

Article

# Oyonite, $\text{Ag}_3\text{Mn}_2\text{Pb}_4\text{Sb}_7\text{As}_4\text{S}_{24}$ , a New Member of the Lillianite Homologous Series from the Uchucchacua Base-Metal Deposit, Oyon District, Peru

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**Abstract:** The new mineral species oyonite, ideally  $\text{Ag}_3\text{Mn}_2\text{Pb}_4\text{Sb}_7\text{As}_4\text{S}_{24}$ , has been discovered in the Uchucchacua base-metal deposit, Oyon district, Catajambo, Lima Department, Peru, as very rare black metallic subhedral to anhedral crystals, up to 100  $\mu\text{m}$  in length, associated with orpiment, tennantite/tetrahedrite, menchettiite, and other unnamed minerals of the system Pb-Ag-Sb-Mn-As-S, in calcite matrix. Its Vickers hardness ( $\text{VHN}_{100}$ ) is 137  $\text{kg}/\text{mm}^2$  (range 132–147). In reflected light, oyonite is weakly to moderately bireflectant and weakly pleochroic from dark grey to a dark green. Internal reflections are absent. Reflectance values for the four COM wavelengths [ $R_{\text{min}}$ ,  $R_{\text{max}}$  (%) ( $\lambda$  in nm)] are: 33.9, 40.2 (471.1); 32.5, 38.9 (548.3), 31.6, 38.0 (586.6); and 29.8, 36.5 (652.3). Electron microprobe analysis gave (in wt %, average of 5 spot analyses): Cu 0.76 (2), Ag 8.39 (10), Mn 3.02 (7), Pb 24.70 (25), As 9.54 (12), Sb 28.87 (21), S 24.30 (18), total 99.58 (23). Based on 20 cations per formula unit, the chemical formula of oyonite is  $\text{Cu}_{0.38}\text{Ag}_{2.48}\text{Mn}_{1.75}\text{Pb}_{3.79}\text{Sb}_{7.55}\text{As}_{4.05}\text{S}_{24.12}$ . The main diffraction lines are ( $d$  in  $\text{\AA}$ ,  $hkl$  and relative intensity): 3.34 (−312; 40), 3.29 (−520; 100), 2.920 (−132; 40), 2.821 (−232; 70), 2.045 (004; 50). The crystal structure study revealed oyonite to be monoclinic, space group  $P2_1/n$ , with unit-cell parameters  $a = 19.1806$  (18),  $b = 12.7755$  (14),  $c = 8.1789$  (10)  $\text{\AA}$ ,  $\beta = 90.471$  (11) $^\circ$ ,  $V = 2004.1$  (4)  $\text{\AA}^3$ ,  $Z = 2$ . The crystal structure was refined to a final  $R_1 = 0.032$  for 6272 independent reflections. Oyonite belongs to the Sb-rich members of the andorite homeotypic sub-series within the lillianite homologous series. The name oyonite is after the Oyon district, Lima Department, Peru, the district where the type locality (Uchucchacua mine) is located.

**Keywords:** oyonite; lillianite homologous series; sulfosalt; copper; antimony; arsenic; Oyon district; Lima department; Peru

## 1. Introduction

Oyonite has been found during a mineralogical investigation of the ore minerals from the Uchucchacua base-metal deposit, Oyon district, Catajambo, Lima Department, Peru. This deposit is the type locality for other four Mn-bearing sulfosalts: uchucchacuaite,  $\text{AgMnPb}_3\text{Sb}_5\text{S}_{12}$  [1], benavidesite,  $\text{MnPb}_4\text{Sb}_6\text{S}_{14}$  [2], manganquadratite,  $\text{AgMnAsS}_3$  [3], and menchettiite,  $\text{AgMn}_{1.60}\text{Pb}_{2.40}\text{Sb}_3\text{As}_2\text{S}_{12}$  [4].

The sample containing oyonite was not found in situ but originates from a sample given to one of the authors (F.N.K.) by the mineral dealer John Veevaert. The material was found in October 2010 from the Nivel 890, Uchucchacua base-metal deposit, Oyon district, Catajambo, Lima Department, Peru, and it is the same material where menchettiite [4] was found. Geological and metallogenic data concerning this mining district have been reported by [2].

