

Miharaite, $\text{Cu}_4\text{FePbBiS}_6$, a new mineral from the Mihara mine, Okayama, Japan

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Abstract

Miharaite, $\text{Cu}_4\text{FePbBiS}_6$, is a new sulfosalt discovered at the Mihara mine, Okayama Prefecture, Japan. It occurs only as minute (<0.3 mm) grains in bornite, closely associated with chalcopyrite, galena, and wittichenite in bornite-rich skarn ores. The crystallographic parameters of miharaite at 25°C are: orthorhombic, space group $Pbmm$, $Pb2m$, or $Pb2_1m$, $a = 10.854(4)$, $b = 11.985(4)$, $c = 3.871(1)\text{\AA}$, $Z = 2$, cell volume = $503.6(3)\text{\AA}^3$. The strongest lines in the X-ray powder pattern are $3.75(60)(130)$, $3.25(70)(021)$, $3.11(55)(320)$, $3.03(100)(211)$, $3.00(90)(040)$, $2.68(80)(301)$, $2.18(60)(411)$. The calculated density is 6.06 g/cm^3 . In reflected light, it is pale gray to grayish-white with slight bireflectance and moderate anisotropism from grayish-blue to pinkish-brown. The optical properties are quite similar to those of wittichenite. Reflectances in air are: 29.6–30.0% in 480 nm, 30.8–31.5% in 546 nm, 31.7–32.6% in 589 nm, 32.1–34.2% in 657 nm. Vickers microhardness is 190–230 kg/cm^2 . The average of six microprobe analyses gave $\text{Cu}_{4.09}\text{Fe}_{1.00}\text{Pb}_{1.01}\text{Bi}_{1.00}\text{S}_{5.91}$ as an empirical formula, very close to the proposed formula $\text{Cu}_4\text{FePbBiS}_6$.

Introduction

During an investigation of the copper bismuth sulfosalt minerals in the ores from the Mihara mine, Okayama Prefecture, a mineral was found similar in optical properties to wittichenite but containing some iron and lead in addition to copper and bismuth. It is a new sulfosalt mineral with a composition of $\text{Cu}_4\text{FePbBiS}_6$. The mineral is named miharaite (pronounced mi-ha-ra-ite) after the location of its first occurrence. The mineral name and designation as a new mineral were approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association in April, 1976. Type materials are deposited in the Institute of Mineralogy, Petrology, and Economic Geology, Faculty

of Science, Tohoku University, Sendai, Japan, and the Department of Mining and Mineral Engineering, Faculty of Engineering, Yamaguchi University, Ube, Japan.

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General description

Miharaite has been found in bornite-rich skarn ore from the stopes on the -11th and -12th levels in the Honpi deposit of the Mihara mine, which are the lowest levels of the mine. The Mihara mine (now closed) is located at Yoshii-cho, Shitsuki-gun, the western part of Okayama Prefecture close to the bor-

der with Hiroshima Prefecture, and is about 20 km west of Takahashi along the Hakubi railway line between Kurashiki and Niimi. The mine is a metasomatic skarn deposit of copper, embedded in the Koyamaichi Paleozoic limestone group (Soeda, 1960; Soeda and Takeno, 1975; Soeda and Hirowatari, 1975). In the Honpi deposit, one of four deposits in the mine, the copper grade of the ore increases with depth, and the bornite in which miharaitite has been found occurs at the lowest levels. The bornite occurs as disseminations in a hedenbergite-garnet-epidote skarn associated commonly with chalcopyrite. Occurrences of copper-bismuth sulfosalt minerals associated with bornite from this deposit were first reported by Soeda (1963), and Sugaki *et al.* (1974a) confirmed by microprobe analyses that the copper-bismuth sulfosalt mineral was wittichenite, Cu_3BiS_3 . Wittichenite occurs both as separate grains and associated with chalcopyrite and/or galena as small granules or drops (10–30 microns) in bornite, and sometimes along grain boundaries of bornite as stringers or chains of drops. From this association, Sugaki *et al.* (1974a) suggested that wittichenite, as well as chalcopyrite, is probably a product of exsolution from a bornite solid solution stable at high temperature.

