

THE CRYSTAL STRUCTURE OF PADERAITE, A MINERAL OF THE CUPROBISMUTITE SERIES

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ABSTRACT

Paderaita from Baita-Bihorului (Rezbanya, Rumania) is monoclinic, a 28.44(8), b 3.90(3), c 17.55(8) Å, $\beta = 106.0(2)^\circ$, space group $P2_1/m$, $Z = 2$. Its crystal structure has been determined from data recorded with $\text{CuK}\alpha$ radiation on a single-crystal diffractometer. There are 20 metal and 22 sulfur atoms in two asymmetric units. Atom co-ordinations include octahedral (Bi), trigonal prismatic (Bi,Pb), trigonal to distorted tetrahedral (Cu), and quasilinear (Ag). Electron-probe microanalysis indicates a composition $\text{Cu}_{5.9}\text{Ag}_{1.3}\text{Pb}_{1.6}\text{Bi}_{11.2}\text{S}_{22}$. This result is supported by the structure analysis, which yields typical atom co-ordinations and bonding for 12 Bi, 1 Pb, 6 Cu, and 1 Ag. The structure of paderaita is related to those of $\text{Cu}_4\text{Bi}_5\text{S}_{10}$, cuprobismutite, and hodrushite. *C*-layers (so called after cuprobismutite) are present in all four structures and determine their common 17.5-Å cell dimension. *C*-layers alternate with predominantly *H*-type (*i.e.*, sheared octahedral) layers (here designated *D*-layers after hodrushite) of different thickness, forming the group of compounds now termed the cuprobismutite series. $\text{Cu}_4\text{Bi}_5\text{S}_{10}$ contains *C*-layers only, whereas cuprobismutite, paderaita and hodrushite feature both *C*- and *D*-layers.

Keywords: paderaita, sulfosalt, new mineral species, crystal structure, hodrushite, cuprobismutite series, Rumania.

SOMMAIRE

La paderaita de Baita-Bihorului (Rezbanya, Roumanie) est monoclinique, a 28.44(8), b 3.90(3), c 17.55(8) Å, $\beta = 106.0(2)^\circ$, $P2_1/m$, $Z = 2$. On en a déterminé la structure sur données obtenues en radiation $\text{CuK}\alpha$ au diffractomètre à cristal unique. Vingt atomes de métal et vingt-deux atomes de soufre occupent deux domaines asymétriques. On distingue quatre types de coordination: octaédrique (Bi), prismatique trigonale (Bi,Pb), tétraédrique (variant de trigonal à difforme) (Cu) et pseudo-linéaire (Ag). L'analyse à la microsonde électronique donne $\text{Cu}_{5.9}\text{Ag}_{1.3}\text{Pb}_{1.6}\text{Bi}_{11.2}\text{S}_{22}$. Etayant cette formule, la structure cristalline révèle les coordinations et liaisons typiques pour douze atomes de Bi, un de Pb, 6 de Cu et un d'Ag. Elle est apparentée aux structures voisines de $\text{Cu}_4\text{Bi}_5\text{S}_{10}$, cuprobismutite et hodrushite. Les couches *C* (ainsi appelées d'après cuprobismutite) se trouvent dans les quatre structures, y déterminant leur commune distance réticulaire de 17.5 Å. Leur alternance avec des couches où domine le type *H* (octaédrique cisailé), couches de différentes épaisseurs (appelées ici couches *D*, d'après la hodrushite), explique la formation de la série dite maintenant "de la cuprobis-

mutite". $\text{Cu}_4\text{Bi}_5\text{S}_{10}$ ne contient que des couches *C*, tandis que les trois autres espèces montrent à la fois des couches *C* et *D*.

(Traduit par la Rédaction)

Mots-clés: paderaita, sulfosel, nouvelle espèce minérale, structure cristalline, hodrushite, série de la cuprobismutite, Roumanie.

INTRODUCTION

Rezbanyite was first studied by Frenzel (1874), but it was not named at the time because of some confusion as to its true identity. Originally Frenzel considered that it was cosalite; only later did he propose and name it as a new species, rezbanyite, having the composition $\text{Pb}_4\text{Bi}_{10}\text{S}_{19}$ (Frenzel 1883). The history of the adjustment of the composition of rezbanyite to $\text{Cu}_2\text{Pb}_3\text{Bi}_{10}\text{S}_{19}$ by Koch (1930) and its present fairly dubious status as a mineral species (Fleischer 1983) have been described by Mumme & Zák (1985). That study of museum and other specimens of what were supposedly rezbanyite-containing materials from Baita-Bihorului (formerly Rezbanya, Rumania) by X-ray diffraction and electron-probe microanalysis (EPMA) resulted in the identification of the bismuthinite derivatives pekoite and hammarite, together with at least one other, less prevalent, mineral containing Ag, that has the average composition (wt. %): Ag 3.26, Pb 6.71, Cu 9.45, Bi 61.4, S 18.9 ($\Sigma 99.72\%$). This mineral proved to be a new species and was named *paderaita* (after Dr. K. Padera, Prague). The name and status as a new mineral were approved by the Commission on New Minerals and Mineral Names of the IMA in 1983.

It therefore seems likely that the original analyses of rezbanyite (Frenzel 1883) were performed not only on a mixture of various bismuthinite derivatives [as has been suspected in these and other laboratories for some time (Harris & Chen 1976, Zák & Prachar 1981, Zák & Hybler 1981, Mumme & Zák 1985)], but the material analyzed also probably incorporated other sulfosalt minerals, including paderaita. This result explains why Ag was reported in the very early analyses carried out by Frenzel (1883) on his specimens of so-called rezbanyite.

