Oscarkempffite, $Ag_{10}Pb_4(Sb_{17}Bi_9)_{\Sigma 26}S_{48}$, a new Sb-Bi member of the lillianite homologous series

Dan Topa[1,*], Werner H. Paar[2], Emil Makovicky[3], Chris J. Stanley[4] and Andy C. Roberts[5]

[1] Natural History Museum-Vienna, Burgring 7, A-1010 Vienna, Austria
[2] A-5020 Salzburg, Pezoltgasse 46, Austria
[3] Department of Geoscience and Resource Management, University of Copenhagen, Østervoldgade 10, DK-1350, Copenhagen K, Denmark
[4] The Natural History Museum, Cromwell Road, London SW7 5BD, England, UK
[5] Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario K1A OE8, Canada

ABSTRACT

Oscarkempffite, ideally $Ag_{10}Pb_4(Sb_{17}Bi_9)_{\Sigma = 26}S_{48}$, is a new mineral species found in old material (1929–30) from the Colorada vein, Animas mine, Chocaya Province, Department of Potosi, Bolivia. It is associated with aramayoite, stannite, miargyrite, pyrargyrite and tetrahedrite. Oscarkempffite forms anhedral grains and grain aggregates up to 10 mm across. The mineral is opaque, greyish black with a metallic lustre; it is brittle without any discernible cleavage. In reflected light oscarkempffite is greyish white, pleochroism is distinct, white to dark grey. Internal reflections are absent. In crossed polars, anisotropism is distinct with rotation tints in shades of grey. The reflectance data (%, air) are: 39.9, 42.6 at 470 nm, 38.6, 41.7 at 546 nm, 38.1, 41.2 at 589 nm and 37.3, 40.6 at 650 nm. Mohs hardness is 3–3½, microhardness VHN_{50} exhibits a range 189–208, with a mean value 200 kg mm^{-2}. The average results of four electron-microprobe analyses in a grain are: Cu 0.24(7), Ag 14.50(8), Pb 11.16(14), Sb 28.72(16), Bi 24.56(17), S 20.87(5), total 100.05(6) wt.%, corresponding to $Cu_{0.24}Ag_{9.92}Pb_{4.00}Sb_{17.36}Bi_{8.64}S_{47.84}$ (on the basis of $Me + S = 88$ apfu). The simplified formula, $Ag_{10}Pb_4Sb_{17}Bi_9S_{48}$, is in accordance with the results of a crystal-structure determination. The density, 5.8 g cm^{-3}, was calculated using the ideal formula. Oscarkempffite has an orthorhombic cell with $a = 13.199(2)$, $b = 19.332(3)$, $c = 8.249(1)$ Å, $V = 2116.3(5)$ Å^3, space group *Pnca* and $Z = 1$. The strongest eight lines in the (calculated) powder-diffraction pattern are [d in Å(I)hkl]: 3.66(35)(122), 3.37(70)(132), 3.34(100)(250), 2.982(55)(312), 2.881(86)(322), 2.733(29)(332), 2.073(27)(004) and 2.062(31)(182). Comparison with gustavite, andorite and roshchinite confirms its independence as a mineral species.

Keywords: oscarkempffite, sulfosalt, new mineral, lillianite homologous series, Animas mine, Chocaya Province, Bolivia.

Introduction

The lillianite homologous series (Makovicky and Karup-Møller, 1977*a,b*) was defined for Pb-Bi-Ag sulfosalts although it was noticed from the start that three antimony-based phases andorite, ramdohrite and fizelyite (Hellner, 1958) belonged to the same structural family. The andorite–

ramdohrite branch of the lillianite series was subsequently studied in detail by Moëlo *et al.* (1989). Phases belonging to the lillianite homologous series are composed of slabs of the slightly distorted PbS archetypal structure, cut and mirror-twinned on (113)$_{PbS}$. The octahedral coordinations present in the slabs are altered to bicapped prismatic coordinations on the composition plane between adjacent slabs. Slab thickness can vary by increments of one or more octahedra, measured diagonally across a slab. The number of octahedra along this diagonal determines the order N of the

