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New structural data reveal benleonardite to be a member of the pearceite-polybasite group

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ABSTRACT

The determination of the crystal structure of benleonardite (S.G. $P\bar{3}m1$; $R = 0.0321$ for 1250 reflections and 102 parameters; refined formula $Ag_{15.0}Cu_{1.0}Sb_{1.58}As_{0.42}S_{7.03}Te_{3.97}$) obtained using data from a gem-quality, untwinned crystal recovered from the type material, revealed that benleonardite exhibits the structure observed for minerals of the pearceite-polybasite group. The structure consists in the stacking of $[Ag_6(Sb,As)_2S_6Te]^{2-}$ *A* and $[Ag_9Cu(S,Te)_2Te_2]^{2+}$ *B* layer modules in which (Sb,As) forms isolated SbS_3 pyramids typically occurring in sulfosalts, Cu links two (S,Te) atoms in a linear coordination, and Ag occupies sites with coordination ranging from quasi linear to almost triangular. The silver d^{10} ions are found in the *B* layer module along two-dimensional diffusion paths and their electron densities, which are evidenced by means of a combination of a Gram-Charlier development of the atomic displacement factors and a split model. In the structure, two S-positions are completely replaced by Te (i.e., Te3 and Te4) and one for one half [S1: $S_{0.514(9)}Te_{0.486}$],

whereas S2 is completely filled by sulfur. This distribution reflects on the crystal-chemical environments of the different cations. On the basis of information gained from this characterization, the crystal-chemical formula of benleonardite was revised according to the structural results, yielding $Ag_{15}Cu(Sb,As)_2S_7Te_4$ (Z = 1) instead of $Ag_8(Sb,As)Te_2S_3$ (Z = 2) as previously reported. Thus, the mineral must be considered a member of the pearceite-polybasite group. A recalculation of the chemical data listed in the scientific literature for benleonardite according to the structural results obtained here leads to an excellent agreement.

***Keywords*:** benleonardite, crystal structure, pearceite, polybasite, Ag-sulfosalt, Bambolla.

INTRODUCTION

Benleonardite, ideally $Ag_8(Sb,As)Te_2S_3$, was identified as a new mineral species by Stanley *et al.* (1986) by studying ore minerals collected from the spoil tips of the abandoned Bambolla mine, Moctezuma, Sonora (Mexico). It was described as forming thin black powdery crusts (1–2 mm thick) with native silver, acanthite, hessite, cervelleite, pyrite and sphalerite. By means of powder-diffraction X-ray investigations, benleonardite was originally given as tetragonal with a = 6.603(5) and c = 12.726(6) Å, but the crystal structure remained unknown. Although benleonardite-like minerals have been found in several occurrences [Zyranov gold deposit, Russia (Aksenov *et al.*, 1969), Ivigtut cryolite deposit, Greenland (Karup-Møller and Pauly, 1979), Gies gold–silver telluride deposit, Montana (Zhang and Spry, 1994; Spry and Thieben, 1996), Mayflower gold–silver telluride deposit, Montana (Spry and Thieben, 1996), Um Samiuki Zn–Pb–Cu–Ag volcanogenic massive sulfide deposit, Egypt (Helmy *et al.*, 1999; Pals and Spry, 2003), black smoker chimney fragments from the Yaman Kasy massive sulfide deposit, southern Urals (Herrington *et al.*, 1998)], no additional structural investigations have been reported in the literature so far.

The simplified formula for benleonardite was given as $Ag_8SbTe_2S_3$ by Stanley *et al.*, (1986). However, such a chemical formula is unbalanced, which is a very unusual characteristic when dealing with Ag-sulfosalts (Bindi and Evain, 2007; Moëlo *et al.*, 2008). Moreover, chemical data reported for benleonardite (and benleonardite-like minerals) in the literature show a general deficiency in Ag+Cu (i.e., <8 atoms per formula unit) coupled with an excess in S (i.e., 3 to 4 atoms per formula unit) when normalized on the basis of 14 atoms, thus reinforcing the suggestion by Spry and Thieben (1996) that the formula proposed by Stanley *et al.* (1986) needs to be modified.

Here we present the determination of the crystal structure of benleonardite obtained using data from a gem-quality, untwinned benleonardite crystal recovered from the type material. We show that benleonardite exhibits the structure observed for the minerals of the pearceite-polybasite group (Bindi *et al.*, 2006a, 2006b, 2007a, 2007b, 2007c, 2013; Bindi and Menchetti, 2009; Evain *et al.*, 2006a, 2006b).

THE HOLOTYPE

A crystal for the X-ray investigation was selected from the type material (catalogue number E.1161 BM 1985, 354). The specimen was collected by the late Alan Criddle on a field excursion to the Sonora Desert led by the late Sid Williams. It consists of black powdery crusts (1–2 mm thick) of benleonardite, acanthite, hessite and cervelleite together with gangue quartz and dolomite (Fig. 1). The hessite contains a vermiform or myrmekitic intergrowth of fine-grained cervelleite (pale-greenish-grey in Fig. 1). The assemblage occupies irregular fractures in a highly altered rock described by Williams (1982) as an intensely silicified rhyolitic vitrophyre.

X-RAY CRYSTALLOGRAPHY

A benleonardite crystal was hand-picked from a polished section of the type material, glued to a glass rod and used for the room temperature data collection, which was carried out on a Oxford Diffraction Xcalibur 3 diffractometer, fitted with a Sapphire 2 CCD detector (see Table 1 for details) using graphite-monochromatized Mo*K*α radiation (λ = 0.71069 Å). Because of the typical ionic conductivity observed in Ag-sulfosalts and the probable presence of twinning (see Bindi *et al.*, 2006a), a rather high sin(θ)/λ cutoff and a full sphere exploration were considered. Intensity integration and standard Lorentz-polarization correction were performed with the *CrysAlis* RED (Oxford Diffraction, 2006) software package. The program ABSPACK in *CrysAlis* RED (Oxford Diffraction, 2006) was used for the absorption correction.