EXPERIMENTAL

The paderaitite crystal used in the present investigation was isolated from a small specimen of Rezbanya material, selected and kindly provided by Dr. L. Zák (Prague). This material comprised a blocky phase (mainly hammarite) at one end, and a fibrous phase (bismuthinite–pekoite intergrowth) at the other. During identification of these two major components by Weissenberg techniques, it was observed that the films of the poorly crystallized bismuthinite–pekoite show evidence of another set of reflections, more or less in the background. These reflections are somewhat sharper than the very diffuse reflections due to the bismuthinite–pekoite. It was also apparent from the films that a crystallographically unique direction in this minor phase (a crystal axis) is subparallel in orientation to the 4-Å axis of the bismuthinite–pekoite intergrowth. This phase was considered a new Bi-sulfosalt mineral.

Several crystals of this mineral were separated, but most of them are intergrown with bismuthinite–pekoite. However, one crystal of the mineral was found that showed reasonable diffraction-characteristics because of the relatively small amount of bismuthinite–pekoite still attached to it or intergrown with it. Unfortunately, the X-ray reflections were found to be quite diffuse, and suffered from absorption due to the thin plate-like nature of the crystal; also some elongate background-type streak-

TABLE 1. CHEMICAL AND CRYSTALLOGRAPHIC DATA FOR PADERAITTE

Space group	: $P2_1/m$	Radiation	: $\text{CuK}\alpha$
Unit cell	: $a = 28.44(8) \text{ \AA}$	μ	: 1349
	$b = 3.90(3) \text{ \AA}$		
	$c = 17.55(8) \text{ \AA}$	Total no. of	
	$\beta = 106.0(2)^\circ$	reflections	: 1723
D(calc)	: 6.91		
Z	: 2	Derived formula:	$\text{Cu}_{5.9}\text{Ag}_{1.3}\text{Pb}_{1.6}\text{Bi}_{11.2}\text{S}_{22}$

ing was noted due to the fibrous bismuthinite–pekoite. The X-ray-diffraction data, together with the EPMA results, indicated that this was in fact a new mineral sulfosalt. Attempts to extract better crystals were not successful, so that it was decided to collect data from this crystal and to attempt a structure solution.

The unit cell was determined from 2-circle diffractometer measurements to be a 28.44(8), b 3.90(3), c 17.55(8) Å, β 106.0(2)° (Table 1). No systematic extinctions were observed on the Weissenberg films collected around the 4-Å axis, allowing the space groups $P2_1/m$ ($P2_1$) or $P2/m$ ($P2$). Reflections with $k = 0,2$ were observed to have the same distribution of intensity, which indicates that all the atoms in the structure would lie in planes normal to b , separated by half the repeat distance of 4 Å. Diffraction measurements of $0k0$ reflections using the 2-circle diffractometer suggested that only those reflections with $k = 2n$ are present, so that the alternatives in space group reduced to $P2_1/m$ and $P2_1$. Of these, $P2_1/m$ was considered the more likely, and a satisfactory solution of the structure was eventually completed using this space group.

Intensity data were collected with $\text{CuK}\alpha$ radiation using ω -scans performed with a 2-circle Stoe single-crystal diffractometer. Numerical absorption-corrections for the small ($0.01 \times 0.15 \times 0.07$ mm) crystal were applied (Sheldrick 1976). The discrepancy between equivalent reflections on each level of data was ~6%, but was accepted as reasonable owing to the rather moderate quality of the data.

Intensity corrections for Lorentz and polarization effects and all subsequent computing were done on a VAX computer using the SHELX76 library of programs.

STRUCTURE DETERMINATION AND REFINEMENT

It was recognized that the unit cell of paderaitite has a simple geometrical relationship to that of hodrushite (Kupčík & Makovický 1968), which results in almost equal volumes of the cells (Fig. 1). The unit-cell contents of paderaitite were therefore assumed to be $2 \times M_{20}\text{S}_{22}$, where M implies (Ag,Cu), Pb and Bi (cf. hodrushite $4 \times$

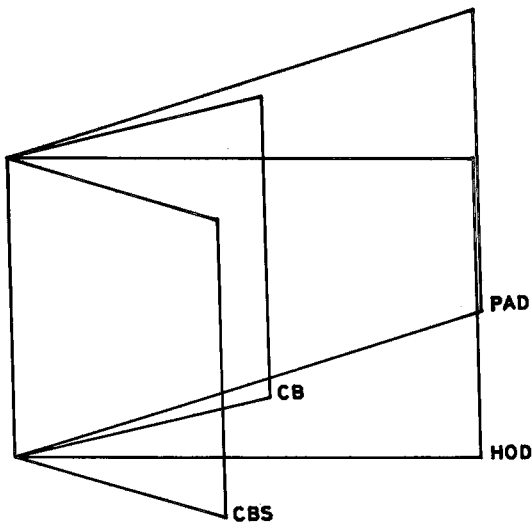


FIG. 1. Relationship between the unit cells of cuprobismutite-related phases. [Projection is onto (010)]. The cells are labeled at their bottom right-hand corners. PAD paderaitite, HOD hodrushite, CB cuprobismutite, CBS $\text{Cu}_4\text{Bi}_5\text{S}_{10}$. The vertical axis is the ~17.5 Å axis that is common to all structures.