Oyonite is associated with orpiment, tennantite/tetrahedrite, menchettiite, and other unnamed minerals of the system Pb-Ag-Sb-Mn-As-S, in calcite matrix.

The new mineral was named oyonite, after the Oyon district, Lima Department, Peru, where the type locality (Uchucchacua mine) is located. The mineral and its name have been approved by the IMA CNMNC, under the number 2018-002. The holotype specimen of oyonite is deposited in the mineralogical collections of the Museo di Storia Naturale, Università degli Studi di Firenze, Via G. La Pira 4, Florence, Italy, under catalogue number 3283/I.

The mineralogical description of oyonite, as well as its crystal structure, are described in this paper.

## 2. Mineral Description and Physical Properties

Oyonite (Figure 1) occurs as black subhedral to anhedral crystals, up to 100  $\mu\text{m}$  in length. Streak is black, and the luster is metallic.



**Figure 1.** Andorite-like minerals occurring with orpiment on calcite. The crystals are not a single phase but a mixture of mainly different andorite-group minerals (i.e., oyonite, menchettiite, ...). The width is 1 mm. Photo by Christian Rewitzer.

In plane-polarized incident light, oyonite is weakly to moderately bireflectant and weakly pleochroic from dark grey to dark green. Internal reflections are absent. Between crossed polars, the mineral is anisotropic, without characteristic rotation tints.

The reflectance was measured in air by means of an MPM-200 Zeiss microphotometer equipped with an MSP-20 system processor on a Zeiss Axioplan ore microscope. Filament temperature was approximately 3350 K. Readings were taken for specimen and standard (SiC) maintained under the same focus conditions. The diameter of the circular measuring area was 0.1 mm. Reflectance percentages in the form [ $R_{\min}$ ,  $R_{\max}$  (%) ( $\lambda$  in nm)] are: 33.9, 40.2 (471.1); 32.5, 38.9 (548.3), 31.6, 38.0 (586.6); and 29.8, 36.5 (652.3).

Oyonite is brittle. Its Vickers hardness ( $\text{VHN}_{100}$ ) is 137  $\text{kg}/\text{mm}^2$  (range 132–147), corresponding to a Mohs hardness of ~3–3.5. Based on the empirical formula, the calculated density is 5.237  $\text{g}/\text{cm}^3$ . The density, calculated based on the ideal chemical formula (see below), is 5.275  $\text{g}/\text{cm}^3$ .

### 3. Chemical Data

A preliminary EDS (Energy Dispersive Spectrometry) analysis performed on the crystal grain used for the structural study did not indicate the presence of elements ( $Z > 9$ ) other than Cu, Ag, Mn, Pb, As, Sb and S.

Quantitative chemical analyses were carried out using a JEOL JXA-8200 electron-microprobe, operating in WDS (Wavelength Dispersive Spectrometry) mode. Major and minor elements were determined at 15 kV accelerating voltage and 30 nA beam current, with 10 s as counting time. For the WDS analyses, the following lines were used:  $PbM\alpha$ ,  $AgL\alpha$ ,  $CuK\alpha$ ,  $MnK\alpha$ ,  $SbL\beta$ ,  $AsL\alpha$ ,  $SK\alpha$ . The standards employed were: galena (Pb), Ag- pure element (Ag), Cu- pure element (Cu), synthetic MnS (Mn), pyrite (Fe,S), synthetic ZnS (Zn), synthetic  $Sb_2S_3$  (Sb), synthetic  $As_2S_3$  (As), synthetic  $Bi_2S_3$  (Bi), and synthetic  $PtSe_2$  (Se). Iron, Zn, Bi, and Se were found below detection limit. The crystal fragment was found to be homogeneous within analytical error. Table 1 gives analytical data (average of 5 spot analyses).

