

## 70. Pilsenite Re-defined and Wehrlite Discredited

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(Communicated by Takeo WATANABE, M. J. A., Dec. 13, 1982)

**Introduction.** The name wehrlite was first used by Huot (1841) to indicate a silver-bearing bismuth telluride from Deutsch-Pilsen, Hungary, studied by Wehrle in 1831, who gave the composition Ag 2.07 wt.%, Bi 61.15, Te 29.74, S 2.33, total 95.29%. Later Sipöcz (1886) gave two additional analyses, one of which was made on a better material, giving Ag 4.37 wt.%, Bi 59.47, Te 35.47, total 99.31%. The X-ray powder diffraction pattern of the material from the type locality was first obtained by Harcourt (1942). Warren and Peacock (1945) accounted for the pattern using a hexagonal cell similar to that of tellurobismuthite  $\text{Bi}_2\text{Te}_3$ , and concluded that wehrlite is a bismuth-tellurium alloy with minor silver and is essentially a non-stoichiometric solid solution close to but not identical with tellurobismuthite after the reference to available analyses.

This interpretation was supported by Thompson (1949), who referred to a fluctuating chemical formula expressed as  $\text{Bi}_{2+x}\text{Te}_{3-x}$  where  $0 < x < 0.5$  and by Strunz (1970) as  $\text{BiTe}$ . However, Sztróky (1946) considered it to be a mixture of some bismuth chalcogenides plus hessite  $\text{Ag}_2\text{Te}$ . In connection with a study on tsumoite (Shimazaki and Ozawa, 1978), the authors investigated the topotypic wehrlite and found it to be a mixture of bismuth telluride with an ideal formula  $\text{Bi}_4\text{Te}_3$  and hessite  $\text{Ag}_2\text{Te}$ . This result can be applied to the interpretation of the original studies, especially as to the nature of silver, and leads to discredit wehrlite as a mixture, although the holotype was not examined. The authors have desired to recover the name pilsenite, which was once given to the material equivalent to wehrlite of Huot by Kenngot (1953) and currently regarded as a synonym of wehrlite (Strunz, 1970), to indicate natural  $\text{Bi}_4\text{Te}_3$ . The proposals to recover pilsenite and discredit wehrlite have been approved by the Commission on New Minerals and Mineral Names, I. M. A. (73-4a, 73-5a). The materials used in this study have been preserved at University Museum, the University of Tokyo, Hongo, Tokyo.

The present and some recent studies on bismuth tellurides indicate that materials described under the name wehrlite are classi-

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fied as pilsenite  $\text{Bi}_4\text{Te}_3$ , tsumoite  $\text{BiTe}$  or tellurobismuthite  $\text{Bi}_2\text{Te}_3$ . Wehrlites studied by Zav'yalov *et al.* (1978) and Zav'yalov (1981) have the chemical composition  $\text{Bi}_{4-x}\text{Te}_{3+x}$  ( $0 < x < 0.28$ ) and the  $c$  periodicity of about  $42\text{\AA}$ . They should be called pilsenite, because these properties are in common with those for pilsenite. The discrediting of mineral name wehrlite will also eliminate the confusion coming from the current usage of this name to indicate an ultrabasic rock.

The first synthetic analogue of natural  $\text{Bi}_4\text{Te}_3$  was prepared by Stasova (1964, 1967), who reported the crystallographic data and its isostructural relation to  $\text{Bi}_4\text{Se}_3$  structurally studied by her (Stasova, 1968). Yamana *et al.* (1979) refined the structure of synthetic  $\text{Bi}_4\text{Te}_3$ , corroborating her study.

The authors would like to thank Dr. G. Niedermayr for supplying us with wehrlite specimen. The computations were performed at the Computing Center of the University of Tokyo.

*Chemical and physical properties.* A tiny tablet of wehrlite from Deutsch-Pilsen, Hungary, supplied by Dr. G. Niedermayr, Mineralogische-Petrographische Abteilung, Naturhistorisches Museum, Wien, was examined by microscope and microprobe. The microscopic observation revealed that it consists of two phases (Fig. 1). Chemical

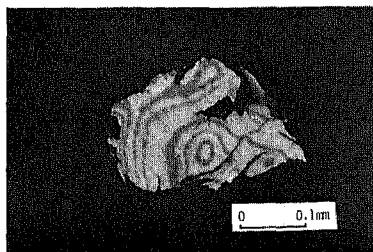


Fig. 1a

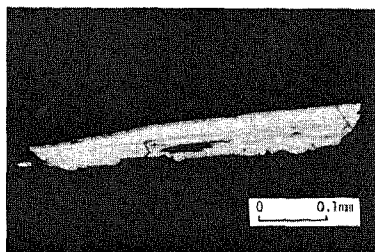


Fig. 1b

Fig. 1. a, b. Polished sections of wehrlite. Thin hessite (grey) is interlayered in pilsenite (white).

and X-ray powder diffraction studies demonstrated the dominant phase to be pilsenite and minor one to be hessite, which is interlayered on such a thin film as less than several microns thick. Both of them are anisotropic between crossed polars and pilsenite has higher reflectance and lower polishing hardness than hessite in the observed orientations. Any further study was not made on account of paucity of material.