TABLE 2. UNIT-CELL DIMENSIONS OF CUPROBISMUTITE RELATED STRUCTURES

Phase	Space group	Cell dimensions (Å)			
$\text{Cu}_4\text{Bi}_5\text{S}_{10}$	C2/m	a = 17.54	b = 3.93	c = 12.85	$\beta = 108.0$
Cuprobismutite	C2/m	a = 17.52	b = 3.91	c = 15.24	$\beta = 101.3$
Paderaitite	F2 ₁ /m	c = 17.55	b = 3.90	a = 28.44	$\beta = 106.0$
Hodrushite	A2/m	c = 17.58	b = 3.93	a = 27.21	$\beta = 92.2$

$\text{MeCu}_4\text{Bi}_5\text{S}_{11}$ where Me is $\sim\text{Bi}$). Cuprobismutite (Ozawa & Nowacki 1975) and $\text{Cu}_4\text{Bi}_5\text{S}_{10}$ (Mariolacos *et al.* 1975) have already been related to hodrushite (Mariolacos *et al.* 1975), as indicated in Table 2 and Figure 1. The common feature of all of these structures was observed to be the so-called C-layer. This type of layer is named after cuprobismutite; the term is used in order to simplify the descriptions that follow. H-layer (*i.e.*, hodrushite-like layer) is not used (in any event) to avoid confusion with the H- and T-layers of Makovicky (1981), which are prevalent in bismuth-lead sulfosalts (*cf.* junoite-type structures; Mumme 1975, Makovicky 1981).

Single to multiple octahedral layers of $(111)_{\text{PbS}}$ with pseudo-hexagonal sulfur co-ordination at the surface are called H-layers (Makovicky 1981) and represent one of the basic types of layers that build up the structures of the Pb-Bi-(Ag-Cu)-sulfosalts. The other main type of layer is the T-layer, composed of $(100)_{\text{PbS}}$ layers with pseudotetragonal sulfur co-ordination at the surfaces. These are the two kinds of regularly alternating layers that comprise the crystal structure of cannizzarite and its homologues (Matzat 1979).

The C-layer is composed of pairs of Bi_2S_7 and CuS_4 groups linked as shown in Figure 2, with

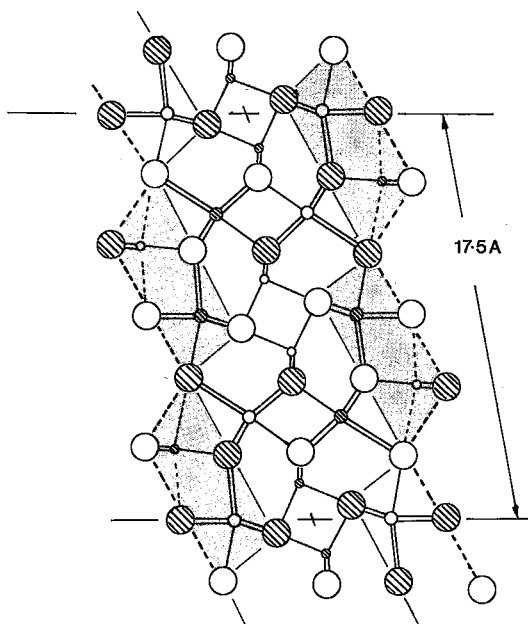


FIG. 2. The C-layer (cuprobismutite-type layer) that determines the 17.5 Å repeat in $\text{Cu}_4\text{Bi}_5\text{S}_{10}$, hodrushite and paderaitite. See text for description. In order of decreasing size, the circles denote S, Pb and Bi, Cu and Ag. Open circles at $\frac{1}{4}$, shaded circles at $\frac{3}{4}$.

$[\text{CuBiS}_{10}]$ lozenges attached to the sides in *en échelon* fashion; it determines the ~ 17.5 -Å axis, which is common to all the structures mentioned in Table 2. This structural layer was therefore assumed to be a feature of paderaitite, and models were based upon

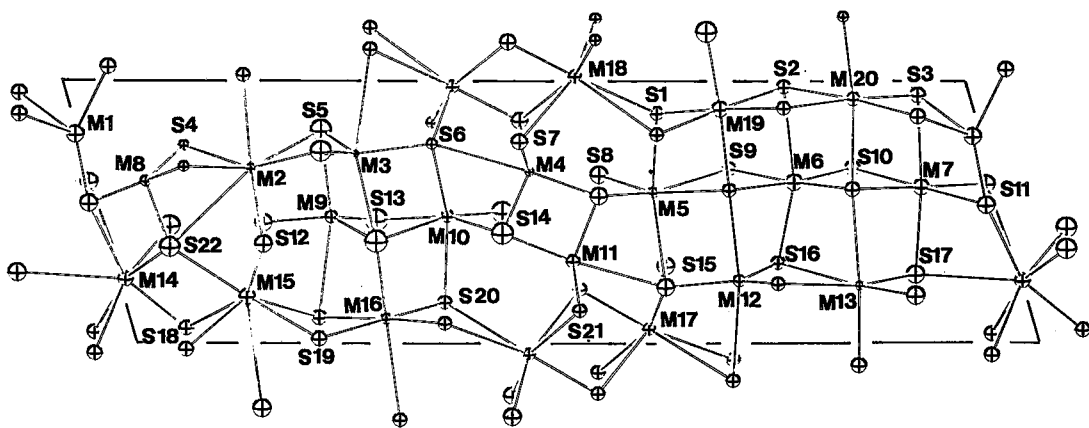


FIG. 3a. Asymmetric unit of the crystal structure of paderaitite. ORTEP drawing with all the atoms refined isotropically. Projection, along a direction close to $[010]$, is rotated 10° about $[100]$ to avoid superposition. \bar{b} points down into the page.