homologue. Substitution $[Ag + (Sb + Bi)]$-for-2Pb is present in the slabs but in most cases it does not involve the prismatic Pb positions. For $N = 4$, relevant for the present study, this substitution spans compositions from $Pb_3Bi_2S_6$ to $PbAg(Bi, Sb)_3S_6$, expressed as the substitution percentage from 0 to 100%. The end-member composition $Pb_3Sb_2S_6$ is unknown, both as a natural or a synthetic phase, and probably cannot exist as a lillianite homologue. Cases of 'oversubstitution', in which the prismatic position is also involved, are known, mostly for the Sb-based cases (Moëlo *et al.*, 1989). For $N = 4$, and a Bi-based case, an ortho-rhombic *Bbmm* structure exists for substitutions of up to ~60%; whereas a monoclinic $P2_1/c$ superstructure is present for substitutions close to 100% (Makovicky and Karup-Møller 1977*b*). The situation for the Sb-based phases is more complicated for the $N = 4$ line, with two highly substituted-to-oversubstituted phases (complicated 6-fold and 4-fold superstructures of the basic lillianite scheme) and several moderately substituted cases present, commonly with other cations modifying the simple Pb-Ag-Sb scheme.

Studies of the mixed antimony-bismuth members of the lillianite homologous series were first limited to a chemical characterization of them by means of electron microprobe analyses. It was established (Mozgova *et al.*, 1987, Moëlo *et al.*, 1989) that extensive Bi-Sb substitution may be present, straddling the 50:50 Sb:Bi divide, although typical gustavites and lillianites have low contents of antimony (e.g. Makovicky and Topa, 2011 and the numerous references in Moëlo *et al.*, 1989). In a similar way, nearly all occurrences of andorite–ramdohrite homologues have only low contents of bismuth (Moëlo *et al.*, 1989). Notable occurrences of mixed Sb-Bi phases are the Alyaskitovoye deposit (Yakutia, Russia) (Mozgova *et al.*, 1987), Flat Head (Montana, USA) (Karup-Møller and Makovicky, unpublished), Julcani (Peru), El Mechero (Peru), Bazoges-en-Paillers (Vendee, France) (all three by Moëlo *et al.*, 1987) and Kutná Hora (Central Bohemia, Czech Republic) (Pažout and Dušek, 2010). Investigations of mixed phases were hampered mostly by extreme variability of Sb:Bi ratios, commonly inside one aggregate or a needle-shaped grain, typical for nearly all investigated occurrences. In spite of it, a successful crystal structure investigation was performed by Pažout and Dušek (2009) on Sb-containing gusta-vite, $PbAgBi_2SbS_6$, from the deposit of Kutná Hora, Czech Republic, with $a = 7.0455$, $b = 19.5294$, $c = 8.3412$ Å and $\beta = 107.446°$, space group $P2_1/c$. Another published structure of

this category from Kutná Hora is that of $Ag_{0.71}Pb_{1.52}Bi_{1.32}Sb_{1.45}S_6$, with $a = 4.254$, $b = 13.309$, $c = 19.625$ Å, space group *Cmcm* (Pažout and Dušek, 2010). This orthorhombic phase has a substitution percentage of only 70.5%, according to the substitution scheme defined above (Makovicky and Karup-Møller, 1977*a,b* and Makovicky and Topa, 2014).

The new investigation of the old material from the Colorada vein, Animas mine, Chocaya Province, Department of Potosi, Bolivia (Ahlfeld and Reyes, 1938, Ahlfeld and Schneider-Scherbina, 1964,) offered a chance to extend further the chemical range of investigated Sb-Bi lillianite homologues with $N = 4$ and led to the definition of oscarkempffite as a new species.

The mineral and its name have been approved by the CNMNC–IMA, under the number IMA-2011–029 (Topa *et al.*, 2011). The name is in honour of Oscar Kempff Bacigalupo (1948–), eminent Bolivian mineralogist and economic geologist, who discovered several large mineral deposits in Bolivia (e.g. the deposit of Don Mario). The holotype specimen of oscarkempffite is deposited in the reference collection of the Naturhistorisches Museum Wien, Wien, Austria, with catalogue number N 9593. Cotype material is deposited in the reference collection of the Natural History Museum, London, UK, with catalogue number BM 20, 3.