The unit-cell found for the selected benleonardite crystal is trigonal (hexagonal setting), with a = 7.623(1) and c = 12.708(1) Å. The c-parameter is almost the same as that found by Stanley *et al.* (1986), 12.726(6) Å, and the a-parameter is related to that originally reported [i.e., 6.606(5) Å] by a factor of sin(120°) [i.e., 7.623 Å × sin(120°) = 6.602 Å], which explains the symmetry change from the trigonal to the tetragonal setting. The refined trigonal unit-cell obtained for benleonardite is very similar to that observed for minerals belonging to the pearceite-polybasite group (Bindi *et al.*, 2007a). Taking into account this similarity, the structure was refined in the space group $P\bar{3}m1$ using the program JANA2006 (Petříček *et al.*, 2006) starting from the atomic coordinates given by Bindi *et al.* (2007b) for the crystal structure of polybasite-*Tac*. The sites with partial (or total) substitution of S by Te were easily identified (i.e., S1, S3 and S4). To mimic the silver electron spreading along diffusion paths, up to third-order non-harmonic Gram-Charlier tensors were used for the Debye-Waller description of the Ag3, Ag4 and Ag5 atoms (Johnson and Levy, 1974; Kuhs, 1984).

Full site occupation (Sb/As and S1/Te1) was assured through constraints and the overall charge balance was ascertained. The final residual R is 0.0179 for 609 reflections [$I > 2\sigma(I)$] and $R = 0.0321$ for all 1250 unique reflections and 102 parameters.

Atomic parameters are reported in Tables 2 to 4, whereas bond distances are given in Table 5. Structure factors and CIF are deposited with the Principal Editor of Mineralogical Magazine at http://www.minersoc.org/pages/e_journals/dep_mat.html.

Unfortunately, the crystal used for the structural study was lost in an attempt to embed it in epoxy to get electron microprobe data. However, the final refined formula can be written as: $Ag_{15.00}Cu_{1.00}(Sb_{1.58}As_{0.42})S_{7.03}Te_{3.97}$, which is in good agreement with those reported by Stanley *et al.* (1986) for benleonardite from the type material, i.e. $Ag_{16.0\text{-}16.1}Cu_{0.0\text{-}0.1}Sb_{1.6\text{-}1.7}As_{0.4\text{-}0.6}S_{6.7\text{-}6.8}Te_{3.9\text{-}4.0}$.

DESCRIPTION OF THE STRUCTURE

On the whole, the benleonardite structure resembles that of the trigonal polytype (*Tac*) of polybasite (Bindi *et al.*, 2007b). It can be described as the succession, along the *c* axis, of two layer modules: a $[Ag_6(Sb,As)_2S_6Te]^{2-}$ *A* module layer and a $[Ag_9Cu(S,Te)_2Te_2]^{2+}$ *B* module layer (Fig. 2).

In the *A* module layer, Ag atoms (Ag1 and Ag2) are triangularly coordinated by S and Te atoms in a quasi-planar environment. Benleonardite represents the first member of the pearceite-polybasite group showing structural disorder also in the Ag positions of the *A* layer. The disorder has been modeled with two split Ag-positions (Ag1–Ag2 = 0.51 Å) with partial occupancy (Table 2). The (Sb,As) atoms are also in a threefold coordination, but in a trigonal pyramidal configuration. The $[Ag(S,Te)_3]$ and $[(Sb,As)S_3]$ subunits are linked together through corners to constitute the *A* module layer.

In the *B* module layer, the silver d^{10} cations are distributed along 2D diffusion paths, in a structure skeleton made of face-sharing tetrahedra (as in argyrodite-type ionic-conductor compounds; Boucher *et al.*, 1993) around the Cu atom (see Fig. 3). It is worth noting that the modes (maxima of density) observed in the diffusion paths do not correspond to the Ag refined positions (Ag3, Ag4 and Ag5) and that and the refined atomic positions do not lie along diffusion paths between modes, the Gram-Charlier expansion of the Debye-Waller factor providing the connecting density. For this reason, the refined Ag positions should not be used to calculate distances (although meaningful distances could be obtained with mode positions).

In the structure, two S-positions are completely replaced by Te (i.e., Te3 and Te4) and one for one half [S1: $S_{0.514(9)}Te_{0.486}$], whereas S2 is completely filled by sulfur. This distribution reflects on the crystal-chemical environments of the different cations. The Cu-S1/Te1 distance [2.317(4) Å] is much longer than both the Cu-S1/Se1' distance in selenopolybasite [2.199(2) Å – Evain *et al.*, 2006b] and that observed for Te-rich polybasite [2.201(2) Å; Bindi *et al.*, 2013], with an 'S1' occupation of $S_{0.91(1)}Te_{0.09}$. Although strongly enhanced (given the high amount of tellurium present in benleonardite), most of the metal–anion bond distances for the crystal studied here show a similar tendency to those in both Te-rich polybasite (Bindi *et al.*, 2013) and selenopolybasite (Evain *et al.*, 2006b).

Table 6 compares the X-ray powder pattern reported by Stanley *et al.* (1986) with that calculated using the structural parameters obtained in this study. Calculated and observed data are in very good agreement.

