardt[9] and Farnham[10], but they are closer to the properties of natural emplectite.

The X–ray powder data of synthesized $CuBiS_2$ are given in Table 2 as compared with those of natural emplectite by Buhlmann[11]. The data of both synthetic and natural emplectites are in good agreement.

The differential thermal analysis was examined on synthetic $CuBiS_2$ in the evacuated silica tube, and two curves were obtained as shown in Fig. 3.

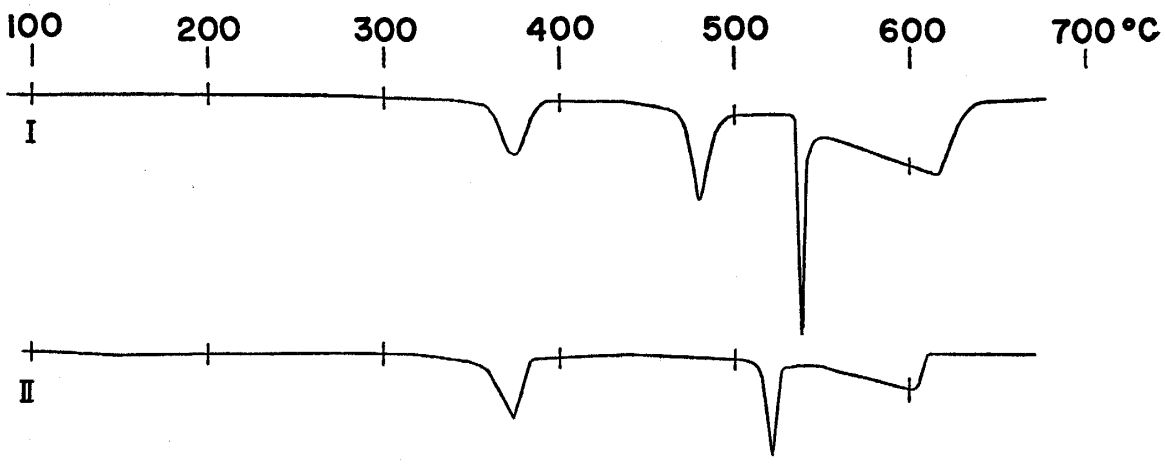


Fig. 3. The curves of differential thermal analysis for synthetic $CuBiS_2$ (emplectite)

They resemble closely with the exception of a endothermic peak starting at 472°C as shown in the curve (I). An endothermic reaction beginning at 360°C is thought to indicate decomposition or inversion of emplectite into wittichenite $Cu_3BiS_3$ and $CuBi_3S_5$ or cuprobismutite respectively. Therefore emplectite is stable only at temperatures below 360°C. The peak starting at 472°C in the curve (I) presents decomposition of cuprobismutite into wittichenite and $Cu_3Bi_5S_9$, and the endothermic peak beginning at 530°C in the curve (I) or at 515°C in the curve (II) shows eutectic melting of mixture of wittichenite and $Cu_3Bi_5S_9$ formed by decomposition of cuprobismutite. In addi-

tion to these peaks, more extensive endothermic reaction which ends at 615°C or 605°C in the curves (I) or (II) respectively is also recognized. It presents liquidation with changing composition of the melt along the liquidus. Buhlmann[12] carried out an experimental study of the $Bi_2S_3$–$Cu_2S$ system, and reported in his paper that emplectite ($\beta$–$CuBiS_2$) changed to cuprobismutite ($\alpha$–$CuBiS_2$) at temperature above 290°C. However our experiment have not made it clear yet whether the relationship between emplectite and cuprobismutite is dimorphous or not. At present the experimental study to confirm it is being continued.

## $FeBi_4S_7$ (New phase)

During the investigation[13] of the phase relation in the system Fe–Bi–S, the phase $FeBi_4S_7$ was found as a stable crystalline phase in the temperature range between 640°C and 718°C. In case of producing the phase, ferrous sulfide (FeS) and bismuth sulfide ($Bi_2S_3$) formed from iron, bismuth and sulfur by the same method described in the previous paper[2], were used as starting materials. They were exactly weighed in the molecular ratio of one ferrous sulfide and two bismuth sulfide, and mixed throughly under aceton in agate motor. After sealing in the evacuated silica glass tube, they were heated in the electric furnace kept at 675°C for 7 days. After heating the content was taken out and ground in the agate motor to mix uniformly under aceton. Then it was again sealed in the evacuated silica tube and heated at 675°C for 12 days. After reheating it was instantly quenched in water. The synthetic product is fully sintered aggregate of grains, 0.1 mm to 0.3 mm in size and megascopically lead-gray in color. Under the reflecting microscope, its color is slightly darker than that of bismuthinite, and has pleochroism changing from light gray or grayish white to gray with light purple tint in air. It shows strong anisotropic property changing its interference color from yellowish gray through dark brownish gray to dark bluish gray under the crossed nicols. Its hardness is approximately the same as bismuthinite. Cleavage parallel to (001) develops distinctly in the grains. When etched with $NHO_3$ (1: 1), it immediately changes the color into black with effervescence. $FeCl_3$ (20%) slowly affects to change its color into brown, while it is negative to HCl (1: 1), KOH (sat.) and $HgCl_2$ (20%).

