Kusachiite, $CuBi_2O_4$, a new mineral from Fuka, Okayama Prefecture, Japan

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Abstract

Kusachiite, $CuBi_2O_4$, has been found in a calcite vein cutting gehlenite-spurrite skarns at Fuka, Okayama Prefecture. It is associated with calcite, henmilite, sillenite, bakerite, tenolite, bultfonteinite, apophyllite, cuspidine and thaumasite. Kusachiite occurs as prismatic crystals or globular aggregates of platy crystals. It is black, opaque with a metallic lustre. Kusachiite is tetragonal with space group $P4/ncc$, $a = 8.511(2)$, $c = 5.823(2)$ Å, $Z = 4$. The strongest lines in the X-ray powder pattern [d in Å (I)(hkl)] are 3.191 (100)(211), 2.695 (18)(310), 1.947 (18)(411), 4.26 (17)(200), 2.913 (16)(002), 2.404 (13)(202), 1.728 (12)(213), and 1.652 (9)(332). The Mohs hardness is 4.5, and the density is 8.5(3) g/cm^3 (meas.) and 8.64 g/cm^3 (calc.). Cleavage is perfect on {110}. Six electron probe analyses gave the following mean values CuO 13.91, Bi_2O_3 86.00 and total 99.91 in wt.%. The empirical formula calculated on the basis of O = 4 is $Cu_{0.960}Bi_{2.027}O_4$ with the simplified formula $CuBi_2O_4$.

KEYWORDS: kusachiite, new mineral, copper, bismuth, oxide.

Introduction

$CuBi_2O_4$ has been synthesized by Boivin et al. (1973), Arpe and Müller-Buschbaum (1976), Kakhan et al. (1979) and others. Unusual three-dimensional antiferromagnetism has been revealed for this compound by García-Muñoz et al. (1990), Konstantinovic et al. (1991) and Yamada et al. (1991). Kusachiite is the natural analogue of the synthetic $CuBi_2O_4$. Kusachiite is named after Dr Isao Kusachi (1942-), Department of Earth Sciences, Faculty of Education, Okayama University, in recognition of his work on skarn minerals from Fuka, Okayama Prefecture, Japan. The mineral species and its name have been approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association. The type mineral of kusachiite is deposited at the National Science Museum, Tokyo, Japan. The present paper deals with the mineralogical properties and mode of occurrence of kusachiite.

Occurrence

Kusachiite was found on calcite crystals grown on cavity walls in a calcite vein of 2 to 8 cm wide. The calcite vein occurs along the boundary between gehlenite–spurrite skarn and crystalline limestone at Fuka. Kusachiite is associated with henmilite (Nakai et al., 1986, and Kusachi, 1992), sillenite (Kusachi and Henmi, 1991), bakerite, tenolite, bultfonteinite, apophyllite, cuspidine and thaumasite. It occurs as prismatic crystals up to 0.5 mm long and globular aggregates up to 2 mm in diameter (Fig. 1).

Physical and optical properties

Kusachiite is black with a metallic lustre. It is grey in reflected light. Internal reflections of deep-red or dark brown are always visible, especially in oil and in badly polished specimen. Bireflectance are weak but distinct. Pleochroism colours are grey with a faint bluish tint and brownish grey. Reflectance values were measured using SiC as a standard. The max./min. values in air are 21.1/19.0, 20.2/18.0, 19.7/17.6 and 19.5/17.3 for 482, 545, 589 and 659 nm, respectively. Those values in oil with refractive index of 1.515 are 7.8/6.5, 7.1/6.3, 6.7/5.8 and 6.6/5.5 for 482, 545, 589 and 659 nm, respectively. Cleavage is perfect on {110}. Vickers microhardness is 292–357 kg/mm^2 (25 g load). The density measured by gravimetric balance is 8.5(3) g/cm^3. The calculated density is 8.64 g/cm^3. Kusachiite is a semiconductor.
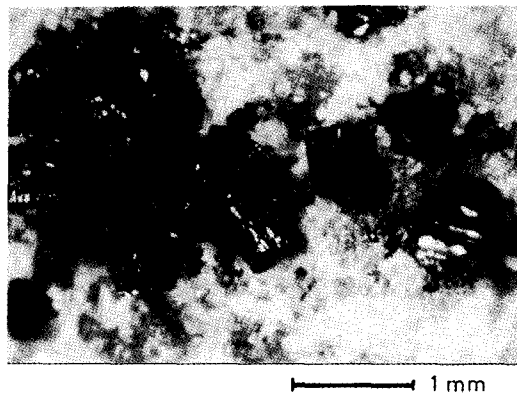
Fig. 1. Photograph of kusachiite crystals on calcite.

