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Sillenite from fuka, okayama prefecture, Japan

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Abstract

Sillenite from Fuka occurs as cubes up to 5 mm across in a calcite vein cutting gehlenite-spurrite skarn, probably as a primary mineral in a new mode of occurrence to this mineral as well as the first description of its idiomorph. The wet and microprobe analyses gave SiO_2 2.22, 1.85; Bi_2O_3 97.74, 96.48; totals 99.96%, 98.33%, respectively. The average yields the empirical formula $Bi_{24.06}Si_{1.95}O_{40}$ (basis O = 40), proving the validity of the ideal formula $Bi_{24}Si_2O_{40}$ advocated after the reference to many synthetic works on $Bi_{24}X_2O_{39-40}$ where X = Fe, Al, Ge, Ti, P, As, and V. The single crystal and X-ray powder works verify the symmetry to be cubic, space group I23, a = 10.110(2)Å, Z = 1. It is optically isotropic, refractive index >2.50; $VHN_{50} = 345 \sim 386$ kg/mm^2, density 9.16 g/cm^3 (meas.), 9.18 g/cm^3 (calc.).

Introduction

Sillenite was firstly found from Durango, Mexico by Frondel (1943), who identified it as the natural analogue of γ-Bi_2O_3 synthesized by Sillén (1938), although traces of Si, Al, Cu, Fe, Ca and other elements were found. In his synthetic works, Sillén (1938) has stated that the impurity content may act either as a stabilizer of this modification or may be an integral part of the composition.

Subsequent natural occurrence of sillenite was found by Correia Neves *et al.* (1974) from Monapo pegmatite, Mozambique, as a secondary mineral. They regarded the chemical composition of this mineral as a simple bismuth sesquioxide. In Japan, the occurrence is known from two granite pegmatites, Fujikawachi, Oita Prefecture and Ishikawa, Fukushima Prefecture (Sakurai, personal communication). All of them were identified by X-ray powder works only without any decisive compositional study on account of the earthy nature and of intimate association with the other secondary bismuth minerals.

While, syntheses of bismuth oxides including minor exotic components with the general formula $Bi_{24}X_2O_{39-40}$ (X = Si, Ge, Ti, Bi, Al, V, As, and P) have been attempted (Aurivillius and Sillén, 1945; Gattow and Fricke, 1963; Surnina and Litvin, 1970; Batog *et al.*, 1973; Ramanan and Gopalakrishnan, 1985; Speer and Jansen, 1986; Horowitz *et al.*, 1989). The combinations of the tri- and pentavalent states of the same element enable to yield +8 for X_2 besides the cases of tetravalent cation only, keeping the relation $O=40$. Also is permitted the formation of compounds with $O=39$, which are fundamentally isostructural with those including two molecules of tetravalent cation only. Some of them have been structurally studied by Abrahams *et al.* (1967, 1979) and by Svensson *et al.* (1979). All of them are cubic, space group I23 (for X = Si), $a=10.07\sim10.23$Å, $Z=1$. The crystallographic data for them are very similar to those for sillenite. As stated later, books on minerals have begun to use $Bi_{12}SiO_{20}$ as the ideal formula of sillenite.

Occurrence

Sillenite was found as aggregates of cubes up to 5 mm across perching on calcite crystals grown on cavity walls in a calcite vein of 2∼8 cm wide (Fig. 1) developed along the boundary between crystalline limestone and gehlenite-spurrite skarns, which are also cut by veinlets of the other minerals. They include hillebrandite, scawtite, foshagite, bultfonteinite, oyelite and tobermorite besides calcite. Although the sillenite-bearing vein comprises henmilite, bultfonteinite, tenorite, and thaumasite besides calcite, all of them are found apart from sillenite aggregates and not in direct contact with the mineral.

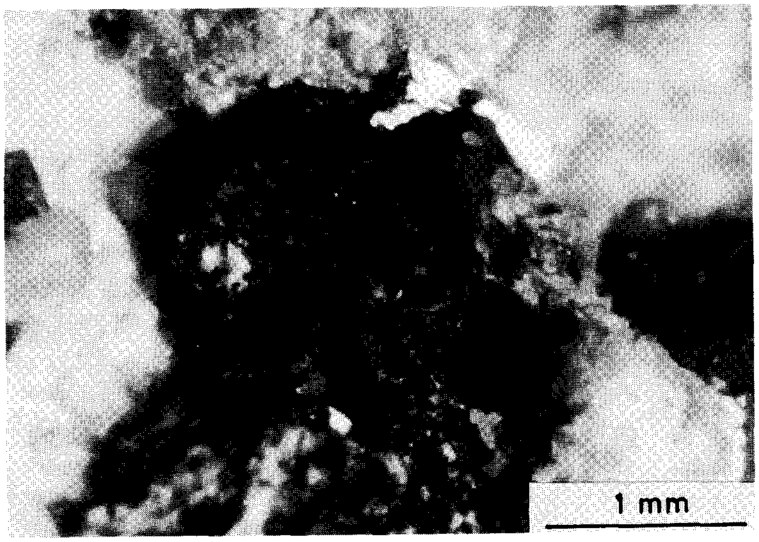

FIG. 1. Photograph of sillenite crystals (cube) on calcite.

Physical properties

Sillenite crystals have various shades of yellow, pale green or reddish brown with an adamantine luster and a light yellowish to brownish white streak. Optically it is isotropic with the refractive index above 2.50. Vickers microhardness using 50 g load is 345 to 386 kg/mm^2. Pycnometrically measured density is 9.16 g/cm^3, which agrees with the calculated value, 9.18 g/cm^3, using the ideal formula. The material is readily soluble in dilute HCl.