Occurrence

Oscarkempffite has been determined in old samples which originate from the expeditions of W. Vaux in 1929–30. The locality which is given on the labels associated with the two specimens of this mineral, is Animas mine, Colorada vein. Chocaya is a typical deposit of the Ag-Sn formation of Bolivia. Its geographical position is 66°33'W and 21°S. It is situated NW of Atocha in the province of Sur Chicas, department of Potosi, Southern Bolivia, and thus very close to the tectonic lineament which separates Paleozoic rocks of the Central Andes from the high planes (= 'altiplano') of Bolivia. The vein-type Ag-Sn deposits occur NE of a volcanic stock of dacitic rocks which has a diameter of 9 km and rises up against the Ordovician plane for more than 900 metres. The volcanic rocks are strongly altered and propylitization, silicification and pyrit-ization are very common.

Colorada, which is the principal vein, follows a distinct fault zone for more than 1800 m along strike. Other veins which parallel the Colorada structure are Arturo and Animas towards the west

and Burton and Judíos towards the east. The Colorada vein has been exploited downwards for almost 750 m in the northern part and 600 m in the Animas section in its southern part. In the upper part of this vein cassiterite was associated with freibergite and members of the stannite–kësterite family. Textures which clearly indicated open space filling have very distinct banding, crustification and cockades.

At the Animas mine, some 70 m from the surface, an extremely rich ore shoot composed of various silver minerals was encountered during the exploitation of the mine. At a depth of 125 m, the ore shoot had a length of 30 m, a thickness of 2 m and the grade of silver was almost 3.5%. The principal silver mineral was freibergite. At the –

235 m level the high-grade zone contained the new mineral species aramayoite, $Ag(Sb,Bi)S_2$, accompanied by stannite, miargyrite, pyrargyrite and freibergite. Aramayoite has been described in detail by Spencer and Mountain (1926).

Oscarkempffite, the new sulfosalt species, is a typical associate of this assemblage containing aramayoite. Though no details about the exact level are given on the labels associated with the specimens, it can be assumed with certainty, that their origin is from the same level as the discovery of aramayoite (–235 m level). The last and more important exploitation at the Animas mine stopped in 1961, after significant amounts of Pb, Ag, Sn and Zn were mined. However, small-scale mining by local mining communities ('cooperativas') at the
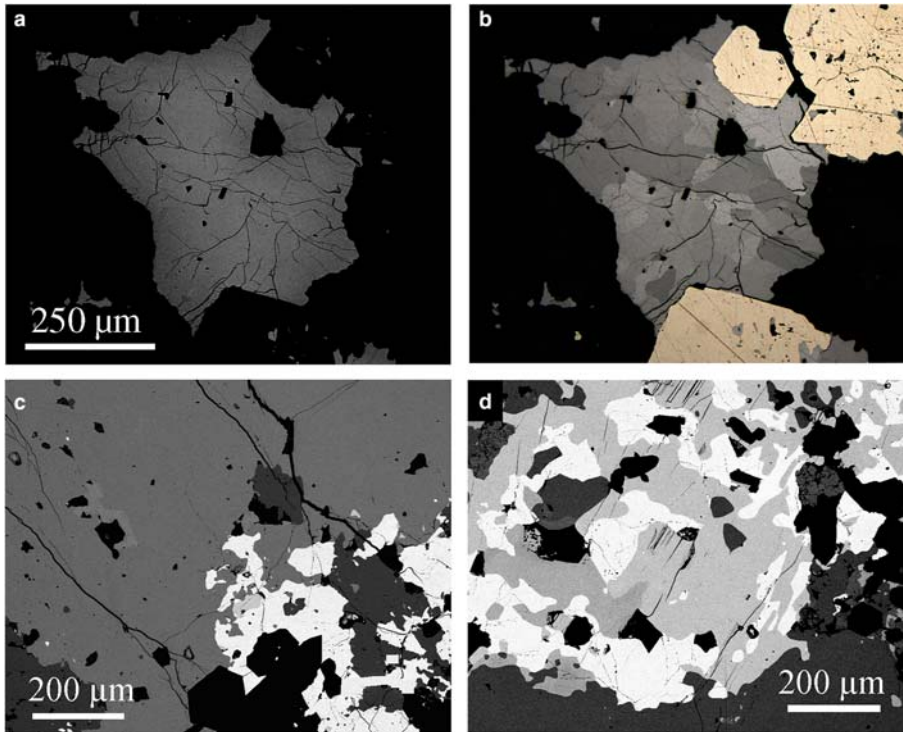

