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TWO NEW PALLADIUM-ARSENIC-BISMUTH MINERALS FROM THE STILLWATER COMPLEX, MONTANA*

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Abstract

Two new Pd-As-Bi minerals from the Stillwater Complex, Montana, are palladobismutharsenide, $Pd_{2.0}As_{0.8}Bi_{0.2}$, and an unnamed mineral, $Pd_{1.94}As_{0.78}Bi_{0.28}$. Palladobismutharsenide is orthorhombic, *Pmcn* or $P2_1cn$, *a* 7.504(4), *b* 18.884(10), *c* 6.841(7)Å; *D*(calc.)=10.8 g/cm³ for *Z*=20, and with strongest lines on a poor powder diffraction pattern of 2.51(9) (071,212), 2.22(10) (081,023,331), and 2.09Å(6) (271,350). The unnamed mineral is hexagonal with diffraction aspect *P6/**c*, *a* 6.625(3), *c* 19.775(13)Å; assuming *Z*=15, *D*(calc.)= 10.7 g/cm³. Strongest powder diffraction lines are 2.33(10) (116,025), 2.16(7) (026,121), and 1.91Å(6) (030). Both minerals are very similar to palladoarsenide under reflected light. Palladobismutharsenide has been synthesized.

Sommaire

Les deux minéraux de Pd-As-Bi provenant du Complexe Stillwater, au Montana, sont le palladobismutharsénide, $Pd_{2.0}As_{0.8}Bi_{0.2}$ et un minéral sans nom $Pd_{1.94}As_{0.78}Bi_{0.28}$. Le palladobismutharsénide est orthorhombique avec groupe spatial *Pmcn* ou $P2_1cn$, *a* 7.504(4), *b* 18.884(10), *c* 6.841(7)Å; *D*(calc.)=10.8 pour *Z*=20; les raies les plus intenses sur un diagramme de poudre de médiocre qualité sont: 2.51(9) (071,212), 2.22(10) (081,023,331), et 2.09Å(6) (271,350). Le minéral sans nom est hexagonal avec *a* 6.625(3), *c* 19.775(13)Å, et dans l'aspect *P6**c*; en supposant *Z*=15, on a *D*(calc.) =10.7. Les raies de poudre les plus fortes sont: 2.33(10) (116,025), 2.16(7) (026,121), et 1.91Å(6) (030). Les deux minéraux ressemblent beaucoup au palladoarsénide en lumière réfléchie. Le palladobismutharsénide a été synthétisé.

Introduction

During the examination of palladium arsenide minerals from the Stillwater Complex, Montana, two new palladium-bismuth-arsenides were discovered (Cabri *et al.* 1975). The minerals were initially considered to be bismuthian palladoarsenide on the basis of their chemical composition. However, the X-ray data of both minerals are different from those of palladoarsenide, and each subsequently proved to be a new and distinct species. The new mineral, palladobismutharsenide**, $Pd_{2.0}As_{0.8}Bi_{0.2}$, is named after its composition; the other mineral, $Pd_{1.94}As_{0.78}Bi_{0.28}$ is unnamed at the moment.

The material for this study came from the same source as previously described by Cabri & Laflamme (1974). The minerals were found in heavy-mineral concentrates from the Banded and Upper zones of the Stillwater Complex, Montana, and ranged in size from approximately 82x95 to 135x165 microns. They occurred either as free grains or as grains closely associated with palladoarsenide, calcite, and an undetermined (Pd,Te,Bi) mineral, and they frequently have silicate inclusions. Three grains were identified as palladobismutharsenide, whereas only one grain of the unnamed mineral was found.

Physical Properties

Palladobismutharsenide is cream-colored and shows no visible pleochroism under reflected light in air or under oil immersion. Anisotropism varies from weak to distinct (or moderate) in air but is distinct under oil immersion, i.e. the mineral goes from grey to extinction in air but polarization effects under oil immersion vary from grey to extinction, brownish grey, or brown.

