

Hydrothermal synthesis of nukundamite and its crystal structure

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Abstract

Crystals corresponding to nukundamite were obtained by hydrothermal synthesis in a temperature gradient. The empirical formula of the synthetic mineral analyzed by electron microprobe is $\text{Cu}_{3.39}\text{Fe}_{0.61}\text{S}_4$. Its crystal data are: trigonal, space group $P\bar{3}m1$, $a = 3.7830(2)$, $c = 11.1950(8)\text{\AA}$; $Z = 1$. The crystal structure has been determined using counter-measured intensities. The characteristic S-S bond recognized in minerals such as covellite and pyrite is confirmed in the structure, and its bond length in the S_2 group is $2.062(20)\text{\AA}$. The metal atoms are in two non-equivalent sites and are tetrahedrally coordinated with sulfur.

Introduction

Nukundamite was recently described as a new mineral from the Undu mine, Nukundamu, Fiji by Rice *et al.* (1979). It had been referred to as idaite or Cu_3FeS_6 , a mineral which corresponds to a synthetic Cu-Fe sulfide with a composition of $\text{Cu}_{5.5}\text{FeS}_{6.5}$.

Idaite was originally described as a supergene sulfide mineral from the Ida mine, southwest Africa, by Frenzel (1958, 1959). He suggested that the composition of idaite was Cu_3FeS_6 , because the optical properties of the mineral were similar to those of a synthetic phase synthesized by himself and by Merwin and Lombard (1937), and the X-ray powder data of a

synthetic and a natural specimen from Jarvis township, Ontario were similar. He also proposed that the synthetic phase has a hexagonal cell $a = 3.90$ and $c = 16.95\text{\AA}$. Later, Yund (1963), on the basis of synthetic experiments under dry conditions, found that the chemical composition of the synthetic phase is $\text{Cu}_{5.5x}\text{Fe}_x\text{S}_{6.5x}$ ($=\text{Cu}_{3.38}\text{Fe}_{0.62}\text{S}_4$) and its cell parameters are $a = 3.77$ and $c = 11.18\text{\AA}$ from the results indexed as a hexagonal cell. From the electron probe microanalyses, Levy (1967), Sillitoe and Clark (1969), and Constantinou (1975) determined that the chemical composition of naturally-occurring supergene idaite is Cu_3FeS_6 . On the other hand, both Frenzel and Ottemann (1967) and Clark (1970) have reported a

Table 1. Experimental results for the hydrothermal synthesis of nukundamite

Run No.	Nutrient materials			Assemblages	Mineralizer	Temp. (°C)	Press. (kg/cm ²)	Heating period (days)	Products
	Weight percent								
	Cu	Fe	S						
HHH 087	55.00	12.00	33.00	bnss+nk+py	5m NH ₄ Cl	450	340	13	nk+bnss+cp
HHH 085	55.00	12.00	33.00	bnss+nk+py	"	400	300	18	nk+bnss+cp
HHH 027	56.50	14.50	29.00	bnss+cp+py	6m NH ₄ Cl	350	300	9	nk+cp+py
HHH 040	56.50	14.50	29.00	bnss+cp+py	5m NH ₄ Cl	350	300	11	nk+bnss+cp
HHH 042	50.00	19.00	31.00	bnss+cp+py	"	350	310	14	nk+cp+bnss
HHH 049	65.00	3.00	32.00	cv+bnss+nk	"	350	315	22	nk+cv+bnss
HHH 053	35.00	28.00	37.00	bnss+cp+py	"	350	285	21	nk+cp+py
HHH 059	65.00	3.00	32.00	cv+bnss+nk	"	300	320	34	nk+cv+bnss
HHH 062	55.00	12.00	33.00	bnss+nk+py	"	300	290	23	nk+bnss+cp
HHH 066	50.00	13.00	37.00	cv+nk+py	"	300	290	20	nk+cv+py
HHH 086	55.00	12.00	33.00	bnss+nk+py	"	250	290	36	nk+dg+cp

bnss: bornite solid solution, cp: chalcopyrite, cv: covellite, dg: digenite, nk: nukundamite, py: pyrite.

hypogene sulfide with the composition of Cu₃FeS₄ and with X-ray powder data in agreement with those of the synthetic phase reported by Yund (1963). Therefore, Sillitoe and Clark (1969) and Clark (1970) considered this to be a new mineral, which differed from supergene idaite originally described by Frenzel (1958).

