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Definitive data on bohdanowiczite, a new silver bismuth selenide

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SUMMARY. Bohdanowiczite was first described in 1967 but incomplete data prevented its acceptance as a new mineral at that time. Additional data on the same material now characterize bohdanowiczite as a new species with the formula:

$$3[(Ag_{0.98}Cu_{0.02})_{0.97}(Bi_{0.97}Pb_{0.03})_{1.02}(Se_{0.83}S_{0.17})_{2.01}]$$

The mineral occurs in intimate intergrowths with clausthalite and wittichenite in polymetallic mineralization at Kletno in Poland. In reflected light bohdanowiczite has a creamy-yellow colour and short polysynthetic twinning is frequently observed. Cell parameters indexed on a hexagonal lattice are $a = 4.183 \pm 0.008$ Å and $c = 19.561 \pm 0.016$ Å. $P\bar{3}m1$ is the most likely space group. The strongest lines of the powder pattern are 2.91(100), 2.03(30), 3.40(20), 6.54(20), 2.09(18), 3.26(18). The calculated density is 7.72 gm/cm^{-3} and the VHN between 63 and 96 kg/mm^2.

BOHDANOWICZITE has appeared in the literature on several occasions (Banaś and Ottemann, 1967, 1969, 1971; Banaś, 1971) although it was first noted in a description of the Kletno deposit of the Polish Sudetes mountains (Banaś, 1965*a*) where it was identified as schapbachite(?). Another occurrence has been reported from the Julianehaab deposit in Greenland (Schönwandt, pers. comm.). None of the previous reports have contained sufficient data for the mineral to be internationally accepted as a new species.

Within the Kletno fluorite deposit, magnetite-bearing skarns are found that contain heavy metal oxides with minor quantities of sulphides. Adjacent to the skarns in a strongly cracked quartz zone, formed by the silicification of crystalline limestone, are nests and veins of uranium-polymetallic-sulphide-selenide mineralization associated with quartz and black fluorite. In this suite pitchblende and secondary uranium minerals (Banaś, 1964, 1966) occur with clausthalite, tiemannite, umangite, klockmannite, wittichenite, and bohdanowiczite (Banaś, 1965*b*; Banaś and Ottemann, 1971). Native silver, naumannite, eskebornite(?), bornite, chalcopyrite, and chalcosine are also recorded. One typical example of these relations studied here contains clausthalite as a host phase showing irregular, lobate emulsion intergrowths with wittichenite, bohdanowiczite, and small quantities of chalcopyrite. This assemblage infills quartz and fluorite and cuts and replaces pitchblende.

Physical and optical properties. These properties were described in detail by Banaś and Ottemann (1971) and are included here in summary for completeness.

Bohdanowiczite has a pale but distinct creamy-yellow colour especially when compared with white clausthalite, and the cream colour remains apparent when compared with the deeper yellow chalcopyrite. The bireflectance of bohdanowiczite can only be observed along grain margins under oil immersion. Table I indicates the reflectance spectrum of the mineral, which has a Vickers micro-indentation hardness between 63 and 96 kg/mm^2.

Bohdanowiczite shows weak but distinct anisotropism, which increases under oil immersion showing pinkish gold colours. Under crossed nicols short polysynthetic twinning is observed.

TABLE I. *Reflectance of bohdanowiczite*

nm	Average R_2%	Average R_1%
434.7	47.3	46.5
486.1	50.0	48.5
520.0	52.2	49.8
546.0	52.5	50.3
589.1	52.8	50.9
653.1	52.3	50.5

Microprobe analysis. Analyses of the closely intergrown phases were performed on a Cambridge Instruments Microscan 5 electron microprobe at an operating voltage of 25 kV and using pure metal standards with galena for Pb and S and pyrite for Fe. The standards and techniques used are described by Bowles (1975) and quantitative correction of the analyses was obtained using the program of Mason, Frost, and Reed (1969).

Microprobe analyses of bohdanowiczite from the present work are given in Table II, with the previous analyses of Banaś and Ottemann (1971) for comparison. The formula $AgBiSe_2$ clearly appears to be correct and there appears to be substitution of lead for bismuth, copper for silver, and sulphur for selenium. The present analyses show ~ 1% lead not previously reported and ~ 2.5% sulphur, which is rather more than the 0.7% reported by the earlier authors. The full formula resulting from the current analyses is: $(Ag_{0.98}Cu_{0.02})_{0.97}(Bi_{0.97}Pb_{0.03})_{1.02}Se_{0.83}S_{0.17})_{2.01}$.

TABLE II. *Microprobe analyses of bohdanowiczite*

				Average	Atomic proportions		Banaś and Ottemann (1971)
Pb	0.56	1.70	1.77	1.34	0.030	1.018	—
Bi	45.19	44.77	44.71	44.89	0.988		44.7
Ag	22.14	22.21	22.58	22.31	0.951	0.972	22.6
Cu	0.17	0.32	0.25	0.25	0.018		—
Fe	n.d.	0.01	n.d.	n.d.	—		—
Co	0.02	0.01	n.d.	0.01	0.001		—
Ni	0.02	0.03	0.02	0.02	0.002		—
S	2.18	2.51	2.73	2.47	0.354	2.011	0.7
Se	29.73	27.72	27.92	28.46	1.657		32.1
Total	100.01	99.28	99.98	99.75			100.1

As, Sb, and Te less than detection limit of 0.01 %.
n.d. = not detected; — = not reported.
Atomic proportions calculated to 4 atoms per formula unit.