It was possible to compare palladobismutharsenide with palladoarsenide directly in one case under reflected light. Palladoarsenide in this association is less anisotropic than palladobismutharsenide, but their reflectances are so similar that it was impossible to distinguish between them in plane-polarized light, even under oil immersion.

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**The name and the mineral have been approved by the Commission on New Minerals and Mineral Names, I.M.A.

The unnamed $Pd_{1.94}As_{0.78}Bi_{0.28}$ mineral is similar to palladobismutharsenide under reflected light. It is cream-colored and shows no visible pleochroism in air or under oil immersion though there is a 2.3% difference between maximum and minimum values at 589 nm (Table 1). Anisotropism is moderate in air and distinct under oil immersion: the mineral goes from grey to extinction in air and from grey to greyish brown under oil immersion.

The reflectance measurements in air with a silicon standard for four standard wavelengths, and the micro-indentation hardness are listed in Table 1.

TABLE 1. REFLECTANCE AND MICRO-INDENTATION HARDNESS

Wavelength nm	Palladobismutharsenide Range[1] %	Unnamed (Pd-As-Bi)-mineral Range[2] %
470	53.6 - 54.5	54.4 - 58.9
546	52.1 - 53.0	51.7 - 54.5
589	53.6 - 54.6	52.0 - 54.3
650	55.8 - 56.1	54.4 - 55.7
Micro-identation hardness(kg/mm^2) VHN_{25g}	429 (373 - 468)[3]	
	450 (429 - 483)[4]	

1 Minimum and maximum values are the mean of two sets of measurements on two grains.
2 As for 1), but for one grain.
3 Three measurements.
4 Seven measurements on another grain.

Chemical Composition

Electron probe analyses of palladobismutharsenide and the unnamed mineral were performed at 25 kV using synthetic Pd_2As, PdSb, PdTe, PtSn, HgS and metallic Bi, Rh, Ni and Ag as standards. The X-ray intensity data were processed by the computer program, EMPADR VII, of Rucklidge & Gasparrini (1969). The results are compared with those of the synthetic Pd-As-Bi compound in Table 2.

On the basis of total atoms = 3.0, the analyses (no. 1-3) of palladobismutharsenide were calculated to $Pd_{1.99}As_{0.81}Bi_{0.20}$, $Pd_{1.99}As_{0.80}Bi_{0.21}$ and $Pd_{2.00}As_{0.80}Bi_{0.20}$, corresponding to the ideal formula, $Pd_2As_{0.8}Bi_{0.2}$. The formula requires the presence of Bi with an As/Bi ratio of approximately 4:1. This requirement is confirmed by the synthetic compound (anal. no. 5 and 6) which has a similar composition and the same symmetry.

TABLE 2. ELECTRON PROBE ANALYSES* OF NATURAL AND SYNTHETIC PALLADOBISMUTHARSENIDE, AND UNNAMED (Pd-As-Bi)-MINERAL

Anal no.	Weight percent Pd	As	Bi	Total	Atomic proportions Pd	As	Bi
1	67.3	19.1	13.4	99.8	1.99	0.81	0.20
2	66.7	18.9	13.5	99.1	1.99	0.80	0.21
3**	67.0	18.9	13.1	99.0	2.00	0.80	0.20
4**	63.7	18.0	18.0	99.7	1.94	0.78	0.28
5**	65.8	19.1	14.9	100.8	1.97	0.80	0.23
6	63.9	18.9	14.7	99.5	1.97	0.81	0.22

1-3 palladobismutharsenide; 4 unnamed (Pd,As,Bi)-mineral;
5-6 synthetic (at 485°C) palladobismutharsenide.
* Other elements searched for, but not detected: Pt,Cu,Au,Sb, Te,Ni,Sn,Ag, and Hg.
** Grain x-rayed with precession and powder cameras.

The analysis (no. 4) of the unnamed mineral gives $Pd_{1.94}As_{0.78}Bi_{0.28}$ on the basis of total atoms = 3.0. The formula corresponds to $Pd_{15.0}As_{6.0}Bi_{2.1}$, indicating an ideal formula of $Pd_{15}As_6Bi_2$. The As/Bi ratio is 3:1.