Miharaite occurs in bornite in the same association and textural setting as wittichenite. It occurs only microscopically, generally several tens of microns in size but up to 0.3 mm, as tiny granular drop-like shapes or irregular masses, closely associated with chalcopyrite, galena, and sometimes wittichenite. Selected examples of these occurrences are shown in Figure 1. Miharaite grains, up to 150 microns, occur in bornite closely associated with chalcopyrite (A), and an irregular intergrowth of miharaitite and galena is found in bornite, with exsolution lamellae of chalcopyrite (B).

Physical and optical properties

In reflected light, miharaitite is pale gray to grayish-white with faint bireflectance and shows moderate anisotropism from grayish-blue to pinkish-brown. No internal reflections were observed. The optical properties are so similar to those of wittichenite that it is almost impossible to distinguish the two by simple microscopic observations. However, when the minerals are in contact with each other, miharaitite appears slightly darker. With chemical etching miharaitite can be readily distinguished from wittichenite. When exposed to HNO_3 (1:1), wittichenite etches slowly and gradually becomes brown, but miharaitite

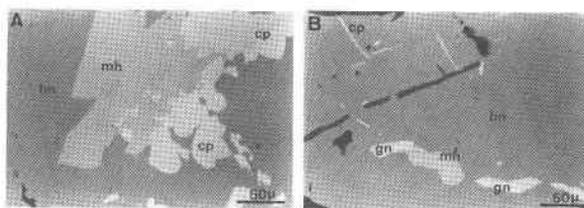


Fig. 1. Photomicrographs of miharaitite intergrown with chalcopyrite and/or galena in bornite. (A) intergrowth with chalcopyrite; (B) intergrowth with galena, and exsolution lamellae of chalcopyrite in bornite. mih: miharaitite; cp: chalcopyrite; bn: bornite; gn: galena.

is not affected; in addition, the former is etched with KCN (20%), whereas the latter does not react to it at all. Miharaite is slightly stained to a bluish tint by KOH (sat.) and is negative to HCl (1:1), FeCl_3 (20%), and HgCl (sat.).

The optical reflectivity of miharaitite was measured with a Leitz microphotometer MPV II at four wavelengths, 480 nm, 546 nm, 589 nm, and 657 nm, as obtained by line filters. The results are compared with those of coexisting wittichenite in Table 1. The conditions of the measurements were as follows: light source, halogen tungsten lamp 10.5 V, 7.1 A; applied potential of a photomultiplier (EMI 9558B) 700 V; objective lens $\times 20$; measured area 30×30 microns. The reflectance standards used included tungsten-titanium carbide and silicon carbide calibrated by Zeiss Ltd., and glass prism 1.9 by Leitz Ltd. Table 1 shows that the reflectance of miharaitite is slightly lower than that of wittichenite in the short wavelength range, but are nearly the same for both in yellow to reddish light.

The Vickers microhardness number ranges from 190 to 230 kg/mm^2 ; this range is similar to those for other copper bismuth sulfosalt minerals as described by Uytenbogaardt and Burke (1971). The measurement was carried out with the Akashi microhardness

Table 1. Reflectance in air and Vickers microhardness of miharaitite compared with coexisting wittichenite

	Miharaite	Wittichenite
<u>Reflectance (%)</u>		
λ (nm)		
480	29.6 - 30.3	30.9 - 34.7
548	30.8 - 31.5	31.7 - 35.4
589	31.7 - 32.6	31.9 - 35.3
657	32.1 - 34.2	31.0 - 34.5
<u>Vicker's hardness (kg/mm^2)</u>		
	190 - 230	180 - 210

tester MVK-D with 25 g load and 15 seconds loading time.

Chemical composition

Miharaite contains Cu, Fe, Pb, Bi, and S, as is clearly indicated by the X-ray scanning photographs of miharaite coexisting with bornite and chalcopyrite shown in Figure 2. Other elements, especially Ag, Sb, or As, which may possibly occur in solid solution in such sulfosalts, have not been detected.

The chemical compositions of six grains of miharaite in two polished specimens were determined by electron probe microanalyzer. The Hitachi electron probe microanalyzer model XMA-5 was used. The conditions of analysis were as follows: accelerating voltage 20 kV, take-off angle 38°, absorption current

0.02 μ A on CuFeS₂, electron beam size 3 μ m on CdS crystal, and crystals of LiF for CuK α , FeK α , PbL α , and BiL α , and ADP for SK α . Synthetic Bi₂S₃, PbS, and natural chalcopyrite were used as standards for Bi and S, for Pb, and for Cu and Fe, respectively.