FIG. 1. (*a*) A BSE photograph of an aggregate of oscarkempffite showing differences in the contents of cations with high Z values as smooth zoning with a higher average Z in the centre. (*b*) The same aggregate in reflected light (crossed polars) displays an irregular mosaic character and pronounced anisotropy; associated with pyrite. (*c*) A large field of Ag-bearing tetrahedrite with another, still richer in silver (lighter) generation deposited in a void. Irregular grains of oscarkempffite penetrate into tetrahedrite on the boundary and enclose a small aramayoite grain. (*d*) A complex round sulfide aggregate interpreted as a replacement of an old unknown mineral aggregate. Oscarkempffite (a 'wreath' of light grains and a grain in the centre) is corroded and cemented by a later, large grain of Bi-rich aramayoite (lighter grey) and another grain of Bi-poorer aramayoite (slightly darker grey, left-hand parts). Small crystals of quartz and a grain of tetrahedrite with a 'cap' of Ag-enriched tetrahedrite (dark grey) are enclosed. At lower corners of the figure, dark semi-decomposed grains of stannite are present. See the text for interpretation.

deeper levels of the Animas mine was still on going at the time of the last visit of one of the authors (WHP, 2004) and probably continues to the present day.

Mineral association

Oscarkempffite forms anhedral grains attaining a size of up to several mm and grain aggregates ranging up to 10 mm across. A back-scatter scanning electron (BSE) photograph (Fig. 1a) of such an aggregate shows differences in the contents of cations with high Z values as smooth zoning with a higher average Z in the centre. The same aggregate in reflected light (Fig. 1b) displays an irregular mosaic character and pronounced anisotropy. The surrounding association is not visible because of high contrast. Figure 1c shows a large field of Ag-bearing tetrahedrite with another, richer in silver (lighter on the BSE image), generation deposited in a void, along with irregular grains of oscarkempffite that penetrate into tetrahedrite on the boundary and enclose a small aramayoite grain. The complex round sulfide aggregate in Fig. 1d is interpreted as a replacement of an old unknown precursor mineral (aggregate) of approximately round shape by oscarkempffite (a 'wreath' of light grains and a grain in the centre) cemented by a large grain of bismuth-rich aramayoite (lighter grey) and another of less bismuthian aramayoite variety (slightly darker grey, lower left part). Small crystals of quartz and a grain of tetrahedrite with a 'cap' of Ag-enriched tetrahedrite variety (dark grey on the BSE image) are enclosed. Close to the lower corners of the figure, dark semi-decomposed grains of stannite are present. Oscar-kempffite overgrew/replaced the original aggregate from the outside and later also the remaining old grain. Much of oscarkempffite was subsequently replaced by aramayoite. Stannite apparently predates aramayoite, as seen in the lower right-hand corner.

Physical properties

The colour of the mineral is greyish black, streak is dark grey; it is opaque with metallic lustre; and non-fluorescent. Hardness (Mohs) is 3–3½, microhardness, VHN_{50}, ranges between 189 and 208, with a mean value 200 kg mm^{-2}. The mineral is brittle with irregular fracture; no cleavage or parting are observed. Density could not be measured because of paucity of available material. Calculated density is 5.8 g cm^{-3} using the empirical formula. No crystal forms and twinning of the anhedral grains and aggregates were observed. The a:b:c ratio calculated from the unit-cell parameters (see below) is 0.683:1:0.429.

Optical properties

In reflected light (plane polars) the colour of oscarkempffite is greyish white. Pleochroism is distinct, white to dark grey; bireflectance is weak to distinct (in oil); no internal reflections were detected. With crossed polars, anisotropism is distinct with rotation tints in shades of grey. Reflectance values in air and oil, (The Natural History Museum, London, UK, WTiC standard, refractive index of oil: 1.515 at 23°C) are given in Table 1. A slight, fairly even decrease of reflectance with increasing wavelength is observed.

Chemical data

Chemical analyses of oscarkempffite (Table 2) were carried out using an electron microprobe JEOL JXA-8600, installed at University of

TABLE 1. Reflectance values in air and oil (WTiC standard, refractive index of oil: 1.515 at 23°C) for oscarkempffite.