NOMENCLATURE REMARKS

The crystal structure of benleonardite is topologically identical to all compounds of the pearceite/polybasite group in their higher temperature form [i.e., 111 pearceite-type structure

(*Tac* polytype); Bindi *et al.*, 2007a]. The real difference is the presence of pure (Te3 and Te4) and partial (S1/Te1) Te-sites. Evain *et al.* (2006b) and Bindi *et al.* (2007d, 2013) already noted that these anion sites are the same where the S-for-(Se,Te) substitution occurs in selenopolybasite and Te-rich polybasite. However, the concentration of Te in benleonardite is much higher, almost dominating three structural sites. Bindi *et al.* (2013) suggested the possible existence of a "*telluropolybasite*" in nature. In this context, benleonardite clearly represents the missing "*telluropolybasite*" member of the pearceite-polybasite group. A recalculation of the chemical data listed in the scientific literature (Table 7) for benleonardite (and benleonardite-like minerals), according to the structural results obtained here, leads to an excellent agreement. Indeed, the mean values for the sums (Ag+Cu), (Sb+As) and (Te+S) in atoms per formula unit (when the data are normalized on the basis of 29 atoms) are 16.11(13), 1.98(19) and 10.91(22), in good accord with the $(Ag,Cu)_{16}(Sb,As)_2(S,Te)_{11}$ stoichiometry of the pearceite-polybasite minerals.

It is interesting to note that very high amounts of Te and Se substituting for S are always associated with low Cu contents and with disordered trigonal structures (*Tac* polytype). Such a feature was already observed and discussed by Evain *et al.* (2006b) and Bindi *et al.* (2013). Benleonardite exhibits this even more strongly, given the fact that some of the analyses given in Table 7 (corresponding to benleonardite and benleonardite-like minerals) show no appreciable concentrations of Cu. This fact seems to contradict what is known for pearceite-polybasite minerals, wherein copper is an essential element for the linearly-coordinated structural site of the *B* module layer. The case of benleonardite shows that the linearly coordinated structural site is able to accommodate larger amounts of silver than recognized previously, thus corroborating the suggestions of Bindi and Menchetti (2009) and raising the possibility that a mineral with Ag > Cu at this site deserves its own name.

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REFERENCES

Aksenov, V.S., Gavrilina, K.S., Litvinovich, A.N., Bespaev, K.H.A., Pronin, A.P., Kosyak, E.A. and Slyasarev, A.P. (1969) Occurrence of new minerals of silver and tellurium in ores of the Zyranov deposits in the Altai (in Russian). *Altai Izvestiya Akademiya Nauk Kazakh SSR, Seriya Geologicheskaya*, **3**, 74–78.

Bindi, L. and Evain, M. (2007) Gram-Charlier development of the atomic displacement factors into mineral structures: The case of samsonite, $Ag_4MnSb_2S_6$. *American Mineralogist*, **92**, 886–891.

Bindi, L., Evain, M. and Menchetti, S. (2006a) Temperature dependence of the silver distribution in the crystal structure of natural pearceite, $(Ag,Cu)_{16}(As,Sb)_2S_{11}$. *Acta Crystallographica*, B**62**, 212–219.

Bindi, L., Evain, M. and Menchetti, S. (2007b) Complex twinning, polytypism and disorder phenomena in the crystal structures of antimonpearceite and arsenpolybasite. *Canadian Mineralogist*, **45**, 321–333.

Bindi, L., Evain, M. and Menchetti, S. (2007d) Selenopolybasite, $[(Ag,Cu)_6(Sb,As)_2(S,Se)_7][Ag_9Cu(S,Se)_2Se_2]$, a new member of the pearceite-polybasite group from the De Lamar Mine, Owyhee county, Idaho, USA. *Canadian Mineralogist*, **45**, 1525–1528.

Bindi, L., Evain, M., Pradel, A., Albert, S., Ribes, M. and Menchetti, S. (2006b) Fast ionic conduction character and ionic phase-transitions in disordered crystals: The complex case of the minerals of the pearceite-polybasite group. *Physics and Chemistry of Minerals*, **33**, 677–690.

Bindi, L., Evain, M., Spry, P.G. and Menchetti, S. (2007a) The pearceite-polybasite group of minerals: Crystal chemistry and new nomenclature rules. *American Mineralogist*, **92**, 918–925.

Bindi, L., Evain, M., Spry, P.G., Tait, K.T. and Menchetti, S. (2007c) Structural role of copper in the minerals of the pearceite-polybasite group: The case of the new minerals cupropearceite and cupropolybasite. *Mineralogical Magazine*, **71**, 641–650.

Bindi, L. and Menchetti, S. (2009) Adding further complexity to the polybasite structure: The role of silver in the *B* layer of the *M*2*a*2*b*2*c* polytype. *American Mineralogist*, **94**, 151–155.

Bindi, L., Voudouris, P. and Spry, P.G. (2013) Structural role of tellurium in the minerals of the pearceite-polybasite group. *Mineralogical Magazine*, **77**, 419–428.

Boucher, F., Evain, M. and Brec, R. (1993) Distribution and ionic diffusion path of silver in γ-Ag_8GeTe_6: A temperature dependent anharmonic single crystal structure study. *Journal of Solid State Chemistry*, **107**, 332–346.

Downs, R.T., Bartelmehs, K.L., Gibbs, G.V. and Boisen, M.B.Jr. (1993) Interactive software for calculating and displaying X-ray or neutron powder diffractometer patterns of crystalline materials. *American Mineralogist*, **78**, 1104–1107.

Evain, M., Bindi, L. and Menchetti, S. (2006a) Structural complexity in minerals: twinning, polytypism and disorder in the crystal structure of polybasite, $(Ag,Cu)_{16}(Sb,As)_2S_{11}$. *Acta Crystallographica*, B**62**, 447–456.