The X–ray powder data for the phase $FeBi_4S_7$ obtained by rapid cooling in water after heating at 675°C are given in Table 3. From the experiment on phase equilibrium relation it was understood to be stable at limited temperatures only from 640°C to 718°C. Therefore it is not clear whether the powder data are those of the stable phase at 675°C or not. There is also a possibility that they may be metastable phase formed during rapid cooling. The density measured by Barman density balance is 6.39 g/cm$^3$, and the density calculated from the lattice constant, a=12.78Å, b=3.96Å, c=11.80Å, $\beta$=104°30′ is 6.41 g/cm$^3$ as Z=2. Both of the values show good agreement.

Table 3. The data of X-ray powder diffraction for synthetic $FeBi_4S_7$

| d (meas.) | I | hkl | d (calc.*) |
|---|---|---|---|
| 11.42 | 8 | 001 | 11.42 |
| 6.19 | 15 | 200 | 6.19 |
| 6.10 | 10 | $20\bar{1}$ | 6.12 |
| 5.72 | 40 | 002 | 5.71 |
| 4.85 | 45 | $20\bar{2}$ | 4.85 |
| 3.81 | 95 | 003 | 3.81 |
| 3.75 | 100 | 202 | 3.75 |
| 3.68 | 60 | $20\bar{3}$ | 3.68 |
| 3.51 | 50 | 111 | 3.50 |
| 3.264 | 20 | $11\bar{2}$ | 3.265 |
| 3.189 | 25 | $40\bar{1}$ | 3.194 |
| 3.091 | 11 | 400 | 3.093 |
| 2.931 | 15 | 203 | 2.932 |
| 2.888 | 50 | $31\bar{1}$<br>$20\bar{4}$ | 2.892<br>2.883 |
| 2.857 | 35 | 310<br>004 | 2.856<br>2.856 |
| 2.787 | 15 | 113 | 2.788 |
| 2.752 | 40 | $40\bar{3}$<br>$31\bar{2}$ | 2.764<br>2.754 |
| 2.663 | 25 | 311 | 2.665 |
| 2.470 | 16 | 402 | 2.473 |
| 2.377 | 13 | 204 | 2.376 |
| 2.368 | 30 | $11\bar{4}$ | 2.366 |
| 2.345 | 35 | 205 | 2.342 |
| 2.287 | 55 | 005 | 2.285 |
| 2.222 | 8 | $31\bar{4}$ | 2.221 |
| 2.199 | 35 | 114 | 2.198 |
| 2.118 | 20 | 602<br>313 | 2.117<br>2.116 |
| 2.110 | 20 | 405 | 2.108 |
| 2.099 | 17 | 510 | 2.099 |
| 2.058 | 4 | 600 | 2.062 |
| 2.039 | 15 | 603 | 2.040 |
| 1.989 | 35 | 511<br>205 | 1.990<br>1.988 |
| 1.961 | 10 | 206<br>315 | 1.963<br>1.958 |
| 1.945 | 11 | 601 | 1.946 |
| 1.914 | 10 | 604 | 1.915 |
| 1.892 | 30 | 006<br>514<br>115 | 1.904<br>1.894<br>1.891 |
| 1.879 | 11 | 404 | 1.877 |
| 1.838 | 55 | 406 | 1.840 |

* Indices were determined by the crystal data of the oscillation and Weissenberg photographs as follows: monoclinic, a=12.78 Å, b=3.96 Å, c=11.80 Å, $\beta=104°30'$.

The differential thermal curve for $FeBi_4S_7$ rapidly cooled from 675°C has a strong endothermic reaction beginning at about 725°C as shown in Fig. 4. It is thought to indicate an incongruent melting by which $FeBi_4S_7$ is decomposed into liquid and $Bi_2S_3$. Also the curve has a small break point at 650°C. It may be interpreted to represent that $FeBi_4S_7$ transforms from metastable to stable phase at 650°C.