X-Ray Data

The crystals (no. 3 and 4) analyzed by electron probe were subsequently studied with an X-ray precession camera using Mo$K\alpha$ radiation. The results (Table 3) show that palladobismutharsenide is orthorhombic with space group either *Pmcn* or $P2_1cn$ with a 7.504(4), b 18.884 (10) and c 6.841(7)Å. The unnamed mineral is hexagonal and shows the diffraction aspect $P6/{**}c$, corresponding to space groups $P6_3/mmc$, $P6_3mc$ or $P\bar{6}2c$, with cell dimensions a 6.625(3) and c 19.775(13)Å. Assuming a density of approximately 10.8 g/cm^3, the number of formula units per cell, Z, is 20 for palladobismutharsenide, ($Pd_2As_{0.8}Bi_{0.2}$), giving D(calc.) 10.8 g/cm^3. Assuming Z=15 for the unnamed mineral ($Pd_{1.94}As_{0.78}Bi_{0.28}$), D(calc.) is 10.7 g/cm^3.

TABLE 3. CRYSTAL DATA OF NATURAL AND SYNTHETIC PALLADOBISMUTHARSENIDE AND UNNAMED (Pd-As-Bi)-MINERAL

	Palladobismutharsenide $Pd_{2.0}As_{0.8}Bi_{0.2}$	Synthetic (485°C) $Pd_{1.97}As_{0.80}Bi_{0.23}$	Unnamed (Pd-As-Bi)-mineral
Space Group	*Pmcn*, $P2_1cn$	*Pmcn*, $P2_1cn$	$P6_3/mmc$, $P6_3mc$, $P\bar{6}2c$
a Å	7.504 (4)	7.467 (4)	6.625 (3)
b	18.884 (10)	18.946 (12)	
c	6.841 (7)	6.797 (5)	19.775 (13)

Gandolfi X-ray powder diffraction patterns of palladobismutharsenide are of poor quality and only a few lines can be observed even on the films taken with a 57.3 mm camera. However, the Gandolfi pattern for the unnamed mineral is of good quality. The patterns were indexed using the strong reflections observed on the single-crystal photographs. The results are compared with the synthetic equivalent of palladobismutharsenide in Table 4. The spacings (and relative intensities) of the strongest lines of the unnamed mineral are 2.33(10), 2.16(7), and 1.91(6) whereas those for palladobismutharsenide are 2.51(9), 2.22(10), and 2.09(6).

Synthetic $Pd_{1.97}As_{0.80}Bi_{0.23}$ and Pd_2As

Charges with bulk composition $Pd_2As_{0.8}Bi_{0.2}$ were prepared from high-purity elements, sealed