224 Evain, M., Bindi, L. and Menchetti, S. (2006b) Structure and phase transition in the Se-rich
225 variety of antimonpearceite,$(Ag_{14.67}Cu_{1.20}Bi_{0.01}Pb_{0.01}Zn_{0.01}Fe_{0.03})_{15.93}(Sb_{1.86}As_{0.19})_{2.05}$
226 $(S_{8.47}Se_{2.55})_{11.02}$. *Acta Crystallographica*, **B62**, 768–774.
227 Helmy, H.M., Kamel, O.A. and El Mahallawi, M.M. (1999) Silver and silver-bearing
228 minerals from the Precambrian volcanogenic massive sulfide deposit, Um Samiuki,
229 Eastern Desert, Egypt. In: Stanley *et al.* (eds) *Mineral deposits: processes to processing*.
230 Balkema, Rotterdam, pp 163–166.
231 Herrington, R.J., Maslennikov, V.V., Stanley, C.J. and Buslaev, F. (1998) Tellurium-bearing
232 phases in black smoker chimney fragments from the Silurian Yaman Kasy massive
233 sulphide orebody, southern Urals, Russia. *17th General Meeting International*
234 *Mineralogical Association*, Toronto, Abst Prog, A119 (Abstract).
235 Johnson, C.K. and Levy, H.A. (1974) *International Tables for X-ray Crystallography*, edited
236 by J. A. Ibers and W. C. Hamilton, Vol. IV, pp. 311-336. Birmingham: Kynoch Press.
237 Karup-Møller, S. and Pauly, S. (1979) Galena and associated ore minerals from the cryolite at
238 Ivigtut, S. Greenland. *Meddelelser om Grønland Geoscience*, **2**, 1–25.
239 Kuhs, W.F. (1984) Site-symmetry restrictions on thermal-motion-tensor coefficients up to
240 rank 8. *Acta Crystallographica*, **A40**, 133–137.
241 Moëlo, Y., Makovicky, E., Mozgova, N.N., Jambor, J.L., Cook, N., Pring., A., Paar, W.H.,
242 Nickel, E.H., Graeser, S., Karup-Møller, S., Balić Žunić, T., Mumme, W.G., Vurro, F.,
243 Topa, D., Bindi, L., Bente, K. and Shimizu, M. (2008) Sulfosalt systematics: a review.
244 Report of the sulfosalt sub-committee of the IMA Commission on Ore Mineralogy.
245 *European Journal of Mineralogy*, **20**, 7–46.
246 Oxford Diffraction (2006) *CrysAlis* RED (Version 1.171.31.2) and ABSPACK in *CrysAlis*
247 RED. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.

248 Pals, D.W. and Spry, P.G. (2003) Telluride mineralogy of the low-sulfidation epithermal
249 Emperor gold deposit, Vatukoula, Fiji. *Mineralogy and Petrology*, **79**, 285–307.
250 Petříček, V., Dušek, M. and Palatinus, L. (2006). *JANA2006, a crystallographic computing*
251 *system*. Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech
252 Republic.
253 Spry, P.G. and Thieben, S.E. (1996) Two new occurrences of benleonardite, a rare silver–
254 tellurium sulphosalt, and a possible new occurrence of cervelleite. *Mineralogical*
255 *Magazine*, **60**, 871–876
256 Stanley, C.J., Criddle, A.J. and Chisholm, J.E. (1986) Benleonardite, a new mineral from the
257 Bambolla mine, Moctezuma, Sonora, Mexico. *Mineralogical Magazine*, **50**, 681–
258 686.
259 Williams, S.A. (1982) Cuzticite and eztlite, two new tellurium minerals from Moctezuma,
260 Mexico. *Mineralogical Magazine*, **46**, 257–259.
261 Zhang, X. and Spry, P.G. (1994) Petrological, mineralogical, fluid inclusion, and stable
262 isotope studies of the Gies gold–silver telluride deposit, Judith Mountains, Montana.
263 *Economic Geology*, **89**, 602–627.
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FIGURE CAPTIONS

Figure 1 – Reflected plane polarized light digital image in oil immersion illustrating a band of benleonardite on a ragged quartz grain to the right with rosettes of acanthite intergrown with low reflecting unidentified phases in a mass of creamy white to off-white hessite. The hessite contains a vermiform or myrmekitic intergrowth of fine-grained cervelleite (pale-greenish-grey). The sample (catalogue number E.1161 BM 1985, 354) is the type specimen for both benleonardite and cervelleite.

Figure 2 – Projection of the benleonardite structure along the *a* axis. The figure emphasizes the succession of the $[Ag_6(Sb,As)_2S_6Te]^{2-}$ *A* and $[Ag_9Cu(S,Te)_2Te_2]^{2+}$ *B* module layers. Grey, light blue, yellow, orange and red circles refer to Ag, Cu, S (S2), S/Te (S1) and Te (Te3 and Te4), respectively.

Figure 3 – Non-harmonic joint probability density isosurface of silver for benleonardite at room temperature. S/Te and Cu atoms have an arbitrary size. Level of the 3D map: 0.05 $Å^{-3}$. The figure illustrates the silver diffusion in the *ab* plane among the various S/Te tetrahedral sites.