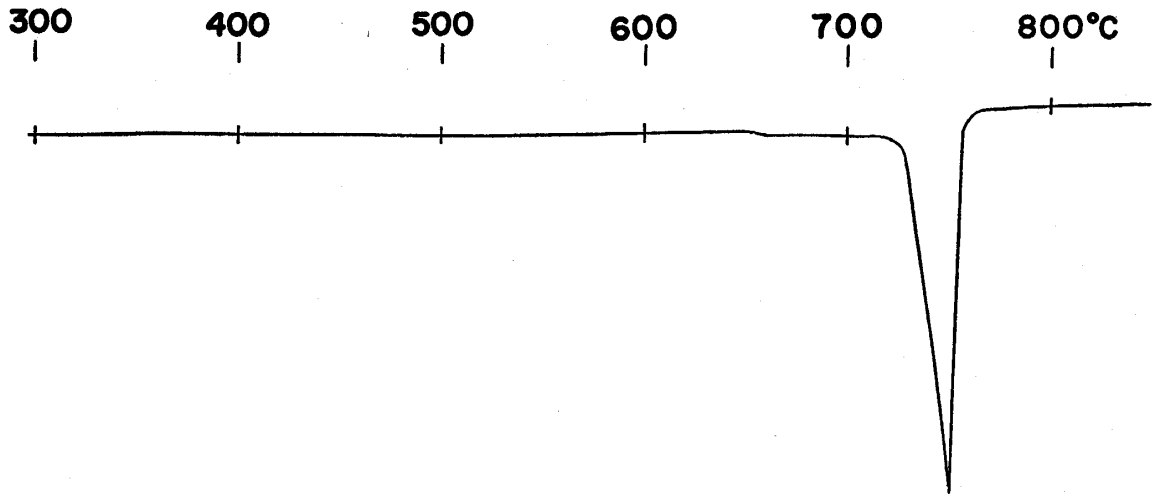


Fig. 4. Differential thermal curve for synthetic $FeBi_4S_7$

## $Cu_{8.4}Fe_{1.2}Bi_{10.8}S_{22}$ (New phase)

$Cu_{8.4}Fe_{1.2}Bi_{10.8}S_{22}$[14] was found as one of the stable phase in the system Cu–Fe–Bi–S during the study[15),19)] of phase equilibrium relation of copper-bismuth sulfide rich portion in the quaternary system. This synthetic phase $Cu_{8.4}Fe_{1.2}Bi_{10.8}S_{22}$ has a similar composition to hodrushite ($Cu_{8.12}Fe_{0.29}Bi_{11.54}S_{22}$) which was described by Koděra, Kupčík and Makovický[17)] as a new sulfosalt mineral from Banská Hodruša, Czechoslovakia, but is not in good accord with it on optical properties and X–ray powder data.

The phase $Cu_{8.4}Fe_{1.2}Bi_{10.8}S_{22}$ was synthesized by reaction between pure metals and crystal sulfur. Namely, electrolytic copper (99.99% in purity), electrolytic iron (99.9%), bismuth (99.9%+) and sulfur (99.98%) weighed exactly in the proportion to 8.4 copper, 1.2 iron, 10.8 bismuth and 22 sulfur in the atomic ratio and sealed together in the Hario glass tube under vacuum of $10^{-3}$mm Hg. The tube was put into a regulated electric furnace and heated at 430°C for 2 days to 4 days after keeping at 350°C for 2 days. By heating, starting materials were completly reacted. The product was taken out from the glass tube after cooling in air and ground into powder under aceton in agate motor to mix uniformly. The powder was again sealed in the evacuated glass tube and kept in furnace at 430°C for 10 days to 14 days and then cooled in air.

The product obtained by reheating became mostly a homogeneous phase

when observed under microscope, but sometimes included a very slight amount of bornite as impurity. It was in powder, not sintered, and dark-gray in color.

Under the ore microscope, it is aggregate of granular crystals from 5 microns to 40 microns in size. It shows grayish white with very slight bluish tint in color presenting weak pleochroism, closely similar to synthetic cuprobismutite and wittichenite. It also shows moderate anisotropism changing interference color from dark bluish gray to yellowish brown in air.