Ottemann and Frenzel (1971) analyzed idaite from various localities, including the type specimen from the Ida mine, and concluded that naturally-occurring idaite have chemical compositions ranging from Cu₃FeS₄ to Cu₅FeS₆. Similar analytical data were obtained by Goble and Smith (1973) and Briggs *et al.* (1977). However, Wang (1976) concluded that the X-

ray powder data for supergene idaite described by Frenzel (1959) are different from those of the synthetic phase or hypogene idaite, and that the cell of the supergene phase is tetragonal, as originally suggested by Levy (1967). Ugarte and Burkin (1977) obtained idaite of composition Cu₃FeS₄ as leaching products of bornite in ferric sulphate solutions at 40°C and determined the cell dimensions to be $a = 5.26$ and $c = 10.46\text{Å}$, similar to those of chalcopyrite.

Thus there are two kinds of minerals described as idaite; one is supergene idaite with a composition of Cu₃FeS₄, and another is a hypogene sulfide with a composition of Cu₅FeS₆. Recently, Rice *et al.* (1979) studied both minerals and concluded that the hypo-

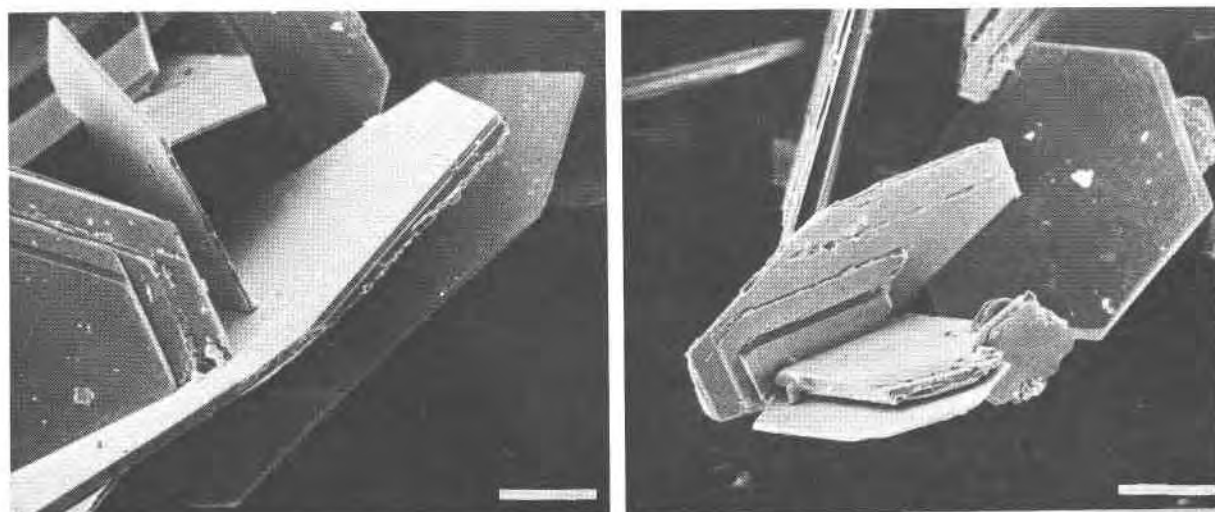


Fig. 1. Scanning electron micrographs for hydrothermally-synthesized nukundamite. Length of scale bar is 150 μm .

gene mineral differs from supergene idaite, and named it nukundamite as a new mineral.