λ (nm)	air		oil	
	R_{min}	R_{max}	R_{min}	R_{max}
400	41.6	44.4	26.0	41.6
420	40.8	43.6	25.4	40.8
440	40.5	43.2	24.7	40.5
460	40.1	42.7	24.3	40.1
470	**39.9**	**42.6**	**24.1**	**39.9**
480	39.7	42.5	23.8	39.7
500	39.4	42.2	23.5	39.4
520	39.0	42.0	23.1	39.0
540	38.7	41.7	22.7	38.7
546	**38.6**	**41.7**	**22.6**	**38.6**
560	38.4	41.5	22.4	38.4
580	38.1	41.3	22.2	38.1
589	**38.1**	**41.2**	**22.1**	**38.1**
600	38.0	41.1	22.0	38.0
620	37.7	40.8	21.7	37.7
640	37.4	40.7	21.7	37.4
650	**37.3**	**40.6**	**21.4**	**37.3**
660	37.1	40.4	21.3	37.1
680	36.9	40.2	21.1	36.9
700	36.8	39.9	21.1	36.8

The reference wavelengths required by the Commission on Ore Mineralogy (COM) are given in bold.

TABLE 2. Analytical results for oscarkempffite and associated minerals.

Nr.	Mineral	NA	Cu	Ag	Fe	Zn	Pb	Sb	Bi	S	total
1	tetrahedrite	16	23.99(30)	19.97(20)	5.64(12)	0.87(13)	-	26.39(39)	-	23.00(14)	99.86(30)
2	tetrahedrite	3	17.38(24)	28.63(01)	4.98(31)	1.34(19)	-	25.55(06)	-	22.18(12)	100.06(04)
3	aramayoite	3	-	34.26(23)	-	-	-	27.70(33)	17.50(44)	20.06(09)	99.52(21)
4	aramayoite	3	-	35.26(28)	-	-	-	30.55(19)	13.48(25)	20.53(03)	99.82(11)
5	aramayoite	3	-	36.34(12)	-	-	-	36.83(68)	5.45(56)	21.05(07)	99.67(11)
6	oscarkempffite	5	0.35(07)	13.98(19)	-	-	12.56(77)	30.13(49)	21.41(20)	21.33(12)	99.76(13)
7	oscarkempffite	4	0.24(03)	14.50(08)			11.16(14)	28.72(16)	24.56(17)	20.87(05)	100.05(06)
8	oscarkempffite	4	0.29(04)	14.48(08)	-	-	10.03(36)	27.12(40)	26.73(37)	21.04(15)	99.96(32)

The data are expressed in wt.%. NA = Number of analyses. Formulae are calculated on the basis of $\Sigma(Me + S) = 29$ apfu for tetrahedrite, 24 apfu for aramayoite and 88 apfu for oscarkempffite, respectively. $N_{chemical}$ and Ag_{subst} are calculated as described in Makovicky and Topa (2014).

1: $Cu_{6.80}Ag_{3.33}Fe_{1.82}Zn_{0.24}Sb_{3.90}S_{12.91}$

2: $Cu_{5.12}Ag_{4.97}Fe_{1.67}Zn_{0.38}Sb_{3.93}S_{12.94}$

3: $Ag_{6.08}Sb_{4.35}Bi_{1.60}S_{11.97}$

4: $Ag_{6.12}Sb_{4.70}Bi_{1.21}S_{11.98}$

5: $Ag_{6.12}Sb_{5.49}Bi_{0.47}S_{11.92}$

6: $Cu_{0.40}Ag_{9.44}Pb_{4.40}Sb_{18.00}Bi_{7.44}S_{48.32}$; $N_{chemical} = 4.08$, $Ag_{subst} = 121\%$

7: $Cu_{0.24}Ag_{9.92}Pb_{4.00}Sb_{17.36}Bi_{8.64}S_{47.84}$; $N_{chemical} = 4.07$, $Ag_{subst} = 124\%$

8: $Cu_{0.32}Ag_{9.92}Pb_{3.68}Sb_{16.40}Bi_{9.44}S_{48.32}$; $N_{chemical} = 4.09$, $Ag_{subst} = 125\%$

Salzburg, Austria, (WDS mode, 25 kV, 20 nA, 5 μm beam diameter, ZAF correction procedure). Other elements (Hg, Tl and As) were sought but not detected. The standards and wavelengths used are chalcopyrite (nat.) CuKα, FeKα, sphalerite (nat.) ZnKα, metal (syn.) AgLα, galena (nat.) PbLα, stibnite (nat.) SbLα and bismuthinite (syn.) BiLα and SKα. Data for oscarkempffite and associated minerals are presented in Table 2.