The X-ray powder data for $Cu_{8.4}Fe_{1.2}Bi_{10.8}S_{22}$ are given in Table 4. Also lattice constants of $Cu_{8.4}Fe_{1.2}Bi_{10.8}S_{22}$ were measured on oscillation and Weissenberg photographs taken with its acicular crystal synthesized by hydrothermal method of thermal gradient transporting as will be mentioned in another

Table 4. The X-ray powder data for synthetic $Cu_{8.4}Fe_{1.2}Bi_{10.8}S_{22}$

| d (obs.) | I | hkl | d (calc.*) | d (obs.) | I | hkl | d (calc.*) |
|---|---|---|---|---|---|---|---|
| 8.15 | 8 | $20\bar{1}$ | 8.15 | 2.529 | 41 | 510 | 2.528 |
| 6.059 | 44 | 002 | 6.12 | 2.421 | 14 | $51\bar{3}$ | 2.420 |
| | | 201 | 6.06 | 2.320 | 9 | 313 | 3.318 |
| 5.879 | 8 | $20\bar{2}$ | 5.878 | 2.298 | 6 | 114 | 2.302 |
| 4.372 | 29 | $40\bar{1}$ | 4.373 | 2.270 | 20 | 602 | 2.274 |
| 4.322 | 15 | 202 | 4.329 | 2.184 | 18 | $80\bar{2}$ | 2.186 |
| 4.210 | 5 | 200 | 4.159 | 2.171 | 30 | 205 | 2.173 |
| 4.007 | 40 | 003 | 4.081 | 2.166 | 30 | 404 | 2.165 |
| | | $40\bar{2}$ | 4.079 | | | $80\bar{1}$ | 2.164 |
| 3.702 | 20 | 111 | 3.693 | | | 512 | 2.164 |
| 3.611 | 73 | 401 | 3.611 | 2.134 | 24 | $31\bar{5}$ | 2.134 |
| 3.558 | 31 | 111 | 3.548 | 2.129 | 18 | $11\bar{5}$ | 2.126 |
| 3.505 | 33 | $40\bar{3}$ | 3.508 | 2.093 | 20 | $71\bar{1}$ | 2.092 |
| 3.336 | 12 | $11\bar{2}$ | 3.328 | 2.078 | 7 | 800 | 2.079 |
| 3.278 | 28 | 203 | 3.282 | 2.034 | 16 | 006 | 2.040 |
| 3.232 | 44 | $31\bar{1}$ | 3.225 | | | 314 | 2.033 |
| 3.214 | 53 | $20\bar{4}$ | 3.214 | 2.028 | 16 | 710 | 2.028 |
| 3.127 | 100 | 112 | 3.124 | | | 603 | 2.020 |
| 3.062 | 75 | 004 | 3.061 | 2.012 | 20 | $51\bar{5}$ | 2.012 |
| | | $31\bar{2}$ | 3.057 | 1.952 | 48 | 513 | 1.953 |
| 3.026 | 10 | 402 | 3.030 | 1.946 | 40 | 020 | 1.945 |
| 2.937 | 16 | $40\bar{4}$ | 2.939 | | | $71\bar{4}$ | 1.944 |
| 2.903 | 18 | $60\bar{1}$ | 2.905 | 1.921 | 15 | 711 | 1.920 |
| 2.881 | 29 | $60\bar{2}$ | 2.885 | 1.852 | 16 | 206 | 1.853 |
| | | $11\bar{3}$ | 2.880 | | | $11\bar{6}$ | 1.852 |
| 2.764 | 27 | $31\bar{3}$ | 2.761 | 1.828 | 10 | | |
| 2.718 | 34 | $60\bar{3}$ | 2.719 | 1.812 | 10 | | |
| 2.685 | 52 | 113 | 2.683 | 1.792 | 10 | | |
| 2.562 | 20 | $51\bar{2}$ | 2.560 | 1.760 | 9 | | |
| | | | | 1.742 | 15 | | |

* Indices were determined by the single crystal data as follows: monoclinic, a=17.50 Å, b=3.89 Å, c=12.88 Å, $\beta$=108.1°.

paper. The unit cell is monoclinic with following parameters: a=17.50 Å, b=3.89 Å, c=12.88 Å, $\beta$=108.1°. The d-value calculated from data of the X-ray powder and single crystal photographs is given in Table 4. It is in a good accordance with the measured d-value.

The density of powdered $Cu_{8.4}Fe_{1.2}Bi_{10.8}S_{22}$ measured by Berman density balance was 6.87 g/cm$^3$. Also the density computed from crystal data was 6.82 g/cm$^3$, as Z=1. Both of the values show very good agreement.