Chemical composition

The chemical composition of kusachiite was obtained by an electron microprobe analyser using Cu_2O and $Bi_{12}GeO_{20}$ as standards. The mean result of 6 analyses gives CuO 13.91, Bi_2O_3 86.00 and total 99.91 in wt.%. No other elements of atomic number greater than 9 were detected. The empirical formula calculated on the basis of O = 4 is $Cu_{0.960}Bi_{2.027}O_4$. This result gives the ideal formula of $CuBi_2O_4$. Prismatic crystals of kusachiite are characterized by a sector structure which is analogous to the hourglass structure and consists of square pyramids along a- and c-axes. The c-sector has the ideal composition of $Cu_{1.001}Bi_{1.999}O_4$ and the a-sector has the composition of $Cu_{0.918}Bi_{2.055}O_4$. Kusachiite is easily soluble in HCl.

X-ray studies

Precession and Weissenberg photographs show that kusachiite is tetragonal with the space group of $P4/ncc$. The unit cell dimensions, refined from the X-ray powder data, are a 8.511(2), and c 5.823(2) Å. The X-ray powder diffraction data of kusachiite are listed in Table 1 together with those of synthetic one, trippekite and schafarzikite for comparison.

Synthesis

Hydrothermal syntheses of kusachiite were preliminarily carried out at temperatures between 20 and 80°C under atmospheric pressure. The starting materials were prepared using reagent grade bismuth oxide and copper sulphate hydrate. The starting mixtures with the ratios from Cu:Bi = 1:1 to 1:5 were dissolved in 1 mol/l nitric acid, and then were added dropwide 5N KOH solution with continuous stirring. The final pH was 13. After

stirring the solutions at constant temperatures for 24 hrs, the crystalline products were filtered out, washed and dried. X-ray powder diffraction revealed that the crystalline products are poorly crystallized kusachiite.

Hydrothermal synthesis was also carried out at 500°C and 1 kbar water pressure. Starting material prepared by the same method mentioned above but with the ratio of Cu:Bi = 1:2 was sealed in gold tubes. After 3 days of run duration, the product was examined by X-ray powder diffraction, which revealed that well crystallized kusachiite was formed. The cell dimensions are a 8.501(2) and c 5.816(2) Å.

Discussion

Kusachiite is the natural analogue of the synthetic $CuBi_2O_4$. The space group of synthetic $CuBi_2O_4$ has been determined to be $P4/ncc$ by Boivin et al. (1973, 1976) and Yamada et al. (1991), and to be $I4$ by Arpe and Müller-Buschbaum (1976). The reflections of $h+k+l = 2n+1$ found in X-ray photographs of kusachiite show that the space goup of kusachiite is not $I4$. The space group of kusachiite was determined to be $P4/ncc$. Kusachiite is closely related to trippkeite and schafarzikite in unit cell parameters and in X-ray powder data, as shown in Table 1. Synthetic $PdBi_2O_4$ has the same structure as kusachiite (Kakhan et al., 1979). X-ray powder data of synthetic $Bu_2Cu_2O_5$ reported by Arjomand and Machin (1975) are very similar to those of kusachiite.