**Table 1.** Chemical data of oyonite.

Element	wt (%) ( $n = 5$ )	Range	Estimated Standard Deviation
Cu	0.76	0.50–1.05	0.02
Ag	8.39	8.08–8.91	0.10
Mn	3.02	2.89–3.22	0.07
Pb	24.70	24.55–25.81	0.25
As	9.54	9.11–9.82	0.12
Sb	28.87	28.24–29.61	0.21
S	24.30	23.63–24.71	0.18
Total	99.58	99.18–100.41	0.23

The empirical formula, based on 20 cations per formula unit, is  $Cu_{0.38}Ag_{2.48}Mn_{1.75}Pb_{3.79}Sb_{7.55}As_{4.05}S_{24.12}$ , with rounding errors. The  $Ev(\%)$  value, defined as  $[Ev(+) - Ev(-)] \times 100/Ev(-)$ , is +1.0. After subtracting minor Cu according to the substitution  $Cu^+ \rightarrow Ag^+$ , the formula can be written as  $Ag_{2.86}Mn_{1.75}Pb_{3.79}Sb_{7.55}As_{4.05}S_{24.12}$ . The ideal formula is  $Ag_3Mn_2Pb_4Sb_7As_4S_{24}$ , which requires (in wt %) Ag 10.17, Mn 3.45, Pb 26.03, As 9.41, Sb 26.77, S 24.17, sum 100.00.

### 4. Crystallography

For the X-ray single-crystal diffraction study, the intensity data were collected using an Oxford Diffraction Xcalibur 3 diffractometer, equipped with a Sapphire 2 CCD area detector, with  $MoK\alpha$  radiation. The detector to crystal working distance was 6 cm. Intensity integration and standard Lorentz-polarization corrections were performed with the *CrysAlis RED* [5] software package. The program ABSPACK in *CrysAlis RED* [5] was used for the absorption correction. Tests on the distribution of  $|E|$  values agree with the occurrence of an inversion center ( $|E^2 - 1| = 0.895$ ). This information, together with the systematic absences, suggested the space group  $P2_1/n$ . We decided to keep this non-standard setting of the space group to make easier the comparison with the other members of the lillianite homologous series [6]. The refined unit-cell parameters are  $a = 19.1806$  (18),  $b = 12.7755$  (14),  $c = 8.1789$  (10) Å,  $\beta = 90.471$  (11)°,  $V = 2004.1$  (4) Å<sup>3</sup>.

The crystal structure was refined with *Shelxl-97* [7] starting from the atomic coordinates of menchettiite [4]. The occurrence of twinning on {100} was considered. The site occupancy factors (s.o.f.) were refined using the scattering curves for neutral atoms given in the *International Tables for Crystallography* [8]. After several cycles of anisotropic refinement, a final  $R_1 = 0.0227$  for 2199 reflections with  $F_o > 4\sigma(F_o)$  was achieved (0.0317 for all 6272 reflections). Crystal data and details of the intensity data collection and refinement are reported in Table 2.

**Table 2.** Crystal and experimental details for oyonite.

Crystal Data	
Crystal size (mm <sup>3</sup> )	0.045 × 0.055 × 0.070
Cell setting, space group	Monoclinic, $P2_1/n$
$a$ (Å)	19.1806 (18)
$b$ (Å)	12.7755 (14)
$c$ (Å)	8.1789 (10)
$\beta$ (°)	90.471 (11)
$V$ (Å <sup>3</sup> )	2004.1 (4)
$Z$	2
Data collection and Refinement	
Radiation, wavelength (Å)	MoK $\alpha$ , $\lambda = 0.71073$
Temperature (K)	293
$2\theta_{\max}$ (°)	64.63
Measured reflections	27568
Unique reflections	6272
Reflections with $F_o > 4\sigma(F_o)$	2199
$R_{\text{int}}$	5.01
$R\sigma$	6.16
Range of $h, k, l$	$-27 \leq h \leq 28,$ $0 \leq k \leq 18,$ $0 \leq l \leq 12$
$R [F_o > 4\sigma(F_o)]$	0.0227
$R$ (all data)	0.0317
$wR$ (on $F_o^2$ )	0.0756
Number of least-squares parameters	206
Maximum and minimum residual peak ( $e \text{ \AA}^{-3}$ )	1.22 (at 1.26 Å from S9) – 2.98 (at 1.00 Å from M8)

Atomic coordinates, site occupancies, and equivalent isotropic displacement parameters are given in Table 3. Selected bond distances are given in Table 4 and bond valence sums are given in Table 5. The crystallographic information file (CIF) is given as Supplementary Material.

**Table 3.** Atomic coordinates, site occupancies, and equivalent isotropic displacement parameters (in Å<sup>2</sup>) for oyonite.