Differential thermal curve obtained for $Cu_{8.4}Fe_{1.2}Bi_{10.8}S_{22}$ in vacuum is shown in Fig. 5. Three endothermic reactions occurred in limited temperature range between 525°C and 650°C in the curve are seen there. Among them the first endothermic peak beginning at 525°C is thought to indicate decomposition of $Cu_{8.4}Fe_{1.2}Bi_{10.8}S_{22}$ to bornite, chalcopyrite and $Cu_3Bi_5S_9$. Although it is not clear on the process of other endothermic reactions, the second peak beginning at 550°C may be high-low inversion of chalcopyrite produced by decomposition $Cu_{8.4}Fe_{1.2}Bi_{10.8}S_{22}$, and the third, more extensive endothermic reaction which has a small peak point at about 600°C and ends at about 640°C may represent melting process of $Cu_3Bi_5S_9$ associated with bornite and chalcopyrite. However, from the result of the long time experiment of the equilibrium on the phase $Cu_{8.4}Fe_{1.2}Bi_{0.8}S_{22}$, it has been ascertained to be unstable at temperatures above 495°C.

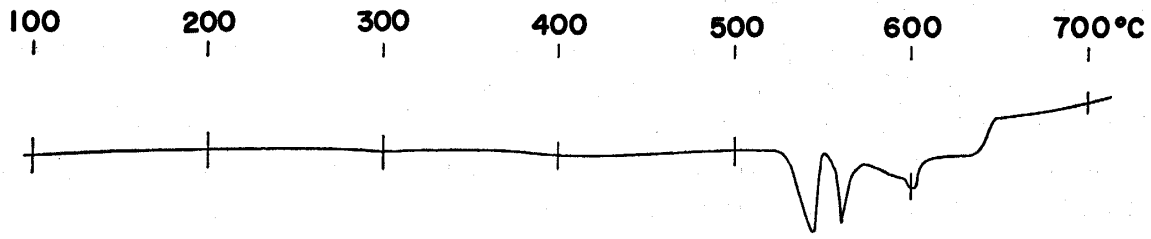


Fig. 5. Differential thermal curve for synthetic $Cu_{8.4}Fe_{1.2}Bi_{10.8}S_{22}$.

## $Cu_3SbS_3$

As a mineral species with composition $Cu_3SbS_3$ or (Cu, Ag, Fe)$_3$ (Sb, As, Bi)$S_3$, the name of stylotypite was formerly known. However it was later confirmed by Schneiderhöhn and Ramdohr[18], and Milton and Axelrod[19] etc. that so-called stylotypite was tetrahedirte, or a mixture of tetrahedrite with enargite and pyrite, and jamesonite, and the name of stylotypite has been consequentially crossed out from a mineral list. However, on the other hand, existence of compound $Cu_3SbS_3$ has been ascertained by the present authors[20),21),22] during a study on the phase equilibrium of the system Cu–Sb–S, as was formerly pointed out by Sommerbland[23], Parravano and de Cesaris[24], and Gaudin and Dicke[25] who carried out experimental works on synthesis or phase relation of minerals in the join $Cu_2S$–$Sb_2S_3$. From the result of the present author's experiment, it is found that the phase $Cu_3SbS_3$ is stable at least in temperature range between

400°C and 610°C. However it is not clear whether compound $Cu_3SbS_3$ is a stable phase at temperatures below 400°C or not although a homogeneous phase was obtained in the case of slowly cooling in air after heating at 400°C. Therefore it may be able to say that $Cu_3SbS_3$ exists as a stable or a metastable phase at low temperature. Tatsuka and Morimoto[26] found that synthesized $Cu_3SbS_3$ is unstable at temperature below 375°C during their study on the system Cu–Sb–S. Also Godovikov, Ilyasheva and Nenasheva[27] synthesized compound $Cu_3SbS_3$ as a new sulfosalt by sintering powdered $Cu_2S$ and $Sb_2S_3$ at 480°C, and described its optical properties, X-ray powder data and DTA curve.

In order to synthesize the phase $Cu_3SbS_3$ cuprous sulfide ($Cu_2S$) and antimony sulfide ($Sb_2S_3$) produced with copper, antimony and sulfur by the method as mentioned in the former paper[2] were employed as starting materials. They were accurately weighed in the molecular ratio of three cuprous sulfide and one antimony sulfide, and then mixed thoroughly under aceton in agate motor. After sealed in the evacuated Hario glass tube, they were heated in an electric furnace at 550°C for 2 days. After heating the product was taken out from the tube, and ground into powder under aceton to be mixed uniformly. Then the powder was again sealed in the evacuated Hario glass tube and heated at 550°C for 2 days. It was cooled in water or air after reheating. When observed under microscope, it became almost a homogeneous phase. The product presents sintered aggregate of fine grains, 10 microns to 100 microns in size, and is megascopically lead-gray in color.