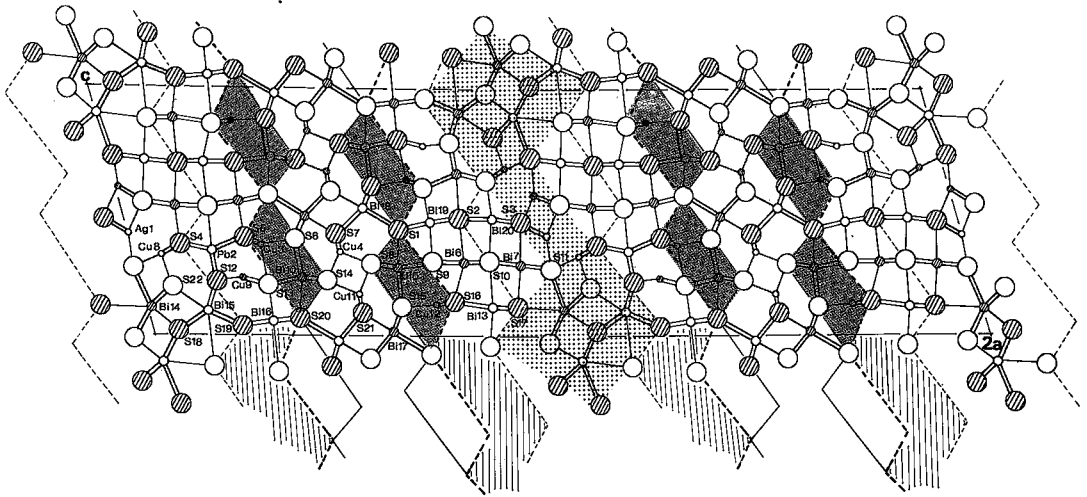


FIG. 3b. Crystal structure of paderaitite projected along [010]. For notation see Figure 2. Two unit cells are drawn to illustrate the relationship between the C-layers (see text: CuBiS_{10} lozenges are close-stippled) and the D-layers (hoderushite H-like layers: incorporating central, joined T blocks, open stippled).

its presence (in its several possible positions) as an entity in the structure.

TABLE 3. ATOMIC PARAMETERS AND ISOTROPIC TEMPERATURE-FACTOR COEFFICIENTS FOR PADERAITITE

Atom	Occup.	x	y	z	U
M1	Ag	0.0004(15)	0.25	0.4125(23)	0.0258(99)
M2	Pb	0.1810(5)	0.25	0.3400(8)	0.0074(34)
M3	Cu	0.3058(29)	0.25	0.3679(46)	0.0484(250)
M4	Cu	0.4937(14)	0.25	0.3413(23)	0.0013(30)
M5	Bi	0.6190(4)	0.75	0.2756(7)	0.0023(28)
M6	Bi	0.7740(6)	0.75	0.2937(9)	0.0127(38)
M7	Bi	0.9187(6)	0.75	0.2819(10)	0.0166(41)
M8	Cu	0.0514(16)	0.25	0.3068(24)	0.0051(29)
M9	Cu	0.2467(17)	0.75	0.2191(26)	0.0075(36)
M10	Bi	0.3811(5)	0.75	0.2286(8)	0.0069(39)
M11	Cu	0.5123(19)	0.25	0.1633(29)	0.0027(85)
M12	Cu	0.6976(17)	0.25	0.1232(22)	0.0037(75)
M13	Bi	0.8210(4)	0.25	0.1185(7)	0.0025(35)
M14	Bi	0.0048(5)	0.75	0.1062(8)	0.0011(34)
M15	Bi	0.1349(6)	0.25	0.0956(9)	0.0146(41)
M16	Bi	0.2824(5)	0.25	0.0552(7)	0.0009(30)
M17	Bi	0.5694(5)	0.75	0.0150(8)	0.0045(33)
M18	Bi	0.4299(4)	0.75	0.4813(7)	0.0047(35)
M19	Bi	0.7203(5)	0.25	0.4613(8)	0.0090(51)
M20	Bi	0.8768(5)	0.25	0.4784(8)	0.0011(31)
S1	S	0.6522(39)	0.75	0.4267(61)	0.0398(280)
S2	S	0.7938(46)	0.75	0.4708(71)	0.0249(320)
S3	S	0.9400(53)	0.75	0.4800(84)	0.0188(464)
S4	S	0.0984(26)	0.75	0.3656(40)	0.0050(150)
S5	S	0.2646(28)	0.75	0.3858(44)	0.0071(130)
S6	S	0.3886(26)	0.25	0.3933(39)	0.0035(159)
S7	S	0.4998(31)	0.75	0.4086(48)	0.0147(305)
S8	S	0.5683(31)	0.25	0.2951(49)	0.0034(316)
S9	S	0.7062(30)	0.25	0.2846(47)	0.0035(280)
S10	S	0.8388(52)	0.25	0.2854(82)	0.0617(445)
S11	S	0.9798(36)	0.25	0.2722(56)	0.0213(363)
S12	S	0.1662(22)	0.75	0.2042(33)	0.0009(58)
S13	S	0.2990(32)	0.25	0.1996(48)	0.0007(63)
S14	S	0.4449(36)	0.25	0.2217(56)	0.0145(209)
S15	S	0.6096(26)	0.25	0.1093(41)	0.0046(199)
S16	S	0.7340(31)	0.75	0.1334(48)	0.0034(179)
S17	S	0.8799(42)	0.75	0.1215(64)	0.0308(339)
S18	S	0.0602(28)	0.75	0.0099(43)	0.0009(39)
S19	S	0.2059(43)	0.75	0.0375(67)	0.0216(214)
S20	S	0.3505(26)	0.75	0.0714(40)	0.0008(46)
S21	S	0.5027(24)	0.75	0.0898(37)	0.0015(63)
S22	S	0.0712(29)	0.25	0.1818(45)	0.0051(79)

The structure was solved by the technique of Fourier and structure-factor recycling, keeping the C-layer as a basic unit and paying attention to the Patterson vector map. The main factor leading to confusion (which could only be recognized in the last stages of the solution) was the presence of a pseudocentre of symmetry in the structure at $(\frac{1}{2} \frac{1}{4} \frac{1}{4})_{\text{Pad}}$ (Fig. 3a). This caused a doubling of many of the Fourier peaks during the structure solution.