Site	s.o.f.	$x$	$y$	$z$	$U_{\text{eq}}$
M1	Sb <sub>0.69(1)</sub> Mn <sub>0.31(1)</sub>	0.13588 (7)	0.33007 (10)	0.12257 (19)	0.0516 (6)
M2	As <sub>0.96(1)</sub> Sb <sub>0.04(1)</sub>	0.06326 (7)	0.62044 (9)	0.1240 (2)	0.0285 (4)
M3	Pb <sub>0.91(1)</sub> Sb <sub>0.09(1)</sub>	0.24633 (3)	0.58190 (5)	0.38468 (9)	0.0473 (2)
M4	Ag <sub>0.80(1)</sub> Cu <sub>0.20(1)</sub>	0.35946 (6)	0.32999 (10)	0.1290 (2)	0.0526 (6)
M5	Sb <sub>1.00</sub>	0.45771 (5)	0.60464 (6)	0.12818 (14)	0.0335 (2)
M6	Sb <sub>1.00</sub>	0.11431 (5)	0.33212 (7)	0.61891 (14)	0.0379 (3)
M7	Sb <sub>0.92(1)</sub> As <sub>0.08(1)</sub>	0.05163 (5)	0.63732 (8)	0.64699 (15)	0.0378 (4)
M8	Pb <sub>1.00</sub>	0.24437 (3)	0.57781 (4)	0.88178 (8)	0.0376 (2)
M9	Mn <sub>0.55(1)</sub> Ag <sub>0.45(1)</sub>	0.36399 (6)	0.34426 (9)	0.61981 (19)	0.0206 (4)
M10	As <sub>1.00</sub>	0.43438 (6)	0.59947 (9)	0.6332 (2)	0.0254 (3)
S1	S <sub>1.00</sub>	0.10164 (17)	0.5080 (3)	0.3380 (5)	0.0387 (10)
S2	S <sub>1.00</sub>	−0.00527 (16)	0.2329 (2)	0.1480 (5)	0.0307 (8)
S3	S <sub>1.00</sub>	0.25202 (18)	0.4302 (2)	0.1411 (4)	0.0360 (8)
S4	S <sub>1.00</sub>	0.16552 (16)	0.7182 (2)	0.1134 (5)	0.0294 (8)
S5	S <sub>1.00</sub>	0.3869 (2)	0.4998 (3)	0.4219 (6)	0.0470 (12)
S6	S <sub>1.00</sub>	0.3468 (15)	0.7112 (2)	0.1078 (6)	0.0302 (9)
S7	S <sub>1.00</sub>	0.09078 (17)	0.5105 (3)	0.8998 (6)	0.0446 (12)
S8	S <sub>1.00</sub>	0.48785 (19)	0.2893 (3)	0.0896 (4)	0.0410 (10)
S9	S <sub>1.00</sub>	0.23509 (15)	0.4183 (2)	0.6086 (5)	0.0327 (9)
S10	S <sub>1.00</sub>	0.16473 (15)	0.7199 (2)	0.6453 (6)	0.0325 (9)
S11	S <sub>1.00</sub>	0.39479 (17)	0.4896 (2)	0.8338 (5)	0.0397 (11)
S12	S <sub>1.00</sub>	0.34339 (15)	0.7228 (2)	0.6462 (5)	0.0283 (8)