Under ore microscope, it has weak pleochroism changing its color from pinkish to brownish white in air. It shows strong anisotropism changing interference color from gray to dark brown under crossed nicols. Its reflecting color is lighter than that of chalcocite, slightly darker with grayish tint than chalcostibite and slightly lighter than tetrahedrite. Its hardness is almost the same as that of chalcocite. When etched by KOH (sat.) it changes its color into dark gray. But, it is negative to $HNO_3$ (1: 1), HCl (1: 1), KCN (20%), $FeCl_3$ (20%) and $HgCl_2$ (sat.).

The X-ray powder data for $Cu_3SbS_3$ are given in the column (1) of Table 5. However it is found that they are not the data of the phase being stable at synthetic temperature of 550°C, but those at room temperature as shown in the DTA although the product was rapidly cooled to room temperature after heating. Thus the X-ray diffraction pattern for $Cu_3SbS_3$ at temperatures of 20°C, 30°C, 40°C, 60°C, 92°C, 110°C 120°C, 140°C, 160°C and 200°C in order was taken. The pattern from 20°C to 110°C did not change, but at 120°C or above, it is seen that some spacings of the pattern disappeared as given in the column (3) of Table 5. Also when spacies taking the powder pattern at 200°C was cooled to 100°C, the diffraction of the spacings which disappeared at 120°C or above came out again as given in column (2) of Table 5. From this fact, it is thought that phase $Cu_3SbS_3$ transforms from the superlattice to subcell form at 120°C or above. The powder pattern (column 3) at 200°C is very similar to that of wittichenite

Table 5. The data of X-ray powder diffraction for synthetic $Cu_3SbS_3$.

| (1) | | (2) | | (3) | | | | (4) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| d (meas.) | I | d (meas.) | I | d (meas.) | I | hkl | d (calc.) | d (meas.) | I | hkl |
| 5.64 | 4 | 5.64 | 3 | 5.64 | 3 | 011 | 5.56 | 5.66 | 20 | 011 |
| 4.56 | 16 | 4.60 | 13 | 4.54 | 20 | 111 | 4.52 | 4.55 | 55 | 111 |
| 4.08 | 2 | | | 4.06 | 2 | 021 | 4.07 | | | |
| 3.92 | 34 | 3.93 | 25 | 3.93 | 25 | 200 | 3.89 | 3.85 | 45 | 200 |
| 3.53 | 5 | 3.53 | 5 | | | | | | | |
| 3.38 | 6 | 3.38 | 5 | 3.37 | 7 | 201 | 3.35 | 3.35 | 20 | 002<br>201 |
| 3.32 | 10 | 3.32 | 10 | 3.31 | 8 | 002 | 3.30 | | | |
| 3.21 | 26 | 3.21 | 25 | 3.20 | 50 | 211 | 3.19 | 3.18 | 50 | 012<br>211 |
| 3.12 | 17 | 3.12 | 15 | 3.12 | 23 | 220 | 3.11 | | | |
| 3.06 | 40 | 3.06 | 50 | 3.05 | 60 | 102<br>031 | 3.04<br>3.05 | 3.08 | 80 | 220<br>102<br>031 |
| 2.935 | 16 | 2.931 | 20 | 2.917 | 17 | 112 | 2.914 | 2.95 | 35 | 112 |
| 2.838 | 100 | 2.836 | 100 | 2.831 | 100 | 131 | 2.840 | 2.861 | 100 | 131 |
| 2.792 | 6 | 2.788 | 10 | 2.784 | 18 | 022 | 2.780 | 2.814 | 25 | 022 |
| 2.629 | 26 | 2.625 | 30 | 2.622 | 55 | 122 | 2.618 | 2.648 | 50 | 122 |
| 2.575 | 13 | 2.574 | 13 | 2.578 | 23 | 230 | 2.577 | 2.578 | 25 | 040<br>230 |
| 2.543 | 8 | 2.543 | 6 | | | | | | | |
| 2.481 | 15 | 2.481 | 10 | | | | | | | |
| 2.452 | 5 | 2.452 | 5 | 2.455 | 2 | 140 | 2.449 | 2.492 | 5 | 310 |
| 2.405 | 8 | 2.401 | 10 | 2.404 | 15 | 231 | 2.400 | 2.401 | 20 | 032<br>231<br>301 |
| 2.364 | 4 | 2.359 | 5 | 2.362 | 13 | 311 | 2.350 | 2.338 | 10 | 311 |
| 2.295 | 8 | 2.295 | 5 | | | | | | | |
| 2.262 | 3 | 2.262 | 3 | | | | | | | |
| 2.199 | 4 | 2.204 | 7 | 2.199 | 3 | 321 | 2.186 | 2.181 | 10 | 013<br>321 |
| 2.041 | 13 | 2.045 | 17 | 2.047 | 18 | 241 | 2.044 | 2.051 | 15 | 330<br>023<br>042 |
| 1.965 | 6 | 1.965 | 5 | | | | | | | |
| 1.924 | 6 | 1.926 | 5 | 1.924 | 7 | 203 | 1.916 | | | |
| 1.903 | 11 | 1.903 | 15 | 1.904 | 25 | 151 | 1.910 | 1.926 | 10 | 151 |
| | | | | 1.890 | 7 | 322 | 1.896 | 1.886 | 20 | 322 |
| 1.860 | 7 | 1.859 | 9 | | | | | | | |
| 1.827 | 6 | 1.831 | 7 | 1.829 | 8 | 250 | 1.823 | 1.824 | 30 | 133<br>250 |
| 1.810 | 20 | 1.807 | 27 | 1.804 | 33 | 133 | 1.803 | 1.812 | 10 | 133<br>250 |
| 1.762 | 11 | 1.763 | 15 | 1.764 | 20 | 341 | 1.763 | | | |
| 1.756 | 12 | 1.755 | 21 | 1.756 | 28 | 052 | 1.750 | 1.765 | 25 | 052 |
| 1.710 | 10 | 1.707 | 10 | 1.714 | 20 | | | | | |
| | | | | 1.703 | 4 | | | | | |
| 1.683 | 8 | 1.684 | 10 | 1.677 | 13 | | | | | |
| 1.661 | 11 | 1.660 | 5 | | | | | | | |