The measured X-ray intensities, mean values of five times counting for ten seconds on each grain and standard, were corrected by the Bence-Albee procedure (1968) using α -factors for sulfide minerals of the Cu-Fe-Pb-Bi-S system (Sugaki *et al.*, 1974b, 1976). The α -factors for the Cu-Fe-Pb-Bi sulfides were obtained by a least-squares calculation based on the relative intensities measured on synthesized sulfide minerals.

The analytical results are listed in Table 2 along with the atomic formula based on 13 ions calculated

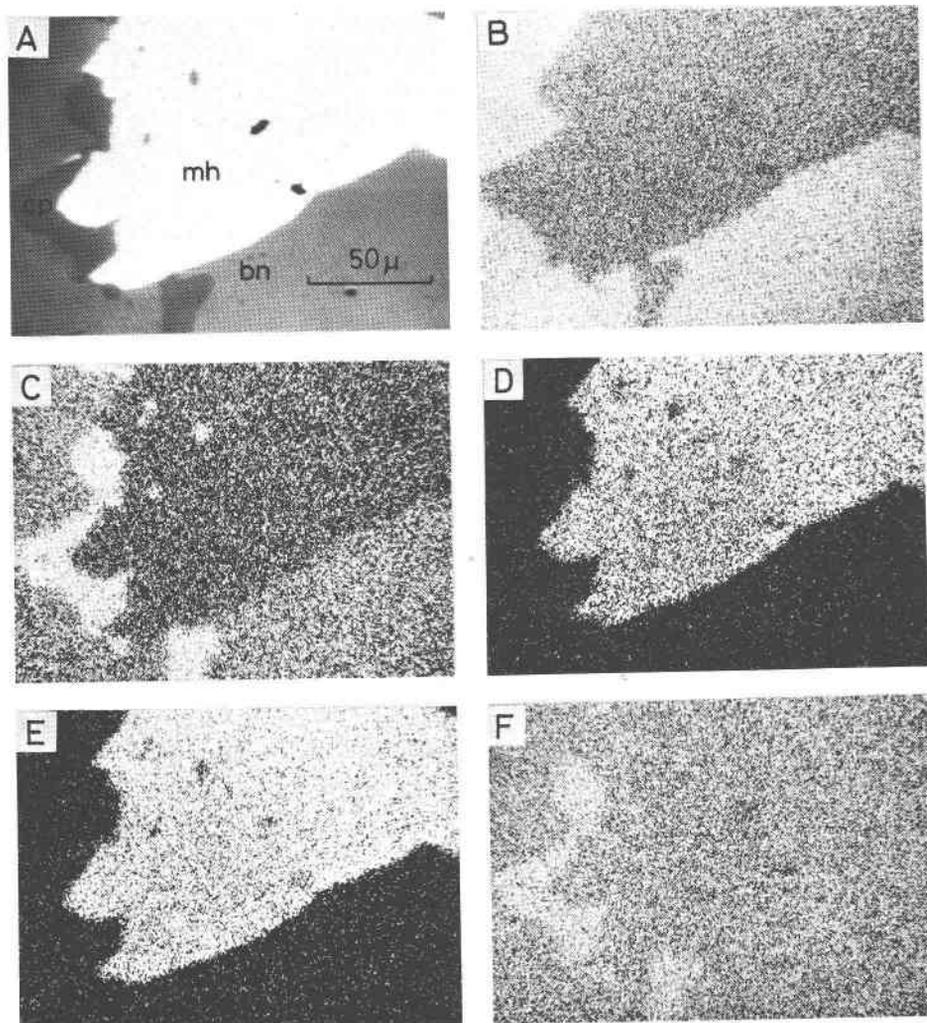


Fig. 2. X-ray scanning microphotographs showing the distribution of elements in an assemblage of miharaite coexisting with chalcopyrite and bornite. (A) reflected electron image; (B) CuK α image; (C) FeK α image; (D) PbL α image; (E) BiL α image; (F) SK α image.

