UNIT CELL AND SPACE GROUP OF VRBAITE $(Tl(As,Sb)_3S_5)$, SELIGMANNITE $(CuPbAsS_3)$ AND SAMSONITE $(Ag_4MnSb_2S_6)$

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ABSTRACT

The following data were obtained by the Weissenberg equi-inclination method. Vrbaite from Allchar: space group *Cmca;* $a_0=13.35$, $b_0=23.32$, $c_0=11.23$ (all $\pm$ 0.05); $a_0:b_0:c_0=0.5725:1:0.5815$; cell contents $Tl_{21}(As,Sb)_{63}S_{105}$. Samsonite from Andreasberg: space group *$P2_1/n$;* $a_0=10.29$, $b_0=8.05$, $c_0=6.61$ (all ±0.05), $\beta=92°41'$ (morph.); $a_0:b_0:c_0=1.278:1:0.821$; cell contents $Ag_8Mn_2Sb_4S_{12}$. Seligmannite from Bingham: space group *Pnmm;* $a_0=8.04$, $b_0=8.66$, $c_0=7.56$ (all ±0.05); $a_0:b_0:c_0=0.928:1:0.873$; cell contents $Cu_4Pb_4As_4S_{12}$.

X-ray powder photographs of aikinite, $CuPbBiS_3$, indicate that it is not a member of the seligmannite-bournonite group.

VRBAITE $(Tl(As,Sb)_3S_5)$

Vrbaite, one of the few known thallium minerals, has been found only at Allchar, northwest of Salonika, Greece. The morphological description of Ježek (1912) established the point symmetry as $2/m\ 2/m\ 2/m$—orthorhombic dipyramidal. The single chemical analysis available, by Křehlík (1912), affords the formula $Tl(As_{.68},Sb_{.32})_3S_5$. The close approach of the As:Sb ratio to 2:1 is here taken as fortuitous. The artificial compound $TlAs_3S_5$ has been found in the system Tl_2S-As_2S_3 by Canneri and Fernandes (1925), but the identity of this substance with vrbaite has not been shown.

A natural crystal from Allchar[1] was examined by the Weissenberg equi-inclination method, using Cu radiation. The interpretation of the films followed the plane group method of Buerger (1935). Rotation photographs were taken about the principal axes, together with 0-, 1- and 2-layer photographs about [100], 0- and 1-layers about [010] and a 0-layer about [001]. The position and intensity of the diffraction effects was entirely consistent with orthorhombic centrosymmetry. The stacking sequence of the reciprocal lattice levels in the {100} projections involved a translation of the 1-layer of $c/2$ and established the lattice type as C-centered. Systematic omissions in the 0-layer about [010] defined a glide {010} in the direction [001], and an additional glide {001} in the direction [100] was defined by the 0-layer about [001]. The space group

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[1] From the Roebling collection of the United States National Museum. No.: R939. Loaned through the courtesy of Dr. William F. Foshag, Curator.

is $D_{2h}^{18} = Cmca$, in accordance with the holohedral morphology. The orientation of the structural cell ($c < a < b$) conforms with the choice of morphological cell by Ježek. The cell dimensions calculated from high order reflections on the 0-layers are given below, together with the x-ray and morphological ratios.

$a_0 = 13.35$ $b_0 = 23.32$ $c_0 = 11.23$ (all ±0.05)
$a_0 : b_0 : c_0 = 0.5725 : 1 : 0.4815$
$a : b : c = 0.5659 : 1 : 0.4836$ (Ježek)

The number of formula units in the unit cell, taking the molecular weight as 534.5 and the specific gravity[2] as 5.3, is 21.0. The calculated specific gravity for Z = 21 is 5.29.

SELIGMANNITE ($CuPbAsS_3$)

Seligmannite is the arsenical analogue of bournonite, $CuPbSbS_3$. Morphological study of material from the Binnenthal by Baumhauer (1901, 1902) and by Solly (1903, 1905, 1912) established the point symmetry as $2/m\ 2/m\ 2/m$—orthorhombic dipyramidal. Chemical analyses later contributed by Prior (1908) yielded the formula given above and confirmed the close relation to bournonite indicated by the morphology. The crystallography of the only other known occurrence of the mineral, at Bingham, Utah, was described in 1928 by Palache. A quantitative analysis of this material was not given, but blowpipe and microchemical tests proved the absence of Sb and the presence of As.