In the final analysis, 20 metal and 22 sulfur atoms were found in the half cell. Based on this number of sulfur atoms, the empirical formula derived from EPMA is $\text{Cu}_{5.5}^+ \text{Ag}_{1.1} \text{Pb}_{1.2} \text{Bi}_{11.0} \text{S}_{22}$, $\Sigma M = 18.8$. If the empirical formula is accepted to indicate less than 20 metal atoms in the half-cell (*i.e.*, 18.8), then up to 3.5 Cu^{2+} atoms can be invoked if all six copper sites are fully occupied. However, whereas the data are not good enough to test for partial occupancy in copper (or other metal) sites, there does not seem to be any reason for partial occupancy of any position, based on the bonding arrangement deduced for paderaitite. The discrepancy in the number of metal atoms was therefore assumed to be due to unavoidable errors in the microprobe data related to the nature of the intergrowth. The closest ideal formula for $M_{20}\text{S}_{22}$ stoichiometry was estimated to be $\text{Cu}_6^+ \text{AgPb}_2 \text{Bi}_{11} \text{S}_{22}$, very close to the empirical formula, but with somewhat more than the measured Pb content (10.6 wt. % Pb instead of the measured 6.71 wt. %). Scaling up the empirical formula to $\Sigma M = 20$ yielded $\text{Cu}_{5.8} \text{Ag}_{1.2} \text{Pb}_{1.2} \text{Bi}_{11.7} \text{S}_{22}$ as the appropriate composition, but this adds a small discrepancy in charge balance if one assumes that all the copper is present as Cu^{1+} . The formula that

satisfied the measured composition, results of the structural analysis, and charge-balance considerations based on Cu^{1+} is $\text{Cu}_{5.9}\text{Ag}_{1.3}\text{Pb}_{1.6}\text{Bi}_{11.2}\text{S}_{22}$. The structure refinement did not contradict this formula.

Neutral scattering factors were used (International Tables for Crystallography, Volume 5, 1984) with corrections for anomalous dispersion (Ibers & Hamilton 1962) for Ag, Cu, Pb and Bi. Refinement of the structure with isotropic temperature-factors for all atoms converged to give $R = 0.17$. As mentioned, all of the crystals of paderaitite studied contain, to some extent, intergrown, fine-grained, poorly crystalline pekoite. This defect, together with the high absorption and the irregular shape of the crystal fragment used for data collection, explains why a better overall agreement was not achieved. Atom positions and isotropic temperature-factors are given in Table 3.

DESCRIPTION OF STRUCTURAL FEATURES

The crystal structure of paderaitite is composed of two types of layer. One of these is the *C*-layer, already referred to above, which incorporates on

either side the attached lozenges of $[\text{CuBiS}_{10}]$ (Fig. 3b). The other is a wider layer of rather mixed nature that contains Bi atoms in octahedral and trigonal prismatic co-ordinations, Pb atoms in trigonal prismatic co-ordination, and Cu in trigonal to tetrahedral co-ordination. The general disposition of this layer in the structure is somewhat reminiscent of the thicker layers found in members of the pavonite homologous series, pavonite and more particularly benjaminite (Makovicky & Mumme 1979). In benjaminite, the thicker layer is composed of 7-octahedra-wide cutouts from the galena structure aligned parallel to $(\bar{1}13)$ of the galena submotif, with $[110]_{\text{PbS}}$ twice the *b* parameter of benjaminite. These are the (sheared) *H*-layers referred to by Makovicky (1981) in his interpretation of the pavonite series of minerals as sheared-layer structures.

In paderaitite, this type of layer is much more complicated. It starts at each edge as a sheared pseudo *H*-layer. It is not ideal *H*-type because two of the polyhedra (Pb2 and Cu9) in this edge are not true octahedra although they maintain the appearance of octahedra in projection. Inasmuch as this layer resembles a sheared *H*-layer similar to those found

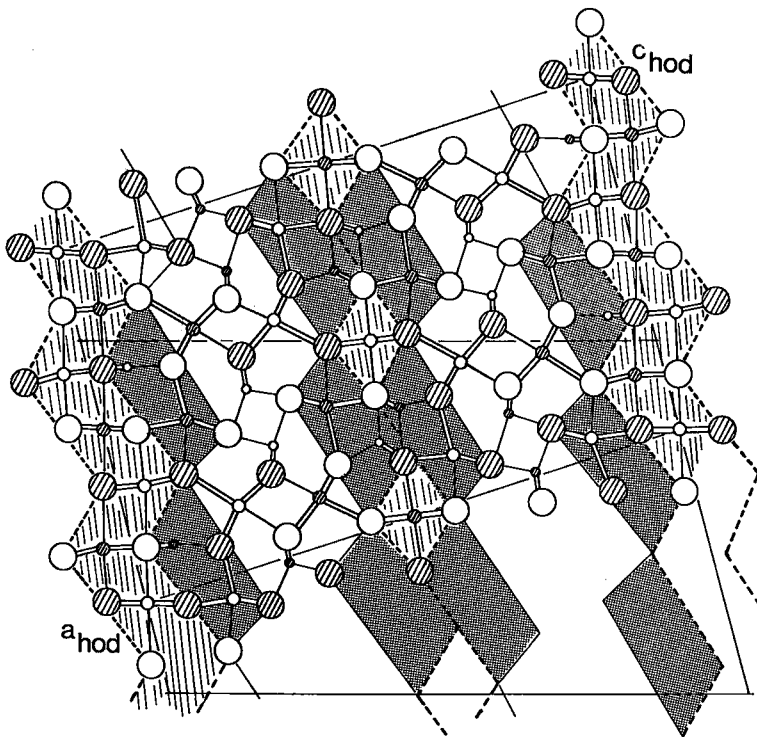


FIG. 4. Crystal structure of hodrushite projected along $[010]$. For notation, see Figure 2. The *H*-layers are hatched with vertical lines (see text). The relationship with the paderaitite cell is illustrated.

in the pavonite series (and also the lillianite homologues, although there they occur in mirror-related configurations), it is aligned parallel to $(331)_{\text{PbS}}$. Therefore its direction of extended growth lies almost normal to that observed for the thicker layers in the members of the pavonite series.