The empirical formula of oscarkempffite varies between $(Ag,Cu)_{9.88}Pb_{4.40}Sb_{18.0}Bi_{7.44}S_{48.32}$ and $(Ag,Cu)_{10.24}Pb_{3.68}Sb_{16.40}Bi_{9.44}S_{48.32}$. It is very close to the simplified formula $Ag_{10}Pb_4(Sb_{17}Bi_9)_{26}S_{48}$. The crystal structure defines oscarkempffite as a

lillianite homologue with the order $N = 4$. The cation ratios resulting from the chemical analysis confirm this assignment, yielding $N = 4.07–4.09$. With respect to the measure of $[Ag + (Bi,Sb)] \leftrightarrow 2Pb$ substitution, typical for the lillianite–gustavite and

TABLE 3. Powder X-ray diffraction data for oscarkempffite.

$I_{rel.}$	d_{meas}/Å	d_{calc}/Å	h	k	l
5	6.292	6.263	2	1	0
5	5.463	5.463	2	2	0
20*	3.904	3.904	2	4	0
30*	3.663	3.672	1	2	2
		3.380	1	3	2
100b	3.354	3.340	2	5	0
20*	3.264	3.263	4	1	0
5	3.053	3.068	1	4	2
40*	2.988	2.991	3	1	2
80*	2.889	2.889	3	2	2
30*	2.741	2.740	3	3	2
10*	2.551	2.550	2	7	0
5*	2.417	2.417	0	8	0
40*	2.263	2.267	1	7	2
20*	2.112	2.111	5	3	2
		2.073	0	0	4
60	2.066	2.062	1	8	2
30*	2.027	2.028	5	4	2
30*	2.008	2.008	6	4	0
		1.933	0	10	0
30	1.931	1.930	5	5	2
20*	1.890	1.889	3	8	2
10*	1.834	1.836	5	6	2
5*	1.803	1.802	4	9	0
50*b	1.766	1.766	2	5	4
10*	1.722	1.722	7	0	2

TABLE 4. Calculated powder X-ray diffraction data for oscarkempffite.*

$I_{rel.}$	d_{calc}/Å	h	k	l
8	6.25	2	1	0
10	5.45	2	2	0
20	3.90	2	4	0
35	**3.66**	**1**	**2**	**2**
70	**3.37**	**1**	**3**	**2**
100	**3.34**	**2**	**5**	**0**
15	3.30	4	0	0
22	3.25	4	1	0
6	3.22	0	6	0
55	**2.982**	**3**	**1**	**2**
25	2.895	2	6	0
86	**2.881**	**3**	**2**	**2**
29	**2.733**	**3**	**3**	**2**
5	2.548	2	7	0
21	2.265	1	7	2
13	2.105	5	3	2
5	2.082	6	3	0
27	2.073	0	0	4
31	**2.062**	**1**	**8**	**2**
29	**2.023**	**5**	**4**	**2**
16	2.002	6	4	0
9	1.9332	0	10	0
9	1.9297	5	5	2
14	1.8863	3	8	2
8	1.8319	5	6	2
5	1.8002	4	9	0
24	1.7610	2	5	4
5	1.7556	4	0	4
5	1.7500	3	9	2
5	1.7484	4	1	4
6	1.7165	7	0	2
6	1.6858	2	6	4
6	1.6680	4	10	0
6	1.6264	8	2	0
7	1.4403	6	4	4
5	1.4140	0	10	4

*Lines used for unit-cell refinement. Indexed on $a = 13.240(5)$, $b = 19.339(7)$, $c = 8.320(4)$ Å; refined on 17 reflections, between 3.904 and 1.772 Å, for which unambiguous indexing was possible, based on the calculated powder pattern derived from the successful determination of the crystal structure; intensities were estimated visually; b = broad line; the pattern was not corrected for shrinkage and no internal standard was used.