A Weissenberg study was made of one of the original crystals from the Bingham occurrence. Cu radiation was used. The crystal was rather large and poorly shaped for x-ray work, and contained a very small irregular portion of another crystal from which it had been broken. Rotation photographs were taken about the principal axes, together with 0-layers about [100] and [001] and a 0- and 1-layer about [010]. The reciprocal lattice was plotted for all of the films to make certain the identification of adventitious spots due to the inclusion mentioned. Nothing was found in the position or intensity of the spots clearly proper to the main body of the crystal that required other than orthorhombic centrosymmetry. The projections on {010} established the lattice type as primitive, and the {100} projection defined a diagonal glide {100} with component $b/2 + c/2$. Other special diffraction effects were absent. The space group is thus either $C_{2v}^{7} = Pnm$ or $D_{2h}^{13} = Pnmm$. The morphology indicates holohedral symmetry so that the correct space group is $Pnmm$.

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[2] Ježek gives three observed values for the specific gravity: 5.271 on 0.272 g. with the pycnometer, 5.333 on 0.272 g. by a hydrostatic method, and 5.302 on 0.458 g. with the pycnometer.

The cell dimensions calculated from high order reflections on the 0-layers are given in Table 1, beyond. The cell contents are 4($CuPbAsS_3$). The observed specific gravity, obtained by the writer on a single small crystal on the microbalance, is 5.38, and the calculated specific gravity is 5.54. The seligmannite from the Binnenthal has G. = 5.44, 5.48, and As:Sb∼41:1. Bournonite has an observed specific gravity of 5.83 ± 0.03, and a calculated value of 5.93 (from the cell dimensions of Oftedal (1932) cited in Table 1).

The x-ray data confirms the isostructural relation of seligmannite and bournonite indicated by the morphology and chemistry, as summarized in Table 1. A complete isomorphous series between these species may exist in point of As-Sb content, but the available analyses show an apparent maximum substitution of As for Sb at about Sb:As = 4:1 at the bournonite end of the series. The composition of these minerals suggests that their structural scheme is of a distorted sphalerite- or wurtzite-type. The pseudocubic cell may be remarked in this connection.

TABLE 1. COMPARISON OF SELIGMANNITE AND BOURNONITE

	Cell Contents	X-ray Cell			Morphological Cell			Space Group
		a_0	b_0	c_0	a	b	c	
Seligmannite	$Cu_4Pb_4As_4S_{12}$	8.04	8.66	7.56	0.9233	1	0.8734	*Pnmm*
					(Binnenthal)			
		0.928	1	0.873	0.9217	1	0.8718	
					(Bingham)			
Bournonite	$Cu_4Pb_4Sb_4S_{12}$	8.10	8.65	7.75	0.9380	1	0.8969	*Pnmm*
					(Brooke and Miller (1852)			
		0.936	1	0.896				

Aikinite, $CuPbBiS_3$, has been classed with bournonite and seligmannite on the basis of the similarity in composition. Adequate crystallographic data are lacking. X-ray powder photographs of aikinite from Berezov differ markedly from those of seligmannite and bournonite, and the mineral probably does not belong in this group.

SAMSONITE ($Ag_4MnSb_2S_6$)

Samsonite is known only from the Samson vein, Andreasberg, in the Harz, Germany. The only analysis available, cited in the original description of Werner and Fraatz (1910), is in very close agreement with the formula given above. The existing morphological data for the species is summarized in a recent study by Palache (1934). The point symmetry is $2/m$—monoclinic prismatic.

A Weissenberg study was made of a measured crystal, employing Cu radiation. Rotation and 0-layer photographs were taken about the principal axes and a 1-layer about [010]. The position and intensity of the diffraction effects were in accordance with monoclinic centrosymmetry. The lattice type, established by the stacking plan of the 0- and 1-layers about [010], is primitive. A diagonal glide {010} with component $a/2+c/2$ was defined by the 0-layer about [010], and a two-fold screw axis was defined along [010]. The space group is $C_{2h}^5=P2/_1n$, confirming the holohedral morphology. The cell dimensions as calculated from high order reflections on the 0-layers are cited below, together with the morphological ratio as averaged by Palache (1934) from the closely agreeing measurements of four observers. The x-ray value for β, calculated from [301]*, a^* and c^*, is less accurate than the morphological value.

$$a_0=10.29 \qquad b_0=8.05 \qquad c_0=6.61 \qquad \text{(all } \pm 0.05)$$
$$a_0:b_0:c_0=1.278:1:0.821 \quad \beta=92°2'$$
$$a:b:c=1.2782:1:0.8198 \quad \beta=92°41'$$

The specific gravity of samsonite was determined on the microbalance by the writer as 5.51. The number of formula units associated with the cell, taking $\beta=92°41'$, are then $1.98\sim 2$, or $Ag_8Mn_2Sb_4S_{12}$ for the cell contents. The calculated specific gravity for Z=2 is 5.56. The monoclinic modification of Ag_3SbS_3 (pyrostilpnite) has an observed specific gravity of 5.94.

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