TABLE 4. X-RAY POWDER DIFFRACTION DATA

	Synthetic[1] $Pd_{1.97}As_{0.80}Bi_{0.23}$			Pallado-bismutharsenide[2] Stillwater Complex Montana			Unnamed (Pd-As-Bi)-Mineral[3] Stillwater Complex Montana					
h k l	d_{calc}	d_{meas}	I_{est}	d_{calc}	d_{meas}	I_{est}	*h k l*	d_{calc}	d_{meas}	I_{est}		
0 3 2	2.993	2.985	½				1 1 2	3.141	3.144	1		
2 3 1	2.906	2.917	½				0 2 2	2.755	2.755	2		
0 4 2	2.761	2.751	½				1 1 4	2.742				
2 4 1	2.692			2.699	2.687	½	0 2 3	2.630	2.663	½		
1 6 1	2.674	2.680	1½	2.672			1 1 6	2.336	2.330	10		
1 4 2	2.590	2.590	8	2.599	2.596	4	0 2 5	2.322				
0 7 1	2.515	2.507	1	2.510	2.505	9	0 2 6	2.164	2.161	7		
2 1 2	2.491	2.485	9	2.505			1 2 1	2.156				
2 5 1	2.477	2.452	1				0.0.10	1.978	1.976	3		
3 1 0	2.468						0 3 0	1.912	1.910	6		
1 7 1	2.383	2.380	4	2.380	2.380	3	0.0.12	1.648	1.648	2		
3 2 1	2.269	2.264	4	2.280	2.276	1½	1 3 0	1.591	1.590	2		
0 8 1	2.236	2.232	10	2.231			2 2 6	1.480	1.481	2		
0 2 3	2.204	2.195	8	2.217	2.224	10	1.2.11	1.384	1.384	3		
3 3 1	2.192			2.201			0.3.10	1.375	1.375	3		
1 1 3	2.154						1 4 0	1.252	1.251	3		
1 8 1	2.142	2.148	4									
0 3 3	2.133	2.127	5	2.139	2.141	1½						
2 7 1	2.086			2.144								
3 5 0	2.080	2.083	9	2.086	2.089	6*						
0 4 3	2.044	2.042	1	2.085								
1 9 0	2.026	2.025	2									
0 9 1	2.011	2.007	2	2.006	2.006	½						
0 5 3	1.945	1.948	2									
2 8 1	1.919	1.922	1									
0.10.0	1.895	1.894	1									
4 0 0	1.867	1.863	5	1.876	1.880	4						
0.10.1				1.820	1.824	½						
1.10.1	1.773	1.774	2	1.769	1.768	½						
0 2 4	1.673	1.673	1									
3 8 1	1.664	1.663	1									
2 6 3	1.651	1.652	2									
4 2 2				1.621	1.623	1						
4 3 2	1.584	1.588	3									
4 4 2	1.547	1.546	2									
2.11.1				1.522	1.520	1						
2.10.2	1.513	1.516	2									
0.10.3	1.453	1.453	3									
2.12.1	1.422	1.418	3	1.420	1.418	1						
3.11.0	1.416			1.415								
3 0 4	1.403	1.405	5									
5 5 0	1.389	1.388	1									
0.11.3	1.371	1.371	3	1.372	1.373	2						
5 5 1	1.361	1.362	3									
0.14.0				1.349	1.349	½						
2.12.2	1.337	1.339	2									
0.14.1	1.327	1.326	1									
5 6 1	1.324											
5 4 2	1.314	1.314	5	1.320	1.319	2						
0.12.3	1.295	1.296	1									
5 7 1	1.284	1.281	4	1.288	1.288	1						
5 1 3	1.244	1.245	5	1.251	1.251	2B						
6 0 0	1.244			1.251								
5 9 0	1.218	1.218	2									
0.11.4	1.210	1.209	5	1.212	1.211	3						

CuKα radiation (λ = 1.5418Å); (1) 114.6 mm Debye-Scherrer camera; (2) 57.3 mm Gandolfi camera; (3) 114.6 mm Gandolfi camera.
* The intensities for this reflection are not uniform creating greater possibility of error in estimation.

For unnamed mineral read 2.752 instead of 2.742.

in evacuated silica-glass tubes, and heated at 710°C for four days. The charges were subsequently subjected to repeated grinding, pelletization and re-annealing at 485°C for a period of 277 days. The quenched products were analyzed by electron probe, and gave compositions, two of which are given in Table 2, ranging from $Pd_{1.97}As_{0.80}Bi_{0.23}$ to $Pd_{1.97}As_{0.81}Bi_{0.22}$ for the major phase (approximately 95%). The minor phases consist of Pd_5As_2 and Pd_2As. Under reflected light the major phase is cream-colored, shows no visible pleochroism, and is distinctly to strongly anisotropic in air. X-ray single-crystal studies (Table 3) confirmed that the major phase $Pd_{1.97}As_{0.80}Bi_{0.23}$ is the synthetic equivalent of palladobismutharsenide. This synthetic phase also has the space group symmetry *Pmcn* or $P2_1cn$, with *a* 7.467(4), *b* 18.946(12) and *c* 6.797(5)Å. The X-ray powder diffraction pattern of this phase (Table 4), gives more detailed data than those of palladobismutharsenide, though the two patterns are similar. The higher resolution of the pattern is attributable to the use of a 114.6 mm Debye-Scherrer camera and also to the long annealing period. The relative intensities of the lines in the two patterns are approximately the same if account is taken of the overlap of lines in the smaller film.