TABLE 1. Details pertaining to the single-crystal X-ray data collection and structure refinement of benleonardite

Crystal data	
space group	$P\bar{3}m1$ (#164)
cell parameters	a = 7.623(1) (Å) c = 12.708(1) (Å) V = 639.5(2) (Å^3)
Z	1
crystal color	black
crystal shape	block
crystal size (mm)	0.031 × 0.045 × 0.062
Data collection	
diffractometer	Oxford Diffraction Xcalibur 3
radiation type	Mo$K\alpha$ (λ = 0.71073)
monochromator	oriented graphite (002)
scan mode	φ/ω
temperature (K)	293
detector to sample distance (cm)	5
number of frames	598
rotation width per frame (°)	0.15
measuring time (s)	90
maximum covered 2θ (°)	75.52 (d = 0.86 Å)
range of h, k, l	$-11 \le h \le 11$, $-13 \le k \le 13$, $-20 \le l \le 20$
collected reflections	11025
R_{int} before absorption correction	0.1054
R_{int} after absorption correction	0.0355
Refinement	
refinement coefficient	F^2
No. of refl. in refinement	1250
No. of observed refl.	609
No. of refined parameters	102
weighting scheme	$w = 1/[\sigma^2(I) + (0.044 \times I)^2]$
$R^{\dagger}$ (obs) / $R^{\dagger}$ (all)	0.0179/ 0.0321
w$R^{2\dagger}$ (obs) / w$R^{2\dagger}$ (all)	0.0167 / 0.0172
diff. Fourier (e$^-$/Å^3)	[-1.94, 1.13]

Note: $^{\dagger}R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$. $wR^2 = [\Sigma w (|F_o|^2 - |F_c|^2)^2 / \Sigma w (|F_o|^4)]^{1/2}$.

TABLE 2. Wyckoff positions, site occupation factors, fractional atomic coordinates, and equivalent isotropic displacement parameters (Å^2) for the selected benleonardite crystal.

atom	Wyckoff	s.o.f.	*x*	*y*	*z*	U_{iso}
Sb	2*d*	0.789(4)	0.3333	0.6667	0.38572(2)	0.0251(7)
As	2*d*	0.211	0.3333	0.6667	0.38572(2)	0.0251(7)
Ag1	6*i*	0.677(7)	0.2848(3)	0.1424(3)	0.3804(1)	0.0526(3)
Ag2	6*i*	0.311(7)	0.3422(3)	0.1711(3)	0.3537(3)	0.0700(8)
Ag3	12*j*	0.307(5)	0.252(3)	0.3641(4)	0.1192(3)	0.0555(8)
Ag4	12*j*	0.134(6)	0.382(3)	0.402(3)	0.1065(8)	0.0635(6)
Ag5	12*j*	0.315(7)	0.3503(4)	0.2803(18)	0.1234(4)	0.0670(6)
Cu	1*a*	1.000	0	0	0	0.0320(2)
S1	2*c*	0.514(9)	0	0	0.1823(2)	0.0271(9)
Te1	2*c*	0.486	0	0	0.1823(2)	0.0271(9)
S2	6*i*	1.000	0.01458(5)	0.50729(5)	0.30681(8)	0.0404(2)
Te3	2*d*	1.000	0.6667	0.3333	0.01650(3)	0.0475(1)
Te4	1*b*	1.000	0	0	0.5	0.0422(1)

TABLE 3 – Anisotropic displacement parameters U_{ij} (Å^2) for the selected benleonardite crystal

atom	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sb	0.0235(9)	0.0235(9)	0.037(1)	0.0118(5)	0	0
As	0.0235(9)	0.0235(9)	0.037(1)	0.0118(5)	0	0
Ag1	0.0542(5)	0.0502(2)	0.0547(6)	0.0271(3)	-0.0002(3)	-0.0001(1)
Ag2	0.093(1)	0.0447(5)	0.089(1)	0.0464(6)	0.042(2)	0.0208(8)
Ag3	0.26(2)	0.0381(7)	0.0516(9)	-0.016(3)	-0.035(3)	0.0024(4)
Ag4	0.169(7)	0.240(9)	0.085(4)	0.170(8)	0.073(5)	0.078(6)
Ag5	0.0356(8)	0.29(1)	0.050(1)	-0.016(2)	0.0068(5)	-0.009(2)
Cu	0.0388(2)	0.0388(2)	0.0186(3)	0.0194(1)	0	0
S1	0.038(3)	0.038(3)	0.006(2)	0.019(1)	0	0
Te1	0.038(3)	0.038(3)	0.006(2)	0.019(1)	0	0
S2	0.0227(3)	0.0418(3)	0.0503(4)	0.0113(1)	-0.0031(2)	-0.0015(1)
Te3	0.0454(1)	0.0454(1)	0.0519(2)	0.02269(7)	0	0
Te4	0.0424(2)	0.0424(2)	0.0417(3)	0.02120(8)	0	0

TABLE 4. Higher-order displacement parameters[†] for the selected benleonardite crystal

	Ag3	Ag4	Ag5
C^{111}	-0.01(4)	0.08(3)	0.001(1)
C^{112}	0.001(9)	0.08(3)	-0.002(2)
C^{113}	-0.008(5)	0.028(7)	-0.0001(4)
C^{122}	0.000(3)	0.09(4)	0.02(1)
C^{123}	0.002(1)	0.028(8)	-0.0005(7)
C^{133}	0.0009(9)	0.006(2)	-0.0001(2)
C^{222}	-0.001(1)	0.11(4)	-0.06(5)
C^{223}	0.0002(3)	0.028(9)	0.005(3)
C^{233}	-0.0005(2)	0.005(3)	-0.0006(6)
C^{333}	-0.0001(2)	0.001(1)	0.0007(2)

Note: [†]Third-order tensor elements C^{ijk} are multiplied by 10^3;

TABLE 5. Main interatomic distances (Å) for the selected benleonardite crystal

Sb/As - S2	2.331(1) (×3)	Cu - S1/Te1	2.317(4) (×2)	Ag1 - S2	2.591(2) (×2)
<Sb/As-S>	2.331	<Cu-S/Te>	2.317	- Te4	2.418(2)
				<Ag1-S/Te>	2.533
Ag2 - S2	2.302(4) (×2)	Ag3‡ - S1/Te1	2.589(6)	Ag4‡ - Te3	2.726(3)
- Te4	2.926(4)	- Te3	2.692(6)	- Te3	2.720(2)
<Ag2-S/Te>	2.510	<Ag3-S/Te>	2.638	<Ag4-Te>	2.723
Ag5‡ - S1/Te1	2.559(5)				
- Te3	2.618(6)				
<Ag5-S/Te>	2.589				

Note: ‡ the bond distances calculated for Ag3, Ag4 and Ag5 correspond to the most probable distance calculated from the modes (maxima) of *jpdf* (joint probability density function) maps.

