Bull. Natn. Sci. Mus., Tokyo, Ser. C, **25**(1, 2), pp. 59–64, June 22, 1999

Pucherite from the Wagu Mine, Fukushima Prefecture, Japan

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Abstract Pucherite from the Wagu mine, Fukushima Prefecture, occurs as a secondary Bi-mineral and forms euhedral crystals and crusts on pegmatitic feldspar ore. It is orange in color with adamantine luster. The representative chemical analysis by EPMA gave Bi_2O_3 72.41, V_2O_5 27.93, Total 100.34 wt. %, yielding the empirical formula $Bi_{1.01}V_{1.00}O_4$ on the basis of O=4. The X-ray powder diffraction pattern is indexed on orthorhombic cell with a=5.338 (2), b=5.072 (2), c=12.04 (1) Å.

Key words: pucherite, chemical composition, X-ray data, pegmatite, Wagu mine

Introduction

Three polymorphs of $BiVO_4$ have been known as pucherite, clinobisvanite and dreyerite. Pucherite is the oldest member described from Pucher shaft of the Wolfgang mine, Schneeberg, Saxony, Germany (Frenzel, 1871). It is not so rare alteration products from native bismuth and bismuth chalcogenide in pegmatite and Bi-bearing hydrothermal veins. During mineralogical survey on pegmatite in Ishikawa area, the third author has recognized orange-colored tiny prismatic crystals in association with ocherous material coating feldspar ore from the Wagu mine. The X-ray and chemical studies have proved it to be pucherite. This paper is for the description of pucherite as the first find in Japan.

Occurrence

There were many mines working for feldspar–quartz ore at Ishikawa-town where is the most famous pegmatite area in Japan. Big crystals of beryl, schorl and almandine, and many species of REE-bearing minerals have been found during the mine operatings. The Wagu mine is located about 3.3 km NWW of Iwaki-Ishikawa railway station of Suigun line. The ore body of the mine was firstly operated before 1944, and after long pause was reoperated in 1980. In this time almost mine activities including the Wagu mine, however, have ceased. The ore bodies are massive pegmatite composed of quartz, albite–oligoclase and K-feldspar in association with muscovite and biotite in weathered granodiorite. The subordinate minerals collected from the second adit include native gold, native bismuth, samarskite, ferrocolumbite, chrysoberyl, monazite, xenotime, zircon, schorl, beryl and allanite (Takeshita & Hashimoto, 1983).

The third author (E. H.) collected the studied material from the second adit and dump in 1980. It is composed of maily albite–oligoclase and muscovite, and includes minor altered Bi-minerals which are covered by grayish black materials and ocherous materials. The original Bi-minerals may be native bismuth and a joseite-like mineral. Along the joint surfaces of albite–oligoclase, also, the ocherous materials are often observed. They are mainly composed of bismutite. Pucherite (NSM M-27916) occurs rarely as spotted aggregates of thin prismatic crystals flattened on {001} less than 1× 0.4×0.1 mm on ocherous material and directly joint surfaces of albite–oligoclase (Fig. 1). It has orange color with adamantine luster. Some minute inclusions up to a diameter of 5 μm in pucherite crystals could be observed by back-scattered electron image (Fig. 2).

Chemical Composition

Chemical analyses were made by using Link Systems energy dispersive X-ray spectrometer (QX 2000) for all elements except H_2O and CO_2. Standard materials are wollastonite for Ca, Bi metal for Bi, GaP for P and V metal for V. Analytical condition was under 15 kV with Falady cup current of 1 nA using a live-time of 60 seconds and the analytical areas are less than $3\times4\,\mu m^2$. The detailed analytical procedure has been reported by Yokoyama *et al.* (1993). In Table 1 the figures of each two analyses of pucherite and minute inclusions in pucherite are compared with related secondary Bi-minerals. The empirical formulae of pucherite are $Bi_{1.01}V_{0.99}O_4$ and $Bi_{1.01}V_{1.00}O_4$ on the basis of O=4, respectively. They are very close to the ideal formula, $BiVO_4$. Though minute inclusions contain major bismuth with minor calcium, phosphorus and vanadium, the characterization by X-ray study could not be made due to their small size.