Kusachiite varies in composition from $CuBi_2O_4$ to $Cu_{0.92}Bi_{2.06}O_4$. The Bi ion is much larger than the Cu ion and cannot occupy the Cu site in the lattice. Bi ions, therefore, cannot exceed 2 per formula unit. The deviation from the stoichiometric composition may arise from defects in the lattice. There may be defects in copper ions, giving kusachiite the chemical formula $Cu_{(1-x)}Bi^{3+}_{(2-x)}Bi^{5+}_x O_4$. If there are defects in both copper and oxygen ions, kusachiite will have the chemical formula $Cu_{(1-x)}Bi^{3+}_2 O_{(4-x)}$. As noted in the chemical composition section, domains grown on {001} have stoichiometric compositions, and those grown on {100} have nonstoichiometric compositions. Thus, kusachiite grown on the {100} may contain some defects. Kakhan et al. (1979) also reported a departure of the composition of synthetic $CuBi_2O_4$ from stoichiometry.

Nonstoichiometric compositions are well known in bismuth minerals such as sillenite and bismuth oxide (Abrahams et al., 1979; Murray et al, 1986; Horowitz et al., 1989; and Kakhan et al., 1979). Nonstoichiometry and domain structure with compositional variations are known in schafarzikite-like minerals (Mellini et al., (1981). Domain structure is also known in clinobisvanite, $BiVO_4$ (Bridge and

TABLE 1. Chemical formulae, space groups, unit cell parameters and powder data of kusachiite, synthetic CuBi$_2$O$_4$, trippkeite and schafarzikite

Name		Kusachiite*		Synthetic[+]		Trippkeite[‡]		Schafarzikite[§]	
Chemical formula		CuBi$_2$O$_4$		CuBi$_2$O$_4$		CuAs$_2$O$_4$		FeSb$_2$O$_4$	
Crystal system		tetragonal		tetragonal		tetragonal		tetragonal	
Space group		P4/ncc		P4/ncc		P4$_2$/mbc		P4$_2$/mbc	
Unit cell	a	8.511		8.510		8.592		8.59	
parameters	c	5.823		5.814		5.573		5.92	
Powder	hkl	d	I	d	I	d	I	d	I
data	110			6.01	1	6.07	57	6.074	8
	200	4.26	17	4.255	18	4.30	14	4.295	15
	210					3.84	8		
	201					3.40	3		
	211	3.191	100	3.184	100	3.16	100	3.223	100
	220	3.011	7	3.009	7	3.04	47	3.037	13
	002	2.913	16	2.906	13	2.79	6	2.960	10
	102	2.759	3	2.751	3				
	310	2.695	18	2.691	23	2.72	34	2.716	18
	112	2.623	8	2.617	7	2.53	15	2.661	9
	311			2.442	1	2.44	1		
	320					2.38	<1		
	202	2.404	13	2.399	15	2.34	36	2.437	17
	212			2.319	1	2.26	15	2.345	3
	321					2.19	3		
	400	2.126	2	2.127	2	1.25	1		
	410					2.08	2		
	222	2.091	2	2.091	1	2.05	2		
	330	2.006	4	2.004	9	2.02	1	2.025	3
	401					2.00	7	2.019	<2
	312	1.976	7	1.975	9			2.001	2
	411	1.947	18	1.945	32	1.95	36	1.9652	20
	420	1.903	3	1.902	5	1.92	7	1.9208	3
	322			1.832	1	1.81	2		
	421			1.807	<1	1.82	3		
	213	1.728	12	1.727	19			1.7553	10
	430					1.72	1		
	402	1.719	5	1.717	5	1.70	11	1.7382	4
	510					1.68	<1		
	412			1.682	1	1.67	14		
	332	1.652	9	1.651	17	1.64	25	1.6711	13

* Present study
[+] Boivin et al. (1973)
[‡] Pertlik (1977)
[§] JCPDS 25-1181

Pryce, 1974). Coexistence of Bi^{3+} and Bi^{5+} is well known in bismuth minerals (Batog et al., 1973; Craig and Stephenson, 1975; and Ramanan and Gopalakrishnan, 1985).

CuBi$_2$O$_4$ has been synthesized at temperatures higher than 500°C (Boivin et al., 1973; Arpe and Müller-Buschbaum, 1976; Kakhan et al., 1979). As mentioned in the synthesis section, kusachiite can be synthesized at temperatures lower than 80°C. The associated minerals are mostly hydrate minerals. It is likely that kusachiite was formed under low-temperature hydrothermal conditions.

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