Table 2. Results of electron probe microanalyses on miharaite from the Mihara mine

	Weight percent						Atomic percent					Chemical formula (Total atoms=13)
	Cu	Fe	Pb	Bi	S	Total	Cu	Fe	Pb	Bi	S	
1	28.00	5.94	22.64	22.90	20.67	100.15	31.24	7.55	7.75	7.77	45.71	Cu _{4.00} Fe _{0.98} Pb _{1.01} Bi _{1.01} S _{5.94}
2	28.17	6.25	22.53	22.45	20.63	100.03	31.33	7.91	7.69	7.59	45.48	Cu _{4.07} Fe _{1.03} Pb _{1.00} Bi _{0.99} S _{5.91}
3	28.42	6.12	22.71	22.78	20.40	100.42	31.68	7.76	7.76	7.72	45.07	Cu _{4.12} Fe _{1.01} Pb _{1.01} Bi _{1.00} S _{5.86}
4	28.23	5.92	23.01	23.06	20.54	100.76	31.46	7.51	7.86	7.81	45.36	Cu _{4.09} Fe _{0.98} Pb _{1.02} Bi _{1.02} S _{5.90}
5	28.29	6.07	22.74	22.72	20.62	100.54	31.45	7.68	7.75	7.68	45.44	Cu _{4.09} Fe _{1.00} Pb _{1.01} Bi _{1.00} S _{5.91}
6	28.31	6.00	22.67	22.60	20.74	100.32	31.43	7.58	7.72	7.63	45.64	Cu _{4.09} Fe _{1.00} Pb _{1.01} Bi _{1.00} S _{5.91}
Average	28.24	6.05	22.72	22.75	20.60	100.36	31.43	7.66	7.76	7.70	45.45	Cu _{4.09} Fe _{1.00} Pb _{1.01} Bi _{1.00} S _{5.91}
Ideal comp.	27.67	6.08	22.56	22.75	20.94	100.00	30.77	7.69	7.69	7.69	46.15	Cu ₄ FePbBiS ₆

from the data. Six analyses show the same results within analytical error. Total relative errors of these analyses are assumed to be less than 1% against the individual values in weight percent on copper, iron, lead, and bismuth, and less than 2% on sulfur. The empirical formula for miharaite of Cu_{4.09}Fe_{1.00}Pb_{1.01}Bi_{1.00}S_{5.91} was obtained from the average of six analyses, and the suggested idealized formula is Cu₄FePbBiS₆.

Crystallography

For the X-ray study, several small grains were picked from the polished sections. Etching proved useful in distinguishing the target mineral from the others. When a polished section was etched by KCN, the effect of the reagent after 20–30 minutes on bornite and wittichenite was strong, leaving only miharaite in optical relief on the surface.

Crystallographic data were determined using a precession camera and the Philips computer-controlled single-crystal diffractometer model PW-1100 at 25°C; the results are shown in Table 3.

Based on the systematic extinctions of $k = 2n$ for $0k0$, $0kl$, and hkl reflections observed on the precession photographs and the data from the single-crystal diffractometer, the space group was determined to be one of three possible, $Pbmm$, $Pb2m$, and

$Pb2_1m$. Precise lattice constants were determined by the least-squares calculation of 54 reflections (corrected in advance by the standard quartz) observed in the range of 2θ between 12° and 20° on monochromatized MoK α radiation. They also coincide, within experimental error, with those obtained from the precession photographs. The density could not be measured because of the minute size of the mineral, but the calculated value is 6.06 g/cm³ with $Z = 2$.

Table 4. X-ray powder diffraction data of miharaite

d(meas)Å	I/I ₀	d(calc)Å	I/I ₀ *	hkl
8.1	1	8.05	—	110
5.45	1	5.43	23	200
5.25	1	5.25	28	120
4.96	1	4.95	28	210
3.75	2	3.75	60	130
3.48	2	{ 3.49	44	111
		{ 3.46	39	310
3.25	3	{ 3.25	71	021
		{ 3.22	6	230
3.16	1	3.15	5	201
3.11	3	{ 3.11	10	121
		{ 3.10	54	320
3.03	10	3.05	100	211
3.00	7	3.00	90	040
2.90	2	2.888	32	140
2.80	1	2.789	9	221
2.70	3	2.693	35	131
2.64	3	{ 2.647	34	410
		{ 2.643	79	301
2.57	1	2.581	10	311
2.47	2	{ 2.474	47	231
		{ 2.471	10	420
2.42	1	2.418	11	321
2.37	2	2.369	31	041
2.25	1	2.245	5	430
		{ 2.193	38	250
2.18	5	{ 2.185	58	411
		{ 2.171	30	241
2.13	1	2.136	11	510
2.09	1	2.083	8	421
2.00	1	2.003	21	151
1.981	2	1.982	48	341
1.935	7	{ 1.942	24	431
		{ 1.936	29	002
1.903	1	1.903	20	251

* Relative intensities were measured by the four circle single-crystal diffractometer.