**Table 4.** Selected bond distances (in Å) in the crystal structure of oyonite.

M1	–S3	2.575 (4)	M2	–S4	2.327 (3)	M3	–S3	2.781 (4)	M4	–S3	2.429 (3)	M5	–S8	2.476 (4)
	–S12	2.624 (4)		–S7	2.372 (4)		–S9	2.789 (4)		–S8	2.540 (4)		–S6	2.531 (3)
	–S6	2.698 (4)		–S1	2.376 (4)		–S5	2.907 (4)		–S4	2.594 (4)		–S2	2.615 (3)
	–S1	2.952 (4)		–S2	3.108 (4)		–S1	2.953 (3)		–S10	2.686 (4)		–S11	3.061 (4)
	–S2	2.985 (3)		–S8	3.337 (4)		–S10	3.187 (4)		–S11	3.236 (4)		–S5	3.076 (4)
	–S7	3.056 (4)		–S7	3.400 (3)		–S4	3.208 (4)		–S5	3.271 (4)		–S11	3.088 (3)
							–S12	3.350 (3)						
							–S6	3.411 (4)						
M6	–S12	2.505 (4)	M7	–S10	2.412 (3)	M8	–S3	2.840 (3)	M9	–S4	2.556 (4)	M10	–S11	2.293 (4)
	–S6	2.531 (4)		–S2	2.525 (4)		–S4	3.023 (4)		–S10	2.557 (4)		–S5	2.326 (4)
	–S9	2.568 (3)		–S7	2.727 (5)		–S9	3.028 (4)		–S5	2.603 (4)		–S12	2.354 (3)
	–S8	2.887 (4)		–S8	2.840 (4)		–S10	3.053 (4)		–S11	2.616 (4)		–S8	3.054 (4)
	–S1	3.222 (4)		–S1	3.175 (5)		–S7	3.074 (4)		–S9	2.648 (3)		–S2	3.178 (4)
	–S7	3.271 (5)		–S1	3.480 (4)		–S11	3.125 (4)		–S2	2.703 (3)		–S5	3.687 (4)
							–S6	3.181 (4)						
							–S12	3.288 (4)						

**Table 5.** Bond valence sums (in valence unit) in oyonite.

Site	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	$\Sigma_{\text{anion}}$
S1	0.22	0.75	0.33			0.12	0.14 0.06				1.62
S2	0.20	0.10			0.64		0.79		0.24	0.08	2.05
S3	0.61		0.52	0.42				0.46			2.01
S4		0.86	0.17	0.27				0.28	0.36		1.94
S5			0.37	0.04	0.18				0.32	0.84 0.02	1.77
S6	0.43		0.10		0.80	0.80		0.18			2.31
S7	0.16	0.76 0.05				0.11	0.46	0.24			1.78
S8		0.06		0.31	0.93	0.31	0.34			0.12	2.07
S9			0.51			0.73		0.27	0.28		1.79
S10			0.17	0.21			1.07	0.26	0.36		2.07
S11				0.05	0.19 0.18			0.21	0.31	0.92	1.86
S12	0.53		0.11			0.86		0.14		0.78	2.42
$\Sigma_{\text{cation}}$	2.15	2.58	2.17	1.30	2.92	2.93	2.86	2.04	1.87	2.64	
Theor.	2.69	3.00	2.09	1.00	3.00	3.00	3.00	2.00	1.55	3.00	

X-ray powder diffraction data (Table 6) were obtained on the same fragment used for the single-crystal study with an Oxford Diffraction Excalibur PX Ultra diffractometer fitted with a 165 mm diagonal Onyx CCD detector and using copper radiation ( $\text{CuK}\alpha$ ,  $\lambda = 1.54138 \text{ \AA}$ ). The working conditions were 40 kV and 40 nA with 1 hour of exposure; the detector-to-sample distance was 7 cm. The program *Crysalis* RED was used to convert the observed diffraction rings to a conventional powder diffraction pattern. The least squares refinement gave the following unit-cell values:  $a = 19.175 (1)$ ,  $b = 12.7775 (9)$ ,  $c = 8.1817 (8) \text{ \AA}$ ,  $\beta = 90.26 (1)^\circ$ ,  $V = 2004.6 (2) \text{ \AA}^3$ .

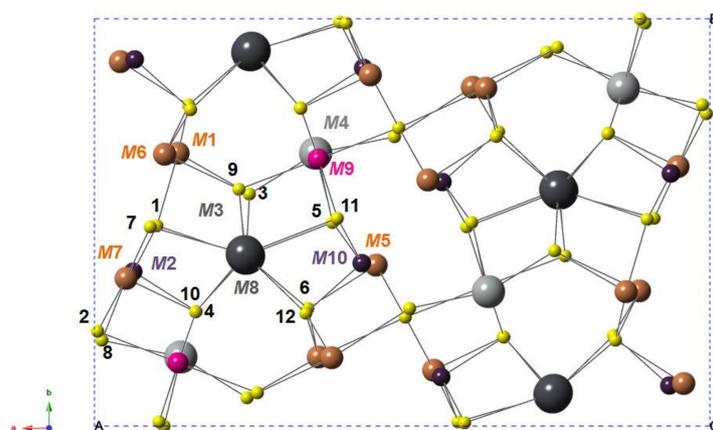
**Table 6.** Observed and calculated X-ray powder diffraction data ( $d$  in Å) for oyonite. The five strongest reflections are given in bold.