(1) At room temperature
(2) At 100°C
(3) At 200°C, indexed with orthorhombic, a=7.78 Å, b=10.32 Å, c=6.60 Å.
(4) Synthetic wittichenite

$Cu_3BiS_3$ given in column (4) of Table 5. Thus, with reference to the crystal data of wittichenite the cell dimensions of high temperature form of $Cu_3SbS_3$ was determined as follows: orthorhmbic, a=7.78 Å, b=10.32 Å, c=6.60 Å. The density of $Cu_3SbS_3$ measured by Barman density balance is 5.20 g/cm$^3$, and its value calculated from crystal data as Z=4 is 5.12 g/cm$^3$.

The curve of differential thermal analysis for $Cu_3SbS_3$ is shown in Fig. 6. It presents two endothermic reactions beginning at 120°C and 615°C with pointed ends at 125°C and 625°C respectively. The former shows an inversion of order-disorder type as mentioned above, and the later, congruent melting directly changing to liquid. However it was not made clear whether the inversion found at 120°C in the DTA curve is of a stable or a metastable phase in the present paper.

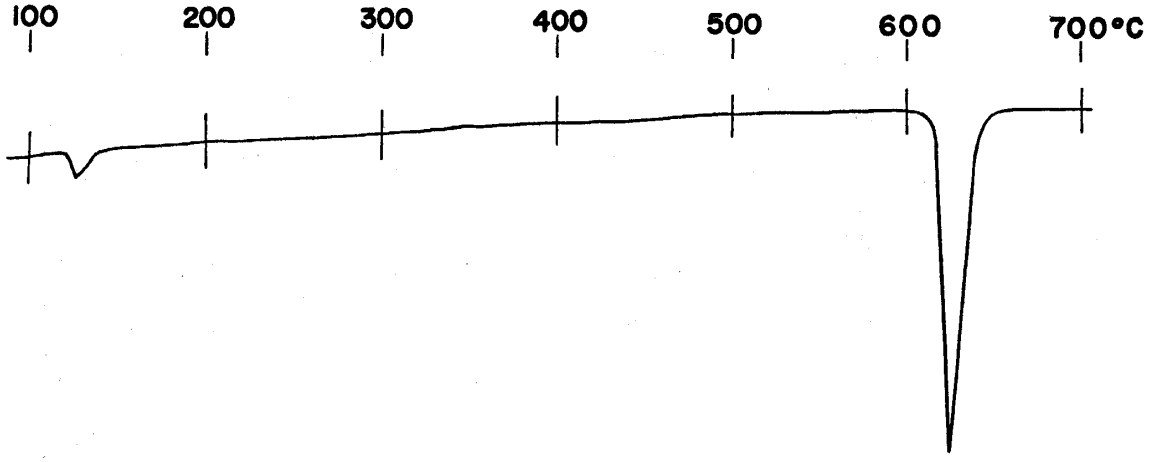


Fig. 6. The curve of differential thermal analysis for synthetic $Cu_3SbS_3$.