Through the centre of the slabs there are 2×2 *T*-blocks ($M14 \times 2$, $M15 \times 2$) and an interspace containing groups 1×4 of Cu, and Ag ($\text{Cu}8 \times 2$, $\text{Ag}1 \times 2$) atoms in trigonal to tetrahedral coordinations. There is a short *H/T* contact that is two units long maintained between the ideal *H* and *T* parts of the layer that occur in this region, *i.e.*, ($M7$, $M13$)/($M14$, $M15$).

The other layer in paderaitite, the so-called *C*-layer, is virtually the same as those in hodrushite, cuprobis-

mutite and $\text{Cu}_4\text{Bi}_5\text{S}_{10}$. Even the $[\text{CuBiS}_{10}]$ lozenges, although not identical to those found in hodrushite, are incorporated, as is also the case in cuprobismutite and $\text{Cu}_4\text{Bi}_5\text{S}_{10}$. Hodrushite is actually made up of two of these *C*-layers, each of which forms between peripheral unit-width galena-like *H*-layers (Fig. 4). Repeated shearing by $\sim \frac{1}{2}a$ along $[001]_{\text{Hod}}$ at the *c* unit-cell interval has resulted in the elimination of another such peripheral *H*-layer. All that remains of it are the single island-like octahedra at $(00\frac{1}{2})_{\text{Hod}}$ and $(\frac{1}{2}\frac{1}{2}\frac{1}{2})_{\text{Hod}}$ (*cf.* also $\text{Cu}_4\text{Bi}_5\text{S}_{10}$, Fig. 5).

Bond-length calculations (Table 4) show that $M5$, $M6$, $M7$, $M10$, $M13$, $M14$, $M15$, $M16$, $M17$, $M18$, $M19$, and $M20$ all have minimum bond-lengths less than 2.70 \AA , with $[1 + 2]$ short bonds set apart from

TABLE 4. BOND LENGTHS AND ANGLES IN PADERAITITE

Interatomic distances					Bond angles				
Ag1 - S3	2.16(4) x1	Cu11 - S21	2.31(4) x2	S3 - Ag1 - S11	144.8	S21 - Cu11 - S21	115.0		
S11	2.37(7) x1	S14	2.41(9) x1	S3' - Ag1 - S3"	79.6	S21 - Cu11 - S14	104.6		
S3'	3.05(7) x2	S8	2.42(8) x1			S21 - Cu11 - S8	118.6		
		S15	3.16(9) x1			S8 - Cu11 - S14	89.1		
Pb2 - S5	3.01(5) x2			S4 - Pb2 - S12	124.2				
S12	3.02(5) x2	Cu12 - S16	2.19(4) x2	S5 - Pb2 - S12	123.9	S16 - Cu12 - S16'	125.7		
S4	3.17(5) x2	S15	2.45(7) x1	S2 - Pb2 - S4	79.4	S16 - Cu12 - S15	117.1		
S2	3.20(6) x1	S9	2.78(7) x1	S2 - Pb2 - S5	77.8	S16 - Cu12 - S9	90.6		
				S4 - Pb2 - S4'	76.0				
		Bi13 - S17	2.57(5) x2	S5 - Pb2 - S5'	80.8	S16 - Bi13 - S16'	74.6		
		S19	2.63(5) x1	S12 - Pb2 - S12'	80.5	S17 - Bi13 - S17'	99.1		
		S10	2.84(8) x1			S10 - Bi13 - S16	80.7		
		S16	3.22(5) x2			S10 - Bi13 - S17	92.8		
Cu3 - S6	2.27(7) x1			S5 - Cu3 - S5'	112.9	S19 - Bi13 - S16	94.3		
S5	2.34(5) x2			S5 - Cu3 - S6	120.2	S19 - Bi13 - S17	91.3		
S13	2.91(7) x1			S5 - Cu3 - S13	103.9				
Cu4 - S14	2.17(7) x1	Bi14 - S18	2.68(6) x1	S7 - Cu4 - S7	119.1	S18 - Bi14 - S22	82.6		
S7	2.26(4) x2	S22	2.78(5) x2	S7 - Cu4 - S14	116.2	S18 - Bi14 - S18'	86.5		
S8	2.47(7) x1	S18	3.01(6) x2	S7 - Cu4 - S8	102.8	S18' - Bi14 - S18"	80.9		
		S17	3.64(6) x1	S8 - Cu4 - S14	93.5				
		S11	3.73(6) x2						
Bi5 - S8	2.50(4) x2			S1 - Bi5 - S8	85.4				
S1	2.56(7) x1	Bi15 - S22	2.66(6) x1	S1 - Bi5 - S9	83.5	S22 - Bi15 - S12	75.1		
S9	3.12(5) x2	S12	2.70(4) x2	S8 - Bi5 - S8'	102.3	S22 - Bi15 - S18	78.9		
S15	3.46(5) x2	S18	3.00(4) x2	S9 - Bi5 - S9'	77.2	S18 - Bi15 - S18'	81.2		
		S19	3.17(7) x2			S12 - Bi15 - S12'	92.5		
Bi6 - S10	2.71(7) x2			S2 - Bi6 - S9	89.3				
S9	2.72(5) x2	Bi16 - S13	2.45(6) x1	S2 - Bi6 - S10	96.7	S13 - Bi16 - S19	92.1		
S16	2.73(6) x2	S20	2.71(4) x2	S16 - Bi6 - S9	81.5	S13 - Bi16 - S20	87.9		
S2	3.00(7) x1	S19	2.87(7) x2	S16 - Bi6 - S10	92.5	S19 - Bi16 - S19'	85.5		
		S16	3.21(7) x1	S9 - Bi6 - S9	91.8	S20 - Bi16 - S20'	92.1		
				S10 - Bi6 - S10	91.9				
		Bi17 - S21	2.59(4) x1	S17 - Bi7 - S10	86.0	S21 - Bi17 - S21'	80.9		
Bi7 - S11	2.65(6) x2	S15	2.61(4) x2	S17 - Bi7 - S11	91.1	S21 - Bi17 - S15	86.1		
S17	2.73(6) x1	S21	3.05(5) x2	S10 - Bi7 - S10'	80.8	S21' - Bi17 - S21"	79.4		
S10	3.01(8) x2	S20	3.6(6) x2	S11 - Bi7 - S11'	94.8	S15 - Bi17 - S15'	96.8		
S3	3.30(8) x1								
		Bi18 - S6	2.56(4) x2						
Cu8 - S11	2.23(7) x1	S7	2.64(7) x1	S4 - Cu8 - S4'	114.1	S7 - Bi18 - S6	89.4		
S22	2.29(6) x1	S7	3.07(7) x2	S4 - Cu8 - S11	115.9	S7 - Bi18 - S7'	81.8		
S4	2.32(4) x2	S1	3.73(7) x2	S4 - Cu8 - S22	105.3	S7' - Bi18 - S7"	79.0		
Cu9 - S12	2.23(6) x1	Bi19 - S5	2.60(4) x1	S13 - Cu9 - S13'	100.7	S5 - Bi19 - S1	97.9		
S13	2.53(5) x2	S1	2.70(6) x2	S13 - Cu9 - S12	127.3	S5 - Bi19 - S2	91.7		
S5	2.83(7) x1	S2	2.83(7) x2			S1 - Bi19 - S1'	92.7		
S19	3.08(8) x2	S9	3.02(6) x1			S2 - Bi19 - S2'	87.1		
						S9 - Bi19 - S1	83.4		
Bi10 - S20	2.65(4) x1			S20 - Bi10 - S13	78.8	S9 - Bi19 - S2	87.0		
S14	2.69(5) x2	Bi20 - S4	2.63(4) x1	S20 - Bi10 - S14	89.2	S4 - Bi20 - S2	91.4		
S13	2.98(5) x2	S3	2.65(8) x2	S13 - Bi10 - S13'	81.9	S4 - Bi20 - S3	90.4		
S6	3.44(5) x2	S2	3.04(8) x2	S14 - Bi10 - S14'	93.0	S2 - Bi20 - S2'	79.9		
		S10	3.25(7) x1			S3 - Bi20 - S3'	94.9		
						S10 - Bi20 - S2	85.6		
						S10 - Bi20 - S3	92.4		