Saini *et al.* (1964) reported that below 455°C synthetic Pd_2As (α-form) is monoclinic, P2/*m*, with *a* 9.24, *b* 8.47, *c* 10.45Å, and β 94°; above 455°C, the phase (β-form) is hexagonal, *P62m*, with *a* 6.650, and *c* 3.583Å. The X-ray powder diffraction data of these two forms [with strong lines: 2.605 (64), 2.352(51), 2.305 (51), 2.216 (100) and 2.149 (100) for α-Pd_2As; 2.423 (100), 2.235 (80), 2.168 (80), 1.913 (64) and 1.238 (80) for β-Pd_2As] are different from those of synthetic $Pd_{1.97}As_{0.80}Bi_{0.23}$, of palladobismutharsenide, and of the unnamed mineral.

Instead of monoclinic symmetry, Bälz & Schubert (1969) reported that α-Pd_2As is orthorhombic, $Cmc2_1$, *a* 3.25, *b* 16.84, and *c* 6.58Å. The X-ray powder diffraction data of this phase are similar to those given by Saini *et al.* (1964).

Related Minerals

Begizov *et al.* (1974) reported a new mineral, palladoarsenide, with formula $(Pd_{1.83}Ag_{0.09}Au_{0.02})_{\Sigma 1.94}As_{1.00}$, from the Oktyabr deposit, U.S.S.R. The mineral was described as the low-temperature polymorph (α-form) of Pd_2As reported by Saini *et al.* (1964) due to the similarity of their X-ray powder diffraction pattern. The chemical formula of this mineral is recalculated to $(Pd_{1.87}Ag_{0.09}Au_{0.02})_{\Sigma 1.98}As_{1.02}$, which is closer to that of palladobismutharsenide than to the unnamed mineral $Pd_{1.94}As_{0.78}Bi_{0.28}$, except that the former mineral contains no Bi. The X-ray powder diffraction data of palladoarsenide are different from those of palladobismutharsenide and of the unnamed mineral.

Razin *et al.* (1973) reported "palladium stibiostannoarsenide", $Pd_{2\pm x}$ (As, Sn, Sb), from the Talnakh deposit, U.S.S.R. The composition $Pd_{2.689}(As_{0.598}Sn_{0.210}Sb_{0.192})_{\Sigma 1.000}$, departs significantly from the ratio $\Sigma Pd/\Sigma(As, Bi)$ = 2:1 for palladobismutharsenide, or 1.8:1 for the unnamed mineral. The reported X-ray powder diffraction data are similar to those of the palladoarsenide reported by Begizov *et al.* (1974), but differ from those of palladobismutharsenide and the unnamed mineral.

It is concluded that the structure of $Pd_2As_{0.8}Bi_{0.2}$ is different from that of Pd_2As and that the presence of Bi in the crystal structure must be essential for palladobismutharsenide and for the unnamed mineral.

Because only one grain of the unnamed mineral was found, and because no synthetic experiments were made, it is considered premature to propose a new name for this mineral. It would be preferable to establish experimentally, or by studying numerous natural occurrences, whether this mineral has a fixed composition or whether a range of compositions is permitted by its crystal structure.

Preservation of Type Material

Single grains of palladobismutharsenide, mounted in polished sections, are preserved at the Royal Ontario Museum, Toronto, M34218 (anal. no. 1, Table 2) and at the U.S. National Museum, Smithsonian Institution, Washington, D.C., NMNH#135407 (anal. no. 2, Table 2). Single grains of palladobismutharsenide and of the unnamed mineral, mounted on glass fibres, are preserved in the Crystal Structure Laboratory, CANMET.

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