*The theoretical pattern was calculated with PowderCell 2.3 software (Kraus and Nolze, 1999) in Debye-Scherrer configuration employing CuKα radiation ($\lambda = 1.540598$ Å), a fixed slit and no anomalous dispersion. Cell parameters, space group, atom positions, site-occupancy factors and isotropic displacement factors from the crystal-structure determination were used.
The strongest lines are given in bold.

fizelyite–andorite substitution lines (both $N = 4$), oscarkempffite is extensively oversubstituted, with a substitution percentage of 120–124%.

Chemical analyses (Table 2) of aggregates shown in Fig. 1d represent the three groups of oscarkempffite chemistries and two types of tetrahedrite illustrated, among which the one richest in Ag represents the minor later phase (Fig. 1c). Among the three analyses of aramayoite, nos. 3 and 4 represent the aggregate in Fig. 1d, no. 5 another aggregate. In conclusion, they show a substantial variability of the Sb/Bi ratio.

Crystallography

A diffractometer with an area detector system was used to perform the single-crystal study (University of Salzburg, Austria). Cell parameters refined from single-crystal data are as follows: orthorhombic system, space group *Pnca*, $a = 13.199(2)$, $b = 19.332(3)$, $c = 8.294(1)$ Å, cell volume $V = 2116.3(5)$ Å^3 and $Z = 1$ for the above formula unit.

Powder X-ray data were collected using a 114.6 mm diameter Debye-Scherrer camera (Cu radiation, Ni filter, $CuK\alpha = 1.54178$ Å). Data are presented in Table 3. The calculated powder data from results of the single-crystal study are shown in Table 4. Cell parameters refined from the powder data are as follows: $a = 13.240(5)$, $b = 19.339(7)$, $c = 8.320(4)$ Å and $V = 2130(2)$ Å^3, in fair agreement with the single-crystal data.

Crystal structure

A fragment with irregular shape and 0.15 mm × 0.05 mm × 0.05 mm in size was mounted and analyzed on a Bruker AXS three-circle diffractometer equipped with a CCD area detector.

The structure of oscarkempffite contains five distinct coordination polyhedra of cations and seven of anions. It contains a mixed (Pb,Bi) site with a trigonal prismatic coordination, a silver site with a distorted tetrahedral coordination in an octahedral arrangement of ligands, which alternates along the 8 Å direction with a mixed ($Sb_{0.88}Bi_{0.12}$) site called Sb1, and a string of alternating Sb2 and a mixed ($Sb_{0.59}Bi_{0.41}$) sites, the latter called Sb3, in the central parts of PbS-like slabs. When proceeding along [100], the arrangement of consecutive atomic planes differs from that in the monoclinic gustavite structure, resulting in orthorhombic symmetry and in –Sb–Sb–Ag–Ag–Sb–Sb– zig-zag [010] chains of coordination octahedra instead of the Ag–Bi–Ag–Bi– chains present in gustavite. The crystal structure is shown in Fig. 2.
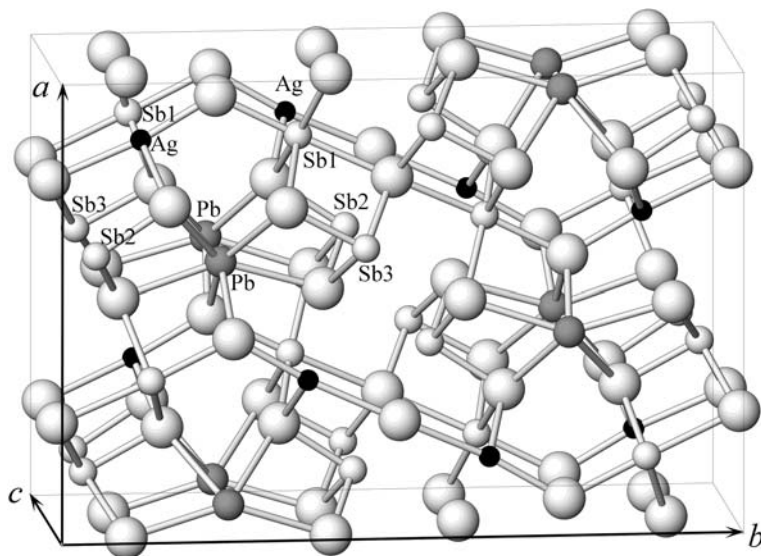

FIG. 2. Cation and anion sites in the crystal structure of oscarkempffite. The unit cell is projected on (001). In the order of decreasing size spheres indicate: S, (Pb,Bi) (grey), (Sb,Bi) (white) and Ag (black). The $(311)_{PbS}$ slabs of the PbS-like arrangement are perpendicular to [010]; they are separated by (010) planes occupied by trigonal coordination prisms of (Pb,Bi).