Our specimen was produced by a hydrothermal method and corresponds to the nukundamite. The synthetic crystals are larger than the crystal of natural nukundamite studied by Rice *et al.* (1979) and therefore were suitable for a X-ray single crystal study. In this paper we describe the chemical composition, crystal data and structure of synthetic nukundamite.

Hydrothermal synthesis of nukundamite

Nukundamite was synthesized under hydrothermal conditions using a thermal gradient transport method similar to that described by Scott and Barnes (1971), Scott (1975), and Sugaki *et al.* (1975, 1976). Hydrothermal syntheses were performed in a gold tube (4 mm inside diameter, 50 mm long), with an aqueous chloride solution as the transporting agent. The results are given in Table 1 together with the compositions of the nutrient materials, the experimental conditions, and the synthesized phases. As described previously (Sugaki *et al.*, 1975), nukundamite ("idaite") coexists with pyrite covellite, bornite, and chalcopyrite at 300° and 350°C. The assemblage nukundamite + chalcopyrite is observed in the temperature range from 250° to 450°C. This assemblage is in conflict with the bornite + pyrite assemblage produced in dry synthesis experiments (Yund and Kullerud, 1966) and has been discussed in detail in Sugaki *et al.* (1975). The hydrothermally-synthesized nukundamite occurs as thin, platy, reddish-brown, hexagonal crystals up to 2 mm in diameter (Fig. 1).

Under the ore microscope, it has very strong pleochroism changing from reddish-orange to yellowish-gray and it also shows very strong anisotropism in greenish-gray under crossed polars. The reflectance of synthetic nukundamite was measured with a Leitz microphotometer MPV II in air and oil. The values for R_c and R_o in air are as shown in Table 2. These values are close to those of natural nukundamite of Rice *et al.* (1979). Twinning with a twin plane of (001) and a perfect cleavage on the basal plane were observed.

Chemical composition and crystal data

The chemical composition of synthetic nukundamite crystals obtained by 11 runs shown in Table 1 was determined by electron probe microanalyses, using procedures similar to those described in Sugaki *et al.* (1975). The mean composition is Cu 56.8 ± 0.4 , Fe

Table 2. Reflectance values for synthetic nukundamite

λ (nm)	406	436	497	546	589	657
In air						
R_o	12.0	11.0	10.6	12.4	16.7	23.8
R_c	21.3	21.3	22.0	22.1	22.2	25.1
In oil						
R_o	5.1	5.1	6.1	7.9	10.1	15.9
R_c	9.8	9.8	11.1	11.2	11.5	15.3

9.0 ± 0.3 , S 33.8 ± 0.2 , total 99.6 weight percent. The empirical formula normalized to four sulfur atoms is $Cu_{3.39 \pm 0.02}Fe_{0.61 \pm 0.02}S_4$. This chemical formula is in good agreement with $Cu_{5.5}FeS_{6.5}$ ($=Cu_{3.38}Fe_{0.62}S_4$) obtained by Yund (1963) in his dry experimental study and with $Cu_{3.37}Fe_{0.66}S_{3.97}$ for natural nukundamite reported by Rice *et al.* (1979).

Cell parameters and the space group were determined from precession and Weissenberg photographs and intensity data measured with an automatic four-circle X-ray diffractometer using $MoK\alpha$ and $CuK\alpha$ radiations. The crystals are generally distorted and twinned with c as the twin axis, and the twinned crystals showed a hexagonal symmetry. Therefore, most of them were not suitable for single-crystal investigation. However, after careful study a small crystal which exhibited almost no distortion in precession photographs was found and was used for single-crystal analysis. The Laue group of this crystal was determined to be $\bar{3}m$, because the principal axis shows three-fold symmetry and a set of mirror planes of {110} is found in the reciprocal lattice reproduced from three-dimensional diffraction data by the precession and Weissenberg method. These results differ from Rice *et al.* (1979), who considered the mineral to be hexagonal from the Laue photographs of inferior crystals. No systematic extinction was found. This indicates that the possible space groups of nukundamite are $P\bar{3}m1$, $P321$, or $P3m1$. The space group is uniquely determined to be $P\bar{3}m1$ by the results of structural analysis.