Table 3. Crystallographic data of miharaite

Crystal system	Orthorhombic
Space group	Pbmm, Pb2m, or Pb2 ₁ m
Cell dimension	a = 10.854 ± 0.004 Å
	b = 11.985 ± 0.004 Å
	c = 3.871 ± 0.001 Å
	Z = 2
Cell volume	503.6 ± 0.3 Å ³
Density (calc.)	6.06 g/cm ³

Table 5. Experimental conditions for the attempted synthesis of miharaite

Run No.	Starting materials	Temp. (°C)	Time (days)	Products
Mh-1	3Cu ₂ S+2CuS+2FeS+2PbS+Bi ₂ S ₃	500	30	bn+liq
Mh-2	"	400	30	aik+gn+cp+bn
Mh-3	"	300	13	gn+aik+wit+cp+bn
Mh-4	"	300	115	aik+gn+cp+bn
Mh-5	Cu ₃ BiS ₃ +CuS+FeS+PbS	500	29	bn+liq
Mh-6	"	400	29	aik+bn+cp
Mh-7	Cu ₃ BiS ₃ +CuFeS ₂ +PbS	400	14	aik+bn+gn+cp
Mh-8	"	300	14	gn+wit+cp+bn+aik

aik: aikinite, gn: galena, cp: chalcopyrite, bn: bornite, wit: wittichenite, liq: liquid

An X-ray powder pattern of miharaite was obtained by a Debye-Scherrer camera, and the data are shown in Table 4. A Rigaku Debye-Scherrer powder camera (114.59 mm in diameter) was used with Ni-filtered CuK α radiation. An internal standard of pure Si ($a = 5.43054\text{\AA}$) was utilized. Calculated d -spacings and indices obtained from the single-crystal study and measured intensities from the automatic single-crystal diffractometer are shown in Table 4.

Synthesis

Attempts to synthesize miharaite in the pure 5-component system were performed using the silica-glass tube technique. The results are summarized in Table 5. Various combinations of starting materials were mixed in the proper proportion of the chemical formula. They were mixed thoroughly in an agate mortar under acetone, placed in sealed evacuated silica-glass tubes and heated at 300° to 500°C for various annealing periods up to four months.

Miharaite was not synthesized in any of these experiments. At 500°C, a liquid phase exists for the composition of miharaite. The assemblage of aikinite, galena, chalcopyrite, and bornite was produced in a long-time experimental run at 300°C. It would appear that the other 300°C runs with wittichenite represent disequilibrium. Attempts to synthesize miharaite are still in progress.

Discussion

Miharaite is a sulfosalt mineral with five essential components. Although many copper-lead-bismuth sulfosalts such as aikinite CuPbBiS₃, gladite CuPbBi₅S₉, nuffieldite Cu₄Pb₁₀Bi₁₀S₂₇ etc. have already been described, a sulfosalt mineral containing iron in addition to these three metallic elements has not

been reported to date. It would appear that miharaite is quite rare in occurrence.

Miharaite could not be synthesized in the dry experiments; at 300°C the assemblage aikinite-galena-chalcopyrite-bornite appears stable. Miharaite is probably stable, therefore, only to some temperature below 300°C.

Recently, we have found miharaite in samples from the Imooka mine, a quartz-vein deposit in granitic rock at Okutsu-cho, Tomada-gun, Okayama Prefecture (Handa, 1951). Miharaite occurs here also in bornite-rich ore. The intimate relationship of miharaite with bornite associated with other copper-bismuth sulfosalts (e.g. wittichenite) is noted, but its significance is not known at this time. The occurrence and properties of miharaite from the Imooka mine will be described in another paper.

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