X-ray studies

The single crystal studies using Weissenberg and precession cameras gave the cubic symmetry with the systematic absence of the reflections with $h+k+l=2n+1$, therefore, possible space group I23 or $I2_13$, the former being preferred after the reference to the structural studies on synthetic $Bi_{24}Si_2O_{40}$ by Abrahams *et al.* (1979) and by Horowitz *et al.* (1989).

The powder diffractometer survey using Cu/Ni radiation gave the pattern essentially identical with that of synthetic $Bi_{24}Si_2O_{40}$ as given in Table 1, where that of the Mozambique material (Correia Neves *et al.*, 1974) is compared. The calculated unit cell parameter of the present material is $a=10.110(2)$Å, $Z=1$.

Chemical composition

Chemical analyses of sillenite were made on the material purified by hand picking and heavy liquid separation. Also, it was subjected to microprobe analyses using a JEOL electron microprobe analyzer operated at 20kV and the sample current was 2×10^{-8}A and 1×10^{-8}A. The employed standards were synthetic Bi_2O_3 (for Bi) and diopside (for Si). Both analyses were very close to theoretical figures for $Bi_{24}Si_2O_{40}$ (Table 2).

Synthesis

The oxide mixture of desired composition was prepared after a simple mechanical mixing of reagent grade Bi_2O_3 and silica gel, and was hydrothermally treated at 450°C and 1 kilobar water pressure for 7 days. The X-ray powder pattern of the product is essentially identical with that of the natural material as given in Table 1. Another run without silica gel treated under the same condition provided the powder pattern of α-Bi_2O_3.

TABLE 1. X-ray powder data for sillenite and synthetic $Bi_{24}Si_2O_{40}$

1.			2.		3.		
I	d(obs.)	d(calc.)	I	d	I	d	h k l
2	7.16	7.1489	1	7.14	2	7.0	110
4	5.05	5.0555	3	5.06	3	5.11	200
5	4.122	4.1274	5	4.137	5	4.17	211
24	3.573	3.5744	23	3.577	20	3.604	220
100	3.197	3.1971	100	3.202	100	3.221	310
22	2.917	2.9185	20	2.922	30	2.945	222
58	2.701	2.7020	65	2.705	70	2.725	321
3	2.528	2.5275	2	2.529	3	2.547	400
8	2.382	2.3830	12	2.384	12	2.402	330,411
11	2.260	2.2607	13	2.262	15	2.278	420
13	2.155	2.1555	17	2.157	18	2.172	332
8	2.063	2.0637	10	2.064	10	2.079	422
13	1.983	1.9827	14	1.983	18	1.9978	431,510
7	1.845	1.8458	9	1.846	15	1.8594	521
25	1.734	1.7339	37	1.734	45	1.7470	433.530
13	1.685	1.6850	18	1.685	20	1.6979	422,600
16	1.640	1.6401	25	1.641	30	1.6528	532,611
		1.5985	1	1.599	6	1.6168	620
3	1.560	1.5600	4	1.560	7	1.5713	541
3	1.524	1.5241	5	1.524	7	1.5354	622
12	1.491	1.4906	18	1.491	20	1.5020	631
2	1.459	1.4593	2	1.460	5	1.4712	444
4	1.430	1.4298	8	1.430	10	1.4402	543,550,710
2	1.402	1.4020	3	1.403			640
4	1.376	1.3758	6	1.376	7	1.3867	552,633,721
2	1.350	1.3510	2	1.351	5	1.3611	642
	a=10.110(2)Å			*a*=10.110(3)Å		*a*=10.184(3)Å	

1. Sillenite, Fuka, Okayama Prefecture, Japan. Cu/Ni radiation. Diffrctometer method. The present study.
2. Synthetic $Bi_{24}Si_2O_{40}$. Cu/Ni radiation. Diffractometer method. The present study.
3. Sillenite. Monapo pegmatite, Mozambique. Camera method. After Correia Neves et al.,(1974).

TABLE 2. Chemical analyses of sillenite

	1.	2.	3.	4.
Weight percentages				
SiO_2	1.85	2.22	2.05	2.10
Bi_2O_3	96.48	97.74	97.95	97.90
Total	98.33	99.96	100.00	100.00
Mole ratios(basis: O=40)				
Si	1.80	2.10	1.95	2
Bi	24.26	23.86	24.06	24

1. Sillenite. Fuka, Okayama Prefecture, Japan. Microprobe analysis. Analyst: H. Akamine.
2. Sillenite. Ditto. Wet chemical analysis. Analyst: I. Kusachi.
3. Sillenite. Average of 1 and 2. Recast to 100%.
4. Theoretical $Bi_{24}Si_2O_{40}$.

Discussion and conclusion

Although the literature survey could not specify who was the first to have used the formula $Bi_{12}SiO_{20}$ to sillenite, mineral books of recent publication refer to above formula (Nickel and Nichols, 1991; Fleischer and Mandarino, 1991). Their usage has been now validated after the studies on the natural material. Also, the assignment of this formula has brought about a taxonomical problem. If, for example, $Bi_{24}Al_2O_{39}$ is found in nature, how to handle it? Is it sillenite or a discrete species? The material from Mozambique has a larger *a* than pure $Bi_{24}Si_2O_{40}$ as seen in Table 1. The detailed chemical study on this material is eagerly requested.

Among afore-mentioned synthetic works on $Bi_{12}SiO_{20}$, Ramanan and Gopalakrishnan (1985) and Horowitz *et al.* (1989) report the success at the temperature as low as 80°C by a reaction in aqueous alkali solutions. The sillenite-bearing calcite vein carries such hydrous minerals as henmilite, bultfonteinite, and thaumasite. That the present sillenite was formed primarily under a low temperature hydrothermal condition is very likely.

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