$I_{\text{obs}}$	$d_{\text{obs}}$	$I_{\text{calc}}$	$d_{\text{calc}}$	$h$	$k$	$l$
-	-	13	9.5900	2	0	0
15	6.05	21	6.0605	1	2	0
10	5.32	14	5.3164	2	2	0
-	-	12	3.8947	0	1	2
25	3.83	25	3.8348	4	2	0
20	3.62	21	3.6183	-2	1	2
-	-	16	3.5986	2	1	2
<b>40</b>	<b>3.34</b>	40	3.3377	-3	1	2
-	-	42	3.3146	3	1	2
<b>100</b>	<b>3.29</b>	100	3.2886	5	2	0
-	-	12	3.1967	6	0	0
10	3.20	14	3.1939	0	4	0
30	3.15	30	3.1505	1	4	0
<b>40</b>	<b>2.920</b>	25	2.9179	-1	3	2
-	-	28	2.9127	1	3	2
30	2.860	30	2.8587	6	2	0
<b>70</b>	<b>2.821</b>	55	2.8240	-2	3	2
-	-	54	2.8146	2	3	2
35	2.678	20	2.6843	-3	3	2
-	-	24	2.6723	3	3	2
20	2.241	11	2.2493	-7	1	2
-	-	12	2.2328	7	1	2
-	-	20	2.0488	-8	1	2
<b>50</b>	<b>2.045</b>	35	2.0447	0	0	4
-	-	20	2.0346	8	1	2
20	1.980	16	1.9779	-4	5	2
10	1.971	14	1.9714	4	5	2
25	1.945	25	1.9460	4	6	0
10	1.919	9	1.9180	10	0	0
5	1.863	9	1.8659	-8	3	2
-	-	9	1.8551	8	3	2
15	1.740	14	1.7419	-5	2	4
-	-	14	1.7309	5	2	4

## 5. Results and Discussion

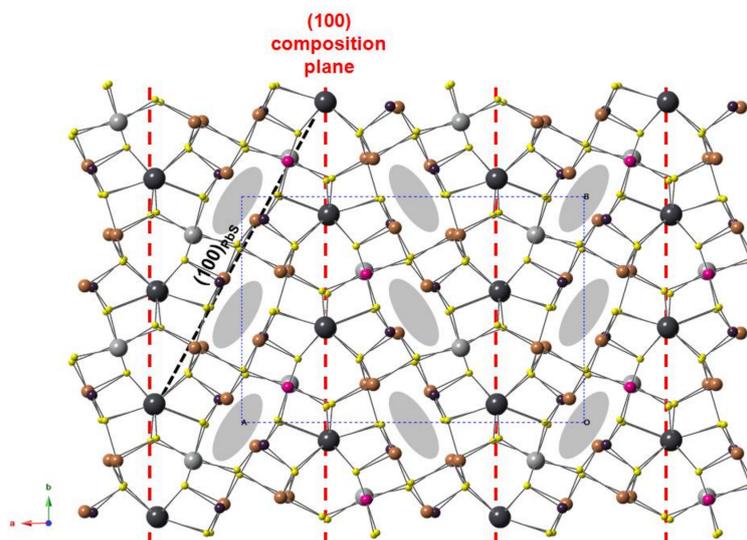
### 5.1. Crystal Structure Description

The crystal structure of oyonite (Figure 2) agrees with those of the  $^{4,4}L$  homologue in the lillianite homologous series [6]. There are 10 metal sites and 12 S sites in the unit cell.



**Figure 2.** Unit-cell content of oyonite as seen down  $c$ . Circles: dark grey = Pb sites; light grey = Ag sites; orange = Sb sites; violet = As site; purple = Mn site; yellow = S sites. Atom labels as in Table 3 (for S sites, only the number is reported).