TABLE 6. X-ray powder diffraction patterns for benleonardite.

	1		2		
hkl	d_{calc} (Å)	I_{calc}	*hkl*	d_{obs} (Å)	I/I_o
001	12.7080	79	001	12.7	70
100	6.6017	33	010	6.62	15
002	6.3540	10	002	6.34	15
101, 011	5.8584	20	011	5.87	15
102, 012	4.5780	2	012	4.61	15
003	4.2360	2	–	–	–
110	3.8115	1	–	–	–
013, 103	3.5652	23	–	–	–
200	3.3009	1	–	–	–
112	3.2685	28	–	–	–
021, 201	3.1948	31	021, 004	3.188	30
004	3.1770	56			
022, 202	2.9292	100	022	2.936	100
014	2.8628	2	014	2.863	25
113	2.8334	5	–	–	–
023	2.6037	21	023	2.608	35
005	2.5416	1	005	2.542	10
210	2.4952	3	–	–	–
211	2.4485	5	n.i.	2.453	15
114	2.4404	54	–	–	–
105	2.3719	1	015	2.376	15
122, 212	2.3225	2	220	2.328	20
024, 204	2.2890	26	221, 024	2.291	10
300	2.2006	22	030	2.206	10
031, 301	2.1683	23	124	2.158	35
123, 213	2.1499	31			
006	2.1180	1	006	2.120	20
115	2.1146	29			
032, 302	2.0794	11	130, 032	2.084	10
106	2.0168	4	016	2.020	15
205	2.0138	19			
214	1.9623	1	n.i.	1.965	10
033	1.9528	7	–	–	–
220	1.9058	43	n.i.	1.914	15
221	1.8847	3	–	–	–
116	1.8514	8	–	–	–
310	1.8310	1	007	1.819	15
222	1.8254	1			
026, 206	1.7826	14	026	1.786	10
125, 215	1.7806	4			
017	1.7504	4	–	–	–
223	1.7380	12	134	1.744	15
313, 133	1.6807	6	–	–	–
401	1.6367	2	–	–	–
224	1.6343	2	–	–	–
216	1.6147	4	–	–	–

042, 402	1.5974	10				
027, 207	1.5907	3		008	1.591	15
008	1.5885	9				
403	1.5378	3				
306	1.5260	2		n.i.	1.531	15
225	1.5247	5				
320	1.5145	1		–	–	–
321	1.5039	4		–	–	–
404, 044	1.4646	6		–	–	–
410	1.4406	3		–	–	–
028, 208	1.4314	6		–	–	–
226	1.4167	5		–	–	–
142, 412	1.4050	5		–	–	–
037	1.4004	2		–	–	–
045	1.3842	3		–	–	–
019	1.3808	2		–	–	–
119	1.3241	2		–	–	–
414, 144	1.3120	4		–	–	–
046	1.3018	3		–	–	–
325	1.3011	2		–	–	–
317	1.2892	2		–	–	–
038, 308	1.2880	4		–	–	–
00<u>10</u>	1.2708	1		–	–	–
330	1.2705	1		–	–	–
145, 415	1.2533	3		–	–	–
332	1.2458	1		–	–	–
421	1.2416	1		–	–	–
422, 242	1.2242	6		–	–	–
228	1.2202	3		–	–	–
054	1.2192	1		–	–	–
243	1.1968	3		–	–	–
146	1.1912	2		–	–	–
02<u>10</u>	1.1859	4		–	–	–
237	1.1630	4		–	–	–
048	1.1445	2		–	–	–
153, 513	1.1418	3		–	–	–
335	1.1364	3		–	–	–
056	1.1205	1		–	–	–
425	1.1200	4		–	–	–
319	1.1181	1		–	–	–
03<u>10</u>	1.1005	1		–	–	–
600	1.1003	3		–	–	–
426	1.0750	3		–	–	–
155	1.0745	1		–	–	–
063	1.0649	1		–	–	–
22<u>10</u>	1.0573	1		–	–	–
520	1.0571	1		–	–	–
239	1.0328	2		–	–	–
247	1.0282	1		–	–	–
11<u>12</u>	1.0203	2		–	–	–
02<u>12</u>	1.0084	2		–	–	–