X-ray powder diffraction data were measured by a Guinier camera with $CuK\alpha_1$ radiation. These results agree with those obtained by Yund (1963) and Rice *et al.* (1979). The cell dimensions calculated by the least-squares method from the powder data at 25°C are $a = 3.7830(2)$, $c = 11.1950(8)\text{\AA}$, $V = 138.75(2)\text{\AA}^3$. These values are in good agreement with $a = 3.782(4)$ and $c = 11.187(8)\text{\AA}$ for natural nukundamite determined by Rice *et al.*

The density of nukundamite, measured by Berman density balance using carbon tetrachloride, is $4.49(3)\text{ g/cm}^3$. This value is in good agreement with the calculated value of 4.53 g/cm^3 for $Z = 1$.

Table 3. Atomic parameters of nukundamite, $\text{Cu}_{3.39}\text{Fe}_{0.61}\text{S}_4$

Atoms		X	Y	Z	B (\AA^2)
M(1)	Cu, Fe	2/3	1/3	0.1547(4)	0.87(7)
M(2)	Cu, Fe	2/3	1/3	0.5790(6)	1.92(13)
S(1)		0	0	0.0921(9)	1.08(14)
S(2)		2/3	1/3	0.3609(9)	0.96(11)

Structural analysis

We selected the most suitable crystal for the structural analysis, but some distortion from handling was unavoidable. The single crystal of nukundamite for intensity measurements has a platy form with dimensions of $0.1 \times 0.15 \times 0.005$ mm. The mineral is so soft and deformable that it is difficult to obtain a distortion-free crystal. Intensities were measured on an automatic four-circle diffractometer (Philips PW 1100), using graphite monochromated $\text{MoK}\alpha$ radiation. The ω - 2θ scan mode was used to a 2θ limit of 120° and scan widths were varied by ω angles. 898 independent reflections were measured, and 544 of them with values less than 2σ were omitted in the least-squares refinement. Corrections were made for Lorentz and polarization factors but not for absorption. The neutral atomic scattering factors were taken from the *International Tables for X-ray Crystallography* (1962).

A three-dimensional Patterson synthesis was made using observable F_o values from 354 reflections. Patterson vectors revealed on the map can be solved assuming metal and sulfur atoms to be located on (0, 0, z) and (2/3, 1/3, z). From the relative peak height and crystallochemical considerations, sulfur atoms were located on two sites of (0, 0, z) and (2/3, 1/3, z) and metal atoms were located on (2/3, 1/3, z_1) and (2/3, 1/3, z_2). Each z parameter was determined by a trial and error method using the Patterson peaks.

Preliminary structural calculations assuming a center of symmetry and using z parameters derived from Patterson maps gave a R value of 0.30. Several cycles of least-squares calculations by the full-matrix, least-squares program (UNICS) were made, varying atomic positions and isotropic temperature factors

for each atom in order to distinguish between copper and iron atoms. A final R value of 0.174 was obtained for 354 independent reflections. Three-dimensional Fourier and difference Fourier syntheses using the final atomic parameters shown in Table 3 were made. Because no unusual features were observed in the Fourier maps, the structure is believed to be correct and to justify the space group $P\bar{3}m1$. The R value is higher than would be desirable which is probably a consequence of lack of corrections for absorption, anomalous dispersion, and site occupancy between copper and iron atoms.