X-ray Crystallography

The X-ray powder diffraction data was obtained by a Gandolfi camera (diameter= 114.6 mm) using Cu/Ni radiation as given in Table 2, in which those of the original material from Schneeberg was compared. The crystal structure of pucherite has been refined with the orthorhombic space group, Pnca (Granzin & Pohl, 1984) The calculated unit cell parameters for the present specimen with indexing refer to their result are a=5.338 (2), b=5.072 (2), c=12.04 (1) Å. These figures are slightly larger than those of the original material from Schneeberg, a=5.326, b=5.056, c=12.00 Å calculated by powder data (ICDD 12-293), and a=5.328 (2), b=5.052 (2), c=12.003 (3) Å by single crystal data (Granzin & Pohl, 1984).

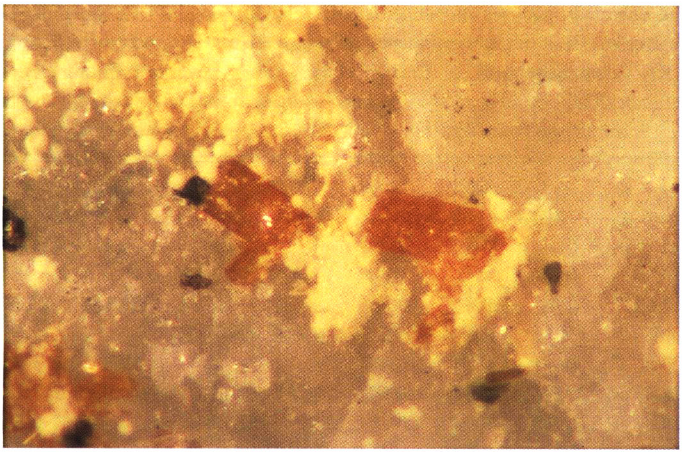

Fig. 1. Photomicrograph of pucherite. Field view, approximately 6×4 mm.

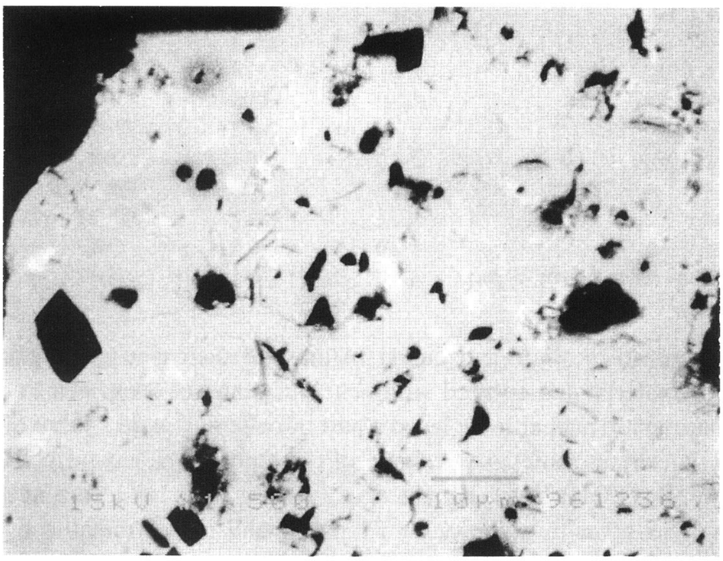

Fig. 2. Back-scattered electron image of pucherite (gray) and enclosed minute Bi-minerals (white). Field view, approximately 83×63 μm.

Discussion

The secondary Bi-minerals are common in pegmatites, hydrothermal quartz veins and skarns which include mainly native bismuth, tetradymite, joseite group minerals and wittichenite. In the present case, native bismuth and a joseite-like min-

Table 1. The chemical analyses of pucherite and related secondary Bi-minerals. 1, 2: pucherite from Wagu mine, 3, 4: mixture composed of mainly bismutite? and others from Wagu mine, 5: $Bi_2(CO_3)O_2$ (ideal bismutite), 6: $CaBi_2(CO_3)_2O_2$ (ideal beyerite), 7: smrkovecite from Smrkovec, Czech (Rídkosil *et al.*, 1996), 8: hechtsbergite from Black Forest, Germany (Krause *et al.*, 1997), 9: ximengite from Ximeng, China (Shi, 1989). n.d.: not determined.