40$\underline{1}\underline{0}$	1.0069	2		–	–	–

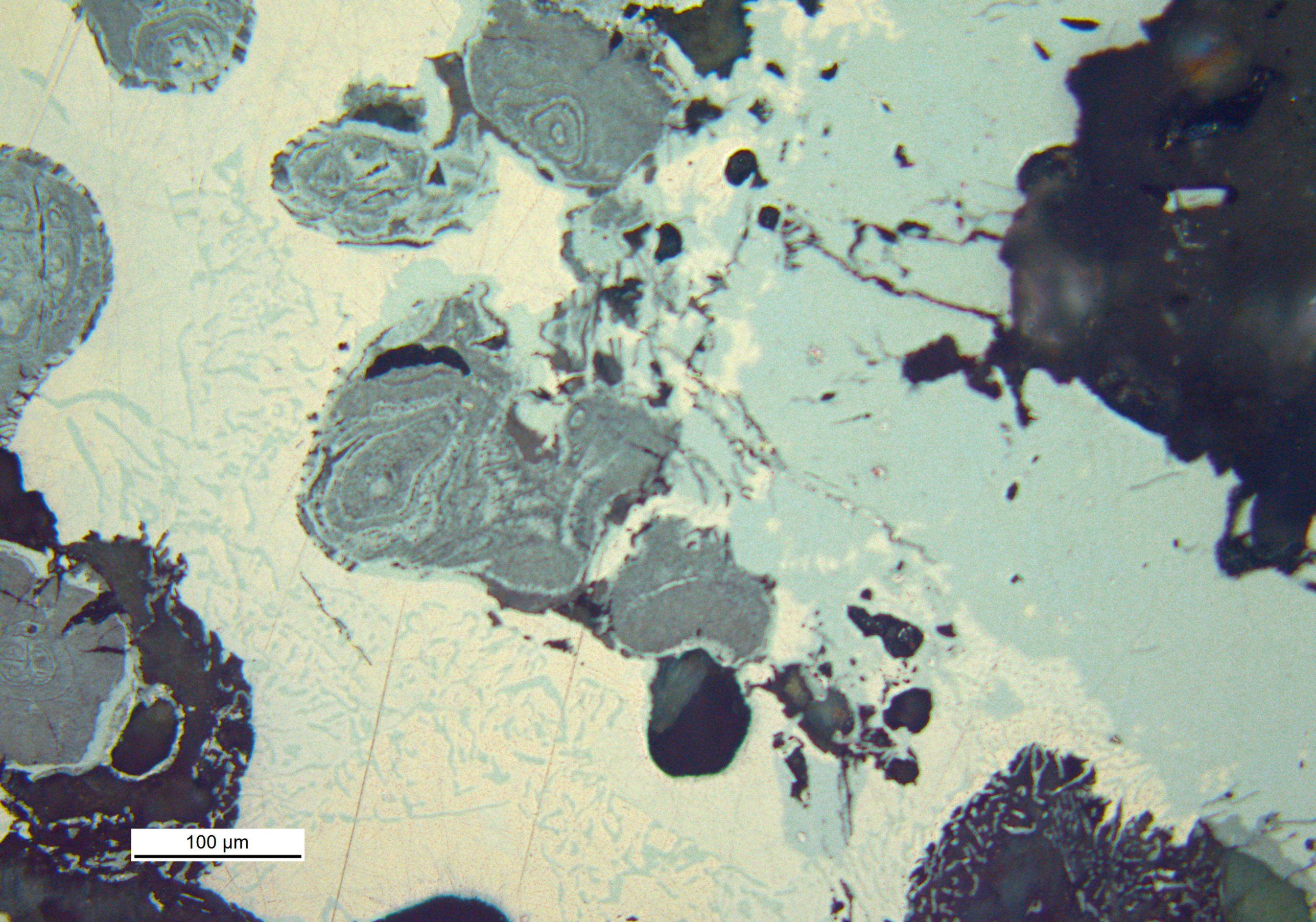
Note: 1 = calculated powder pattern and indexing for benleonardite of this study. *d* values calculated on the basis of a = 7.623(1) Å, c = 12.708(1) Å, and with the atomic coordinates and occupancies reported in Table 2. Intensities calculated using XPOW software version 2.0 (Downs *et al.*, 1993). 2 = observed powder pattern and indexing originally reported by Stanley *et al.* (1986).

TABLE 7 – Electron microprobe data (wt% of elements) of 'benleonardite' minerals from different deposits (data from literature) and atomic ratios calculated on the basis of 29 atoms.

	Bambolla						*Gies*			
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Ag	63.80	65.00	65.00	65.10	65.60	64.50	62.52	62.99	62.70	63.40
Cu	0.10	0.00	0.00	0.00	0.00	0.10	1.90	1.65	1.90	2.10
Sb	9.00	7.40	7.80	7.60	7.20	7.30	6.25	5.33	6.70	4.40
As	0.70	1.80	1.20	1.10	1.80	1.40	1.16	1.70	0.90	2.60
Te	18.60	18.40	18.70	18.50	18.70	18.70	19.38	19.06	19.60	18.80
S	8.00	8.10	8.20	8.10	8.00	8.00	8.16	8.33	8.40	8.60
total	100.20	100.70	100.90	100.40	101.30	100.00	99.37	99.06	100.20	99.90
Ag	16.01	16.11	16.10	16.23	16.22	16.14	15.52	15.60	15.41	15.38
Cu	0.04	0.00	0.00	0.00	0.00	0.04	0.80	0.69	0.79	0.87
Sb	2.00	1.63	1.71	1.68	1.58	1.62	1.37	1.17	1.46	0.95
As	0.25	0.64	0.43	0.39	0.64	0.50	0.41	0.61	0.32	0.91
Te	3.95	3.86	3.92	3.90	3.91	3.96	4.07	3.99	4.07	3.86
S	6.75	6.76	6.84	6.80	6.65	6.74	6.83	6.94	6.95	7.03
Ag+Cu	16.05	16.11	16.10	16.23	16.22	16.18	16.32	16.29	16.20	16.25
Sb+As	2.25	2.27	2.14	2.07	2.22	2.12	1.78	1.78	1.78	1.86
Te+S	10.70	10.62	10.76	10.70	10.56	10.70	10.90	10.93	11.02	10.89