Estimated standard deviation for bond angles is 0.9° .

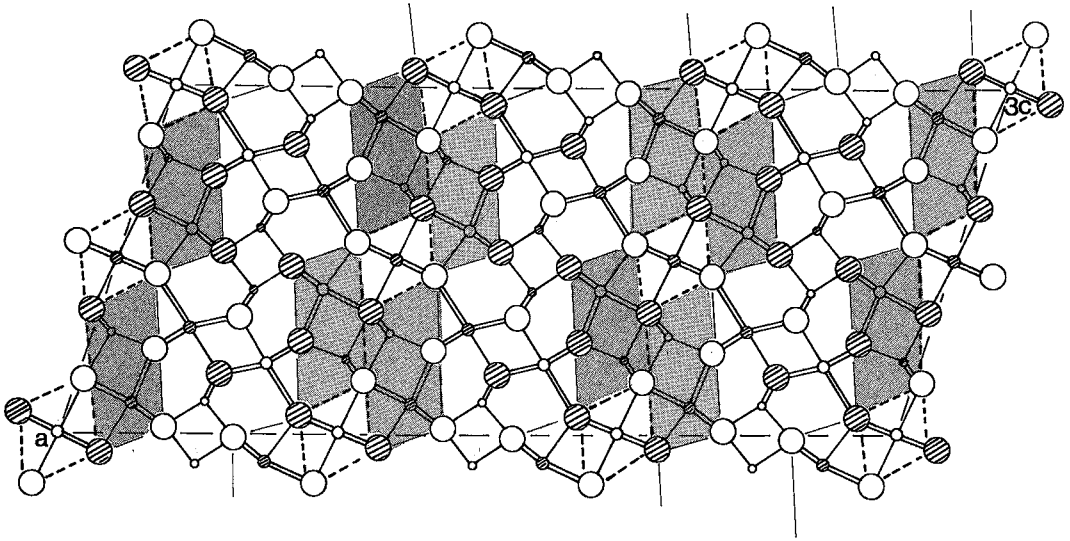


FIG. 5. Crystal structure of $\text{Cu}_4\text{Bi}_5\text{S}_{10}$ projected along $[010]$. The figure incorporates three unit-cells joined along c . For notation, see Figure 2.

the remaining longer bond-interactions, a situation typical of Bi. $M2$ (minimum bond equals 3.02 \AA) is the only site with all-round longer bonding-interactions typical of Pb. Therefore, these are the sites (respectively) of the Bi and Pb atoms. There are

11.2 Bi and 1.6 Pb atoms indicated by the microprobe analysis if the chemical formula is normalized to 22S , so that the bonding arrangements mentioned above confirm the overall analytical formula. Of the sites that accommodate the Cu atoms,