TABLE 5. Comparative data for oscarkempffite and related minerals.

Mineral	oscarkempffite	gustavite[1]	andorite VI[2]	roshchinite[3]
Formula	$Ag_{10}Pb_4Sb_{17}Bi_9S_{48}$	$Ag_4Pb_4Bi_9Sb_3S_{24}$	$Ag_6Pb_6Sb_{18}S_{36}$	$Ag_{9.5}Pb_5Sb_{25.5}S_{48}$
Substitution (%)	124	100	100	120
Crystal system	orthorhombic	monoclinic	orthorhombic	orthorhombic
Space group	*Pnca*	*P2₁/c*	*Pn2₁a*	*Pmna*
Cell parameters (Å)				
a	13.199	7.046	13.005	12.946
b	19.332	19.529	19.155	19.048
c	8.294	8.342	25.622	16.932
α, β, γ (°)	90, 90, 90	90, 107.45, 90	90, 90, 90	90, 90, 90
Z	1	1	1	2
R_1 factor (%)	3.7	5.88	4.89	-
Ref[4].	1	2	3	4, 5

[1]Also gustavite with less Sb substitution, $Ag_4Pb_4Bi_{11.2}Sb_{0.8}S_{24}$, with $a = 7.056$, $b = 9.691$, $c = 8.222$ Å, $β = 106.9°$, space group $P2_1/c$, $R_1 = 2.76\%$, by Makovicky and Topa (2011). [2]Or senandorite. [3]Tentative crystal structure refinement of Petrova *et al.* (1986). [4][1]: this study; [2]: Pažout & Dušek (2010); [3]: Sawada *et al.* (1987); [4]: Spiridonov *et al.* (1990); [5]: Petrova *et al.* (1986).

Details of the crystal structure and the interesting geometric relationships between the structures of orthorhombic oscarkempffite and monoclinic gustavite $PbAgBi_3S_6$ will be treated in another paper.

Relation to other species

Oscarkempffite is essentially a pure Ag-(Sb, Bi)-Pb sulfosalt with only trace amounts of copper and without As. It is a lillianite homologue $N = 4$ as confirmed by the N value calculated from the chemical analysis. With respect to the measure of $(Ag + Bi) \leftrightarrow 2Pb$ substitution, typical of the lillianite–gustavite and fizelyite–andorite substitution lines, oscarkempffite is extensively oversubstituted, with a substitution percentage of 124%, far beyond the 100% value of gustavite, $PbAgBi_3S_6$ (Makovicky and Karup-Møller, 1977*a,b*) and the ~100% value of senandorite (andorite VI; Sawada *et al.*, 1987). In this, it resembles the partly heterogeneous 'bismuthian andorites' from Julcani, Peru, analysed by Moëlo *et al.*, (1989) without crystallographic studies. They are distinguished by higher contents of copper, constant presence of arsenic (mostly between 1.2 and 2.5 wt.%), substitution percentages between ~101 and 119% and very variable Sb:Bi ratios (Moëlo *et al.*, 1989).

The orthorhombic Sb-Bi member of the lillianite homologous series from Kutná Hora (Czech Republic), investigated by Pažout and Dušek (2010) has the composition $Ag_{0.71}Pb_{1.52}Bi_{1.32}Sb_{1.45}S_6$. It has

a substitution percentage of only 70.5% and its lattice, with $a = 4.254$, $b = 13.309$, $c = 19.625$ Å, space group *Cmcm*, corresponds to a classical unit cell of lillianite. Oscarkempffite also resembles roshchinite (Spiridonov *et al.*, 1990) from Kvartsitovye Gorki deposit, Kazakhstan, for which published data indicate a substitution value of 120%. In roshchinite, however, Bi is absent, As is present in 3.5 wt.%, and the crystal structure has not been worked out beyond the subcell of the andorite type (Petrova *et al.*, 1986). Comparative data for oscarkempffite and related minerals are given in Table 5.

Acknowledgements

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