	Mayflower		*Ivigtut*	*Emperor*	*Um Samiuki*		
	11	**12**	**13**	**14**	**15**	**16**	**17**
Ag	60.76	63.07	61.70	63.00	64.87	65.50	64.83
Cu	2.68	0.55	0.00	0.18	0.30	0.00	0.31
Sb	6.94	6.98	7.10	5.81	6.60	6.99	6.88
As	1.15	1.01	0.00	1.57	1.71	1.20	1.66
Te	18.97	18.75	17.00	19.99	19.24	18.78	19.98
S	8.78	8.56	8.80	8.22	8.47	8.27	8.38
total	99.28	98.92	94.60	98.77	101.19	100.74	102.04
Ag	14.85	15.74	15.98	15.85	15.88	16.22	15.81
Cu	1.11	0.23	0.00	0.08	0.12	0.00	0.13
Sb	1.50	1.54	1.63	1.30	1.43	1.53	1.48
As	0.40	0.36	0.00	0.57	0.60	0.43	0.58
Te	3.92	3.95	3.72	4.25	3.98	3.93	4.12
S	7.22	7.18	7.67	6.95	6.99	6.89	6.88
Ag+Cu	15.96	15.97	15.98	15.93	16.00	16.22	15.94
Sb+As	1.90	1.90	1.63	1.87	2.03	1.96	2.06
Te+S	11.14	11.13	11.39	11.20	10.97	10.82	11.00

Note: analyses 1-6: Stanley *et al.* (1986); analyses 7-8: Spry and Thieben (1996); analyses 9-10: Zhang and Spry (1994); analysis 11-12: Spry and Thieben (1996); analysis 13: Karup-Møller and Pauly (1979); analysis 14: Pals and Spry (2003); analysis 15-17: Pals and Spry (2003).


100 µm

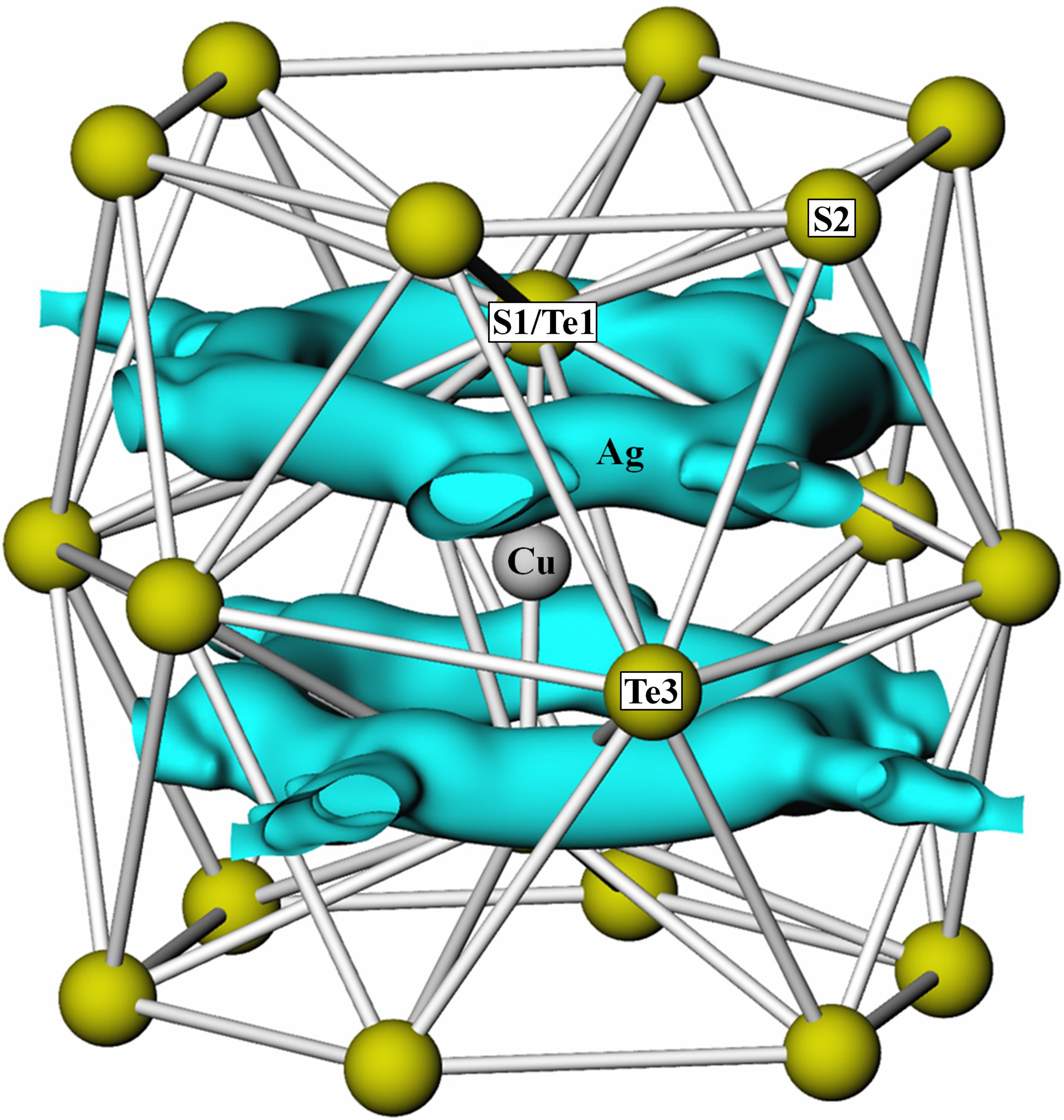
B

A

B

c

b_p


S2
S1/Te1
Ag
Cu
Te3