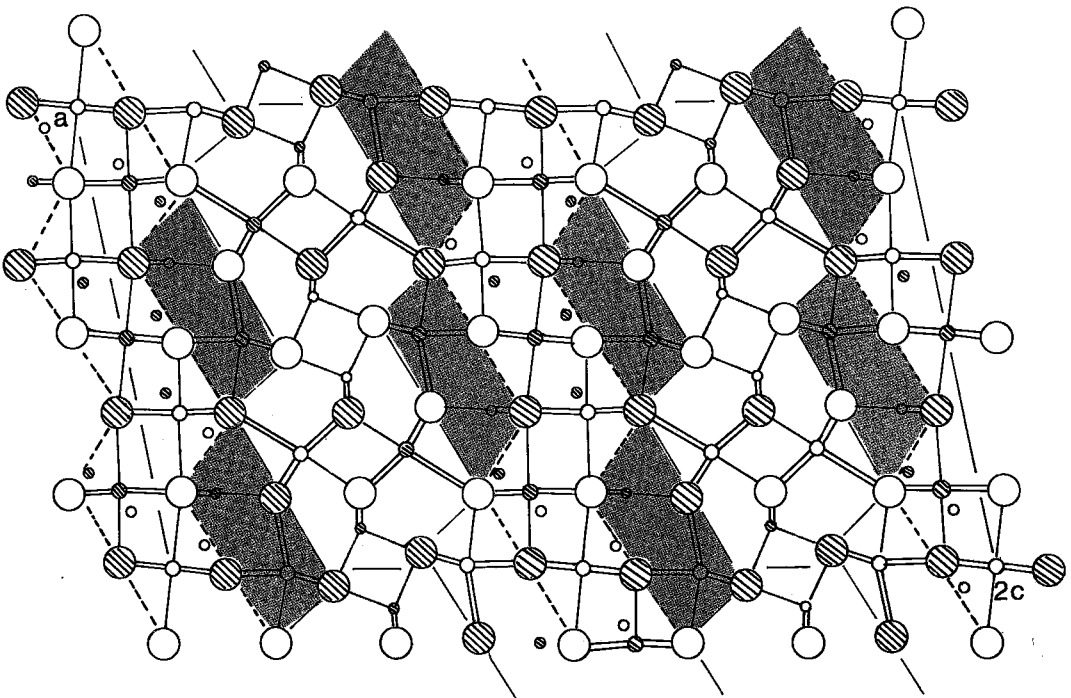


FIG. 6. Crystal structure of cuprobismutite projected along $[010]$. For notation, see Figure 2.

M8 and *M12* are trigonal, *M3* and *M9* are distorted trigonal to tetrahedral, and *M4* and *M11* are distorted tetrahedral. *M1* is a distorted tetrahedral site that primarily contains Ag. The co-ordination of *M1* (or Ag1) tends between a kinked linear S11–Ag1–S3 configuration, which is usual for Ag, to a distorted tetrahedron when the two bonds to S3 and S3' are included in the bonding arrangement.

Overall, therefore, the results of the structure analysis support closely the empirical formula obtained by EPMA. There is some partial substitution of the 12 bismuth sites by the 0.3Ag and the 0.6Pb that cannot be accommodated in *M1* (Ag1) and *M2* (Pb2), but it is not obvious from the results of the refinement which of these or other sites contain the Ag and Pb.

THE CUPROBISMUTITE SERIES OF STRUCTURES

The relationship between hodrushite and paderaitite has been discussed above. In fact, hodrushite and paderaitite, together with cuprobismutite, are all related to, and derived from, the $\text{Cu}_4\text{Bi}_5\text{S}_{10}$ crystal structure.

In $\text{Cu}_4\text{Bi}_5\text{S}_{10}$, the *C*-layers are joined as shown in Figure 5. It is seen that the sheared join referred to above in hodrushite (Fig. 4) is repeated between each *C*-layer in $\text{Cu}_4\text{Bi}_5\text{S}_{10}$. In hodrushite, the sheared join alternates with the *H*-layer of unit width, whereas in cuprobismutite (Fig. 6) it is completely eliminated, and unit-width (distorted and Cu-containing) *H*-layers alternate with the *C*-layers. There is a jump in the size of the approximate *H* layers to paderaitite (Fig. 3b), where the *C*-layers alternate with now distorted *H*-like layers, that approximate to 4 octahedra wide. A preliminary nomenclature is suggested (Table 5), based on the layer disposition encountered here and described above. In this notation *C* is used for the *cuprobismutite*-type layer in the structure; *D* (after hodrushite) is used for the *hodrushite*-like *H*-layer. $\text{Cu}_4\text{Bi}_5\text{S}_{10}$ becomes ${}^1\text{C}^0\text{D}$ or ${}^\infty\text{C}$ (that is, *C*-layers only, sheared together); hodrushite ${}^2\text{C}^1\text{D}$ (two *C*-layers sheared together, alternating with a unit-width hodrushite *H*-like layer); cuprobismutite ${}^1\text{C}^1\text{D}$ and paderaitite ${}^1\text{C}^4\text{D}$.

TABLE 5. LAYER DISPOSITIONS IN CUPROBISMUTITE-SERIES PHASES

Member	C-Layer width	P-Layer width	Layer configuration	Nomenclature symbol
$\text{Cu}_4\text{Bi}_5\text{S}_{10}$	∞	0	-1C-(0D)-1C-(0D)-1C-	${}^1\text{C}^0\text{D}({}^\infty\text{C})$
Cuprobismutite	1	1	-1D-1C-1D-1C-1D-	${}^1\text{C}^1\text{D}$
Paderaitite	1	4	-4D-1C-4D-1C-4D-	${}^1\text{C}^4\text{D}$
Hodrushite	2	1	-1C-1C-1D-1C-1C-	${}^2\text{C}^1\text{D}$

The crystal structures are all apparently $\text{Cu}_4\text{Bi}_5\text{S}_{10}$ -related, this compound having the simplest of the known structures in the series and the one upon which they are all based. However, this compound has not yet been reported in nature, and it is reasonable to expect that the mineral series be named after a member that is a mineral. The best choice at this stage is the next, least complicated, mineral member of the series, which happens to be cuprobismutite. It is suggested, therefore, that the structural series become known as the *cuprobismutite series*. This choice of name is all the more acceptable because cuprobismutite was the first mineral discovered of the series as it is known to date.

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