X-ray data. It was not possible to isolate a pure bohdanowiczite sample for the X-ray diffraction studies but the identities of the closely intergrown clausthalite and wittichenite were clearly confirmed by X-ray powder photographs and microprobe analysis. A bohdanowiczite-clausthalite intergrowth proved to be the most satisfactory material for deriving the bohdanowiczite powder diffraction data. Masking of bohdanowiczite reflections by those of the cubic, face-centred clausthalite ($a = 6.083$ Å) was very limited and comparison with synthetic $AgBiSe_2$ (Geller and Wernick, 1959) indicated that only two bohdanowiczite *d*-spacings were likely to have been obscured, both being multi-indexed and relating to high-angle lines with $d < 1.40$ Å. These are indicated by a note in Table III.

TABLE III. *X-ray powder data for bohdanowiczite*

hkil	d_{calc} Å	d_{obs} Å	*I*	*hkil*	d_{calc} Å	d_{obs} Å	*I*
0001	19.56	—	—	$11\bar{2}6$	1.760	—	—
0002	9.78	—	—	$20\bar{2}3$	1.745	—	—
0003	6.52	6.54	20	$10\bar{1}10$	1.721	1.722	3
0004	4.89	—	—	$20\bar{2}4$	1.699	1.699	5
0005	3.91	—	—	$11\bar{2}7$	1.674	—	—
$10\bar{1}0$	3.62	—	—	$20\bar{2}5$	1.644	1.641	1
$10\bar{1}1$	3.56	3.56	3	00012	1.630	1.630	6
$10\bar{1}2$	3.40	3.40	20	$10\bar{1}11$	1.596	—	—
0006	3.26	3.26	18	$11\bar{2}8$	1.589	—	—
$10\bar{1}3$	3.17	3.17	2	$20\bar{2}6$	1.583	—	—
$10\bar{1}4$	2.91	2.91	100	$20\bar{2}7$	1.520	—	—
0007	2.79	—	—	$11\bar{2}9$	1.507	1.507	1
$10\bar{1}5$	2.66	2.66	5	00013	1.505		
0008	2.45	2.43	1	$10\bar{1}12$	1.487	—	—
$10\bar{1}6$	2.42			$20\bar{2}8$	1.455	1.455	5
$10\bar{1}7$	2.21	2.21	2	$11\bar{2}10$	1.429	—	—
0009	2.17	2.17	1	00014	1.397	*	
$11\bar{2}0$	2.09	2.09	18	$20\bar{2}9$	1.391		
$11\bar{2}1$	2.08			$10\bar{1}13$	1.390		
$11\bar{2}2$	2.05	2.03	30	$21\bar{3}0$	1.369	—	—
$10\bar{1}8$	2.03			$21\bar{3}1$	1.366	*	
$11\bar{2}3$	1.992	1.995	1	$21\bar{3}2$	1.356		
00010	1.956	—	—	$11\bar{2}11$	1.355		
$11\bar{2}4$	1.923	—	—	$21\bar{3}3$	1.340	—	—
$10\bar{1}9$	1.864	—	—	$20\bar{2}10$	1.329	—	—
$11\bar{2}5$	1.844	—	—	$21\bar{3}4$	1.319	1.319	3
$20\bar{2}0$	1.811	1.805	1	00015	1.304	1.305	1
$20\bar{2}1$	1.804			$10\bar{1}14$	1.304		
$20\bar{2}2$	1.781	1.781	2	$21\bar{3}5$	1.292	—	—
00011	1.778			$11\bar{2}12$	1.286	1.286	4

* *d*-spacings very probably lost due to masking by the clausthalite impurity, cf. synthetic $AgBiSe_2$ (Geller and Wernick, 1959); values for reflections $11\bar{2}6$ and $20\bar{2}7$ would be similarly obscured, but no measured *d*-spacings are listed for these reflections in the synthetic data.

The measurements were made on photographs taken in a 114.6 mm diameter camera with Cu-*Kα* radiation ($\lambda = 1.5418$ Å).

Powder data for bohdanowiczite (Table III) were obtained from photographs taken in a 114.6 mm diameter Debye-Scherrer camera using Cu-*Kα* radiation and ThO_2 as an internal standard. Intensities were visually estimated by comparison with an intensity scale. No allowance was made for any preferred orientation effects that might have been introduced during the preparation of the sample mount. In fact some equatorial enhancement was noted in the powder photographs for orders of the 0001 reflection, a behaviour that would be consistent with the presence of a basal cleavage. The bohdanowiczite *d*-spacings were indexed in conjunction with those of the synthetic $AgBiSe_2$ of

Geller and Wernick (1959). The method of least squares employed on seventeen unambiguous reflections gave the cell parameters of bohdanowiczite as $a = 4.183 \pm 0.008$ Å, $c = 19.561 \pm 0.016$ Å, $a{:}c = 1{:}4.676$ and $V = 296.4 \pm 1.4$ Å^3. By analogy with the synthetic material the most probable space group is $P\bar{3}m1$. The structural synthesis of Geller and Wernick (1959) indicates that there are three formula units to the unit cell, which with the atomic ratios given in Table II permits a calculated density of 7.72 gm/cm^3 to be determined.

It should be noted that in a description of the structurally related mineral matildite, Harris and Thorpe (1969) determine the *a* parameter from single crystal studies to be twice that recorded by Geller and Wernick (1959) for synthetic $AgBiS_2$. The powder data quoted here index satisfactorily using an *a* parameter similar to that obtained for synthetic $AgBiSe_2$ but it is possible that detailed single-crystal investigation might reveal a comparable situation and yield an *a* cell parameter for bohdanowiczite of about 8.4 Å.

The name bohdanowiczite proposed by Banaś and Ottemann (1967) is retained and is in acknowledgement of the work of Professor dr. h.c. eng. Karol Bohdanowicz of Cracow (1864–1947). Both the name and the description of the mineral have now been approved by the Commission on New Minerals and Mineral Names.

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