Wt. %	1	2	3	4	5	6	7	8	9
SiO_2	0	0	0	0			0.02		
CaO	0	0	1.42	1.30		9.19			
Bi_2O_3	72.62	72.41	88.87	90.03	91.37	76.38	85.16	83.02	76.34
CO_2	n.d.	n.d.	n.d.	n.d.	8.63	14.43			
P_2O_5	0	0	0.54	0.44			12.74	3.60	22.92
V_2O_5	27.87	27.93	0.57	0.60			0.03	15.18	
As_2O_5	0	0	0	0			0.17	0.52	
H_2O	n.d.	n.d.	n.d.	n.d.			1.65	*1.59	0.76
total	100.49	100.34	91.40	92.37	100	100	99.77	100.31	100.02
	O=4	O=4			O=5	O=8	O=6	O=6	**O=4
Si									
Ca						1			
Bi	1.01	1.01			2	2	2.01	2.03	1.01
C					1	2			
P							0.98		0.99
V	0.99	1.00						0.95	
As							0.01	0.03	
H							1.00	1.01	0.26

*: calculation. **: in anhydrous part.

eral are recognized in albite and quartz. Almost of their rim have been altered to grayish black material and covered with ocherous material composed of mainly bismutite. Subsequently pucherite replaced a part of ocherous material, but the source of vanadium is uncertain same as a example of the report on a secondary Bi-vanadate, hechtsbergite, $Bi_2O(OH)(VO_4)$ (Krause *et al.*, 1997). Since no occurrences of primary V-minerals as colusite group and sulvanite found in polymetallic hydrothermal vein are expected in this case, the source of vanadium may be bituminous material included in pegmatitic vein or vanadium ion exsolved in underground water. The chemical composition of minute inclusion in pucherite indicates small amounts of calcium, phosphorus and vanadium contents. If these minor components are ignored, this may corresponds to that of bismutite. However, it is possible to consider that calcium may be derived from minor beyerite or kettnerite, and phosphorus and vanadium may be derived from such minerals as ximengite (Shi, 1989), smrkovecite (Rídkosil *et al.*, 1996)–hechtsbergite (Krause *et al.*, 1997) solid solution or petijeanite (Krause *et al.*, 1993)–schumacherite (Walenta *et al.*, 1983) solid solution excluded the possibility of

Table 2. X-ray powder data for pucherite.

h k l	Wagu mine			Schneeberg		h k l	Wagu mine			Schneeberg	
	$d_{obs.}$	$d_{calc.}$	I	d	I		$d_{obs.}$	$d_{calc.}$	I	d	I
0 0 2	6.01	6.02	m	5.985	16	3 0 2	1.708	1.706	vw	1.703	16
0 1 1	4.68	4.67	s	4.644	55	2 1 5	1.685	1.686	vvw	1.681	16
1 0 2	3.99	3.99	s	3.982	55	3 1 1	1.663	1.663	vvw	1.659	20
1 1 1	3.52	3.52	vs	3.499	100	2 0 6	1.598	1.604	vw	1.596	16
0 1 3	3.16	3.15	vw			1 3 1		1.598			
1 1 2		3.14		3.125	10	0 2 6	1.570	1.574	w	1.567	25
0 0 4	3.02	3.01	m	2.992	45	2 2 4		1.569			
1 1 3	2.72	2.71	vvs	2.702	100	0 3 3	1.560	1.558	vw	1.554	40
2 0 0	2.67	2.67	w	2.658	20	3 1 3	1.551	1.549	w	1.544	25
1 0 4				2.614	<2	3 0 4				1.531	<2
0 2 0	2.54	2.54	m	2.528	25	2 1 6				1.525	<2
2 0 2	2.45	2.44	vvw	2.438	2	1 2 6	1.511	1.509	vw	1.505	16
1 1 4	2.32	2.33	vw			1 3 3	1.497	1.496	m	1.491	35
2 1 1		2.32		2.312	35	1 0 8				1.445	10
1 2 1				2.237	<2	2 3 1	1.417	1.418	vw		
0 1 5	2.18	2.18	w	2.168	25	3 2 2		1.416		1.413	20
1 2 2	2.14	2.14	m	2.133	40	0 3 5	1.379	1.384	vvw	1.380	10
2 1 3	2.04	2.04	vw	2.030	16	3 1 5		1.377			
2 0 4	1.993	1.997	m	1.992	45	2 2 6	1.358	1.356	vvw	1.345	16
1 2 3		1.989				4 0 0	1.333	1.335	vw	1.333	16
0 2 4	1.942	1.939	s	1.934	40	3 2 4				1.308	20
1 0 6	1.884	1.878	vw	1.872	20	0 2 8				1.292	20
2 2 0	1.836	1.838	w	1.832	40	0 4 0	1.266	1.268	vw		
1 1 6				1.759	2						

Wagu mine: a=5.338 (2), b=5.072 (2), c=12.04 (1) Å. Schneeberg: a=5.326, b=5.056, c=12.00 Å (ICDD 12-293).

vanadium contamination from surrounding pucherite.

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