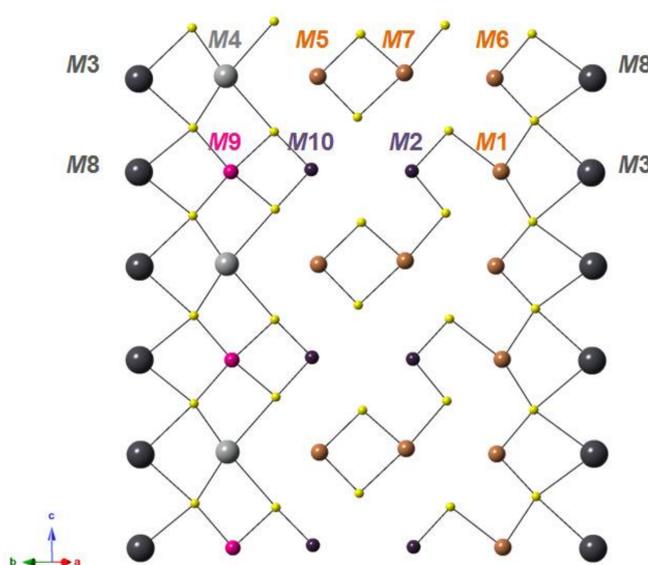
The general organization of oyonite, as seen down *c*, is shown in Figure 3. The crystal structure is formed by the alternation of  $(311)_{\text{PbS}}$  slabs, four octahedra thick along  $(100)_{\text{PbS}}$  and unit-cell twinned by reflection on  $(311)_{\text{PbS}}$  planes. The crystal structure of oyonite shows a two-fold superstructure with respect to the short 4 Å axis of the substructure.



**Figure 3.** General organization of oyonite, as seen down *c*. Within each slab, separated by the  $(100)$  composition plane,  $(100)_{\text{PbS}}$  planes occur (one of them is shown by the black dashed line). Lone electron-pair micelles are shown as grey ellipses.

Two independent sites are located on the composition planes  $(100)$  of the unit-cell twinning, i.e., *M3* and *M8*. They show a bicapped trigonal prismatic coordination, with a pure Pb occupancy (at *M8*) or a mixed (Pb,Sb) occupancy (at *M3*), with a Pb:Sb atomic ratio of 91:9. The chemical composition of the  $(100)$  composition plane is  $[(\text{Pb}_{1.91}\text{Sb}_{0.09})\text{S}_2]^{+0.09}$ , that can be simplified as  $(\text{Pb}_2\text{S}_2)$ .

Only one kind of  $(311)_{\text{PbS}}$  slab occurs in the crystal structure of oyonite, formed by one kind of diagonal  $(100)_{\text{PbS}}$  plane (Figure 4).



**Figure 4.** Organization of the  $(100)_{\text{PbS}}$  layer in oyonite, as seen perpendicular to  $(110)$ .

On the border of the plane, mixed (Ag,Cu) and (Mn,Ag)-centered octahedra (i.e., M4 and M9 sites, respectively) on one side, and Sb and (Sb,Mn)-centered sites alternate (M6 and M1 sites, respectively). In the center of the plane, a pure Sb site (M5) alternates with a pure As site (M10) along *c* in one column and mixed (Sb,As) and (As,Sb) sites in the other column (M7 and M2 sites, respectively). The composition of the diagonal (100)<sub>PbS</sub> plane is (Cu<sub>0.20</sub>Ag<sub>1.25</sub>Mn<sub>0.86</sub>Sb<sub>3.65</sub>As<sub>2.04</sub>S<sub>10</sub>), that can be simplified as (Ag<sub>1.5</sub>MnSb<sub>3.5</sub>As<sub>2</sub>S<sub>10</sub>). Thus, the simplified chemical composition of oyonite is given by  $2 \times \text{Pb}_2\text{S}_2 + 2 \times (\text{Ag}_{1.5}\text{MnSb}_{3.5}\text{As}_2\text{S}_{10}) = \text{Ag}_3\text{Mn}_2\text{Pb}_4\text{Sb}_7\text{As}_4\text{S}_{24}$ .

The chemical formula, as obtained through the single-crystal X-ray diffraction study, is Cu<sub>0.40</sub>Ag<sub>2.48</sub>Mn<sub>1.74</sub>Pb<sub>3.82</sub>Sb<sub>7.48</sub>As<sub>4.08</sub>S<sub>24</sub> (*Z* = 2).