Description of the crystal structure

Interatomic distances and bond angles are given in Table 4 and the structure is shown in Figure 2. The structure is characterized by pairs of S_2 and MS_4 tetrahedra. The S_2 group is surrounded by six metal atoms, and its S-S distance is $2.062(20)\text{\AA}$. This value agrees with the mean S-S distance (2.06\AA) in orthorhombic sulfur (Caron and Donohue, 1965), but is slightly shorter than the S-S bond length of 2.071 or 2.086\AA of covellite as given by Evans and Konnerd (1976) or Ohmasa *et al.* (1977). S-S bonds are also found in other sulfide structures such as FeS_2 , CoS_2 ,

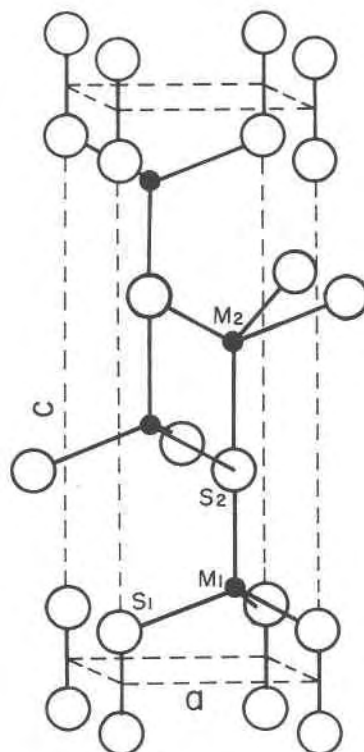


Fig. 2. The crystal structure of nukundamite.

Table 4. Interatomic distances and bond angles for nukundamite

Interatomic distances			Bond angles	
M(1)-S(1)	x3	2.294(13) Å	S(1)-M(1)-S(2)	107.8(5)°
M(1)-S(2)		2.308(11)	S(1)-M(1)-S(1)	111.0(2)
M(2)-S(2)		2.442(12)	S(2)-M(2)-S(2)'	107.1(5)
M(2)-S(2)'	x3	2.285(13)	S(2)''-M(2)-S(2)'	111.7(2)
M(2)-M(2)'		2.811(12)		
S(1)-S(1)'		2.062(20)		

and NiS_2 (Elliott, 1960) and $\text{Cu}_4\text{Bi}_4\text{S}_9$ (Takéuchi and Ozawa, 1975). Sulfur is in tetrahedral arrangement around M(1) and M(2). Two tetrahedrons of M(1)- S_4 and M(2)- S_4 share a corner and their base S_3 triangles are oriented opposite to each other. The bond lengths of M(1)-S(1)₃ (2.294Å) and M(1)-S(2) (2.308Å) are slightly shorter than those for most common sulfide or sulfosalt minerals, 2.33–2.37Å (Ohmasa *et al.*, 1977). The M(2)-S(2)₃ bond length (2.285Å) is slightly shorter than M(1)-S(1) (2.294Å) and the bond length of M(2)-S(2) (2.442Å) is the longest of the M-S bond groups in the nukundamite structure. The M(2)- S_4 tetrahedron is distorted from the regular tetrahedron. Two M(2)- S_4 tetrahedra share an edge in the structure and the M(2)-M(2) distance is shortened to 2.811Å. A similar structure is found, for example, with respect to the Fe-Fe distance of 2.804Å in cubanite (CuFe_2S_3) (Szymanski, 1974).

Although the crystal structure of hydrothermally-synthesized nukundamite has been determined as mentioned above, we do not understand why the ratio of copper and iron atoms has a very constant value of 3.39 to 0.61, and so more detailed work on the structural analysis would be helpful. X-ray single-crystal study of supergene idaite has not yet been made. The X-ray powder data for idaite by Frenzel (1960) are distinctly different from our data for synthetic nukundamite, and more study on the composition and crystal structure of idaite is indicated.

Acknowledgments

We thank Dr. S. D. Scott of the University of Toronto and Dr. C. W. Rice of the University of Aberdeen for critical reading of the manuscript. A part of the expense for this study was supplied from the Ministry of Education of Japan as the Grant-in-Aid for Scientific Researches.

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