## Acknowledgments

The authors wish to express their thanks to Messrs. Shuichi Nomiyama, Toshifumi Sasaguri and Tetsuro Yamamoto for their help in the experimental works.

A part of the expense for this study was defrayed by the Grant for Scientific Researches from the Ministry of Education of Japan.

## References

1) A. Sugaki and H. Shima: Proc. IMA–IAGOD Meeting' 70, IMA Vol., (1971), p. 270–271
2) ———, ———: Mem. Fac. Eng. Yamaguchi Univ., **15,** 15–31 (1965)
3) ———, ———: Ditto, **15,** 33–47 (1965)
4) ———, ———: Ditto, **16,** 109–118 (1965)
5) T. Ozawa and Y. Takeuchi: 6'th Int. Congr. Crystallography, Col. Abst. (1972) p. 70
6) A. Sugaki and H. Shima: Mem. Fac. Eng. Yamaguchi Univ., **16,** 99–106 (1965) (in Japanese.)

7) M. N. Short: "Microscopic Determination of the Ore Minerals", U.S.G.S. Wash. Bul. 914 (1940), p. 125–147
8) P. Ramdohr: "Die Erzmineralien und Ihre Verwachsungen", Akademin-Verlag., Berlin (1955), s. 546–548
9) W. Uytenbogaardt: "Table for Microscopic Identification of Ore Minerals", Princeton Univ. Press, Princeton (1951), p. 82–83
———, and E. A. J. Burke: "Table for Microscopic Identification of Ore Minerals", Elsevier pub. Co., Amsterdam (1971), p. 294–295
10) C. M. Farnham: "Determination of the Opaque Minerals", McGraw-Hill Book Co., New York (1931), p. 61–62
11) E. Buhlmann: Untersuchun im system Cu–Bi–S, Dissertation, Ruprecht-Karl Univ., Heidelberg, (1965) s. 91–93
12) ———: N. Jb. Miner. Mh., 137–141 (1971)
13) A. Sugaki, H. Shima and S. Nomiyama: Jour. Mineral. Soc. Japan, **10,** 110–111 (1970) Abs. (in Japanese.)
14) A. Sugaki and A. Kitakaze: Jap. Assoc. Pet. Min. Econ. Geol., **67,** 104–105 (1972) Abs. (in Japanese.)
15) ———, ——— and T. Yamamoto: Ditto, **67,** 105 (1972) Abs. (in Japanese.)
16) ———, ———, ———: Abs. Annual Meeting Mineral Soc. Japan, p. 39 (1972) (in Japanese.)
17) M. Kodéra, V. Kupčík and E. Makovický: Miner. Mag., **37,** 642–648 (1970)
18) H. Schneiderhöhn and P. Ramdohr: "Lehrbuch der Erzmikroskopie", Bd II, (1931) s. 420–421
19) C. Milton and J. M. Axelrod: Amer. Mineral., **36,** 696–703 (1951)
20) H. Shima: Jour. Mineral. Soc. Japan, **8,** 357 (1967) Abs. (in Japanese.)
21) ———: Jap. Jour. Pet. Min. Econ. Geol., **59,** 167 (1968) Abs. (in Japanese.)
22) A. Sugaki, H. Shima and A. Kaneyasu: Mining Geology, **19,** 75 (1969) Abs. (in Japanese.)
23) H. Sommerbled: Z. anorg. Chemie, **18,** 420–447 (1898)
24) N. Parravane and P. de Cesaris: Atti Accad. Kincei, (5) 21, I, 789 (1912)
25) A. M. Gaudin and G. Dicke: Econ. Geol., **34,** 49 (1939)
26) K. Tatsuka and N. Morimoto: Abs. Annual Meeting, Mineral. Soc. Japan, p. 40 (1972) (in Japanese.)
27) A. A. Godovikov, N. A. Ilyasheva and S. N. Nenasheve: Proc. IMA–IAGOD Meeting '70, Joint-symp. Vol. (1971) p. 32–34