Microprobe analyses, using JEOL XMA-5 and standard materials composed of metallic Bi, Te, Ag, synthetic PbS and chalcopyrite, were made on pilsenite and hessite areas. Quantitative correction

for atomic number, absorption and fluorescence effects were performed by the method proposed by Sweatman and Long (1969). The compositions at four points on pilsenite area are Bi 64.7–66.0 wt. % (average 65.2), Pb 0.9–1.3 (1.1), Ag 0.0–0.3 (0.1), Fe 0.0–tr., Te 30.6–31.2 (31.0), S tr.–0.1 (0.1), the average corresponding to  $(\text{Bi}_{3.87}\text{Pb}_{0.07}\text{Ag}_{0.01})_{\Sigma 3.95}(\text{Te}_{3.01}\text{S}_{0.04})_{\Sigma 3.05}$ , or ideally  $\text{Bi}_4\text{Te}_3$ , on the basis of  $(\text{Bi} + \text{Pb} + \text{Ag}) + (\text{Te} + \text{S}) = 7$ . Hessite occurs as very thin film in pilsenite, impeding the exclusive bombardment of electron beam. The

Table I. X-ray powder patterns for wehrlite from Deutsch-Pilsen, Hungary and synthetic  $\text{Bi}_4\text{Te}_3$

1			2			hkil	hkl	remarks
I	d <sub>obs</sub>	d <sub>calc</sub>	I	d <sub>obs</sub>	d <sub>calc</sub>			
m	4.68	4.66	m	4.68	4.65	0009	333	
w	3.79	3.79	w	3.79	3.79	0112	110	
vs	3.25	3.24	vs	3.24	3.24	1017	322	
w	3.00							hessite
w	2.89							hessite
*	2.61							
s	2.36	2.36	s	2.36	2.36	011.14	554	
w	2.30							hessite
s	2.22	2.22	s	2.23	2.23	1120	101	
w	2.17	2.17	w	2.17	2.17	101.16	655	
vw	2.13							hessite
s	1.998	1.997	m	1.999	1.994	000.21	777	
s	1.833	1.833	s	1.836	1.835	0227	331	
w	1.649	1.648	vw	1.647	1.646	011.23	887	
m	1.622	1.620	m	1.621	1.621	202.14	644	
*	1.552	1.552	vw	1.552	1.552	022.16	664	
s	1.485	1.486	s	1.486	1.485	112.21	876	
vw	1.449	1.451	w	1.449	1.451	022.19	775	
m	1.415	1.414	m	1.416	1.416	2137	421	
m	1.397	{1.398 1.396}	w	1.396	{1.396 1.395}	{000.30 101.28}	{10.10.10 10.9.9}	
vw	1.343							
vw	1.328	1.327				213.13	643	
m	1.308	1.309	m	1.310	1.310	123.14	653	
wb	1.284	1.283	wb	1.284	1.285	3030	211	
m	1.183	{1.183 1.182}	w	1.183	{1.183 1.182}	{112.30 022.28}	{11.10.9 10.10.8}	
m	1.144	1.144	w	1.142	1.143	011.35	12.12.11	
w	1.111	1.112	vw	1.113	1.113	2240	202	
	$a_h = 4.446$ (2) Å			$a_h = 4.453$ (2) Å				
	$c_h = 41.94$ (2)			$c_h = 41.88$ (2)				
	$a_r = 14.21$ (1)			$a_r = 14.19$ (1)				
	$\alpha_r = 18.00$ (1)°			$\alpha_r = 18.05$ (1)°				

1: Wehrlite from Deutsch-Pilsen, Hungary. Cu/Ni radiation. Camera method ( $\phi = 114.59$  mm). \* Spotty. 2: Synthetic  $\text{Bi}_4\text{Te}_3$ . Cu/Ni radiation. Camera method ( $\phi = 114.59$  mm).

best analyses for hessite area gave Ag 50.7 wt.%, Bi 12.7, Pb 0.6, Te 37.5, S 0.1, total 101.6%. Deducting Bi etc. due to pilsenite, the remnant is recalculated to  $(\text{Ag}_{1.89}\text{Pb}_{0.01})_{\Sigma 1.90}(\text{Te}_{0.99}\text{S}_{0.01})_{\Sigma 1.00}$  on the basis of  $(\text{Te}+\text{S})=1$ .

*X-ray diffraction studies.* X-ray powder diffraction photographs were taken for wehrlite and synthetic  $\text{Bi}_4\text{Te}_3$  prepared by heating the stoichiometric quantities of Bi and Te metals in an evacuated silica glass tube for 7 days at 640°C, at which the sample is expected to have reached a liquid state according to Brown and Lewis (1962), then annealing for 6 days at 413°C. They are shown in Table I with their unit cell dimensions computed by a least-squares programme. Because a very small quantity of pilsenite was available, no single crystal suitable for structure determination was obtained. However, its powder pattern and precession photographs correspond to those for synthetic  $\text{Bi}_4\text{Te}_3$  (Yamana *et al.*, 1979), confirming that pilsenite is essentially the natural analogue of synthetic  $\text{Bi}_4\text{Te}_3$ . The crystallographic data as well as their chemical compositions for bismuth tellurides which Zav'yalov *et al.* (1978) and Zav'yalov (1981) described under the name wehrlite are also identified as those for pilsenite. Thus, re-defined pilsenite is rhombohedral,  $R\bar{3}m$ ,  $a$  4.446 (2),  $c$  41.94 (2) Å,  $Z=3[\text{Bi}_4\text{Te}_3]$ .

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