## 5.2. Relation to the Other Species

Oyonite belongs to the andorite sub-series of the Sb-rich homeotypic members within the lillianite homologous series ([9]). Following the calculation procedure for the order *N* and the  $\text{Ag}^+ + \text{Me}^{3+} = 2\text{Pb}^{2+}$  substitution proposed by [6], considering minor cations, the homologue order from chemical analysis is *N* = 3.58, slightly smaller than the crystallographic value *N* = 4 indicated by the crystal structure refinement, whereas the substitution percentage is 83%. The idealized chemical composition corresponds to *N* = 4 and a substitution percentage of 75%.

The simplified chemical formula of the members of the andorite homeotypic series is  $\text{Ag}_x\text{Pb}_{3-2x}\text{Me}^{3+}_{2+x}\text{S}_6$ , where *Me* = (Sb,Bi). Within this series, the classification of its members can be indicated by the percentage of the andorite component *And<sub>n</sub>*, where *n* (%) = 100 *x*. In ideal oyonite, *n* = 75. Following [6] and [10], mineral species belonging to the andorite series have compositions close to integer values of *m* in the general formula  $\text{Ag}_{16-m}\text{Pb}_{16+2m}\text{Sb}_{48-m}\text{S}_96$ , where  $m = 16 \times [1 - (n/100)]$ . The known species have *m* = 8 (uchucchacuaite [11] and menchettiite [4]), 6 (fizélyite [12]), 5 (ramdohrite [13]), 1 (quatrandorite [14]), 0 (senandorite [15]), −1 (andreadiniite [16]), −2 (arsenquatrandorite [17]), −3 (roshchinite [18]), and −5 (jasrouxite [19]). Oyonite, having an andorite component *And*<sub>75</sub>, corresponds to a new member in the sequence, having *m* = 4.

Oyonite is the third member of the andorite series where Mn plays a structural role. Based on 12 S atoms per formula unit (*Z* = 2), these three minerals have formulae  $\text{AgMnPb}_3\text{Sb}_5\text{S}_{12}$  (uchucchacuaite [1,11]),  $\text{AgMn}_{1.5}\text{Pb}_{2.5}\text{Sb}_3\text{As}_2\text{S}_{12}$  (menchettiite [4]), and  $\text{Ag}_{1.5}\text{MnPb}_2\text{Sb}_{3.5}\text{As}_2\text{S}_{12}$  (oyonite). Oyonite is related to uchucchacuaite through the heterovalent substitutions  $0.5^{M1}\text{Sb}^{3+} + ^{M5}\text{Pb}^{2+} + 0.5^{M9}\text{Mn}^{2+} = 0.5^{M1}\text{Mn}^{2+} + ^{M5}\text{Sb}^{3+} + 0.5^{M9}\text{Ag}^+$  and by the substitution of Sb-by-As at the M2 and M10 sites. It differs from menchettiite for a higher *And* component, related to a higher (Ag+Sb) content in the (311)<sub>PbS</sub> layers (e.g., Sb at M1 and Ag at M9). A comparison between site occupancies in the three Mn-rich members of the andorite group is given in Table 7.

**Table 7.** Summary of site occupancies in Mn-bearing ramdohrite-type minerals.

	Uchucchacuaite [11]	Menchettiite [4]	Oyonite (This Work)
M1	Sb	Mn <sub>0.60</sub> Pb <sub>0.40</sub>	Sb <sub>0.69</sub> Mn <sub>0.31</sub>
M2	Sb	As <sub>0.57</sub> Sb <sub>0.43</sub>	As <sub>0.96</sub> Sb <sub>0.04</sub>
M3	Pb	Pb <sub>0.65</sub> Sb <sub>0.35</sub>	Pb <sub>0.91</sub> Sb <sub>0.09</sub>
M4	Ag	Ag	Ag <sub>0.80</sub> Cu <sub>0.20</sub>
M5	Pb	Sb <sub>0.77</sub> Pb <sub>0.23</sub>	Sb
M6	Sb	Sb	Sb
M7	Sb	Sb <sub>0.68</sub> As <sub>0.32</sub>	Sb <sub>0.92</sub> As <sub>0.08</sub>
M8	Pb	Pb	Pb
M9	Mn <sub>0.9</sub> Ag <sub>0.05</sub> Sb <sub>0.05</sub>	Mn	Mn <sub>0.55</sub> Ag <sub>0.45</sub>
M10	Sb	As	As

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2075-163X/8/5/192/s1>, CIF: oyonite.

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