

**SELENOPOLYBASITE, [(Ag,Cu)₆(Sb,As)₂(S,Se)₇][Ag₉Cu(S,Se)₂Se₂],
 A NEW MEMBER OF THE PEARCEITE–POLYBASITE GROUP
 FROM THE DE LAMAR MINE, OWYHEE COUNTY, IDAHO, USA**

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ABSTRACT

Selenopolybasite, ideally [(Ag,Cu)₆(Sb,As)₂(S,Se)₇][Ag₉Cu(S,Se)₂Se₂], is a new mineral species from the De Lamar mine, Owyhee County, Idaho, USA. It occurs as black anhedral to subhedral grains up to 400 μm across, closely associated with naumannite, covellite, pyrite and calcite. Selenopolybasite is opaque with a metallic luster and possesses a black streak. It is brittle, and neither fracture nor cleavage was observed; the Vickers microhardness (VHN₁₀₀) is 131 kg/mm² (range 125–141) (corresponding Mohs hardness: 3–3½). The density could not be measured owing to the small grain-size. The calculated density is 6.548 g/cm³ (on the basis of the empirical formula). In plane-polarized reflected light, selenopolybasite is light grey, weakly to moderately birefractant, and weakly pleochroic from grey to a violet-blue grey. Between crossed polars, it is anisotropic, with no characteristic rotation-tints and no internal reflections. Reflectance values (*R*_{min} and *R*_{max}) for the four standard COM wavelengths are 32.8, 34.1 (471.1 nm), 31.0, 32.9 (548.3 nm), 30.2, 31.8 (586.6 nm), and 29.3, 30.0% (652.3 nm), respectively. Selenopolybasite is trigonal, space group *P*3̄m1, with unit-cell parameters: *a* 7.5950(4), *c* 12.0731(6) Å, *V* 603.12(5) Å³, *c* : *a* 1.5896, *Z* = 1. The strongest eight X-ray powder-diffraction lines [*d* in Å(*hkl*)] are: 3.1731(48)(201), 3.0183(84)(004), 2.8880(48)(022), 2.8880(100)(202), 2.5466(23)(023), 2.3629(34)(114), 2.2237(28)(024) and 1.8987(31)(220). Average results of 10 electron-microprobe analyses gave the chemical formula [(Ag_{5.67}Cu_{0.20}Bi_{0.01}Pb_{0.01}Zn_{0.01}Fe_{0.03})Σ_{5.93}(Sb_{1.86}As_{0.19})Σ_{2.05}(S_{6.68}Se_{0.34})Σ_{7.02}][Ag₉Cu(S_{1.79}Se_{0.21})Σ_{2.00}Se₂], on the basis of 29 atoms and according to results of the structure refinement. The name chosen, selenopolybasite, recalls its status as the Se-dominant analogue of polybasite. Moreover, as it shows the 111 unit-cell type, the full name for the polytype is selenopolybasite-*Tac*, the Se-dominant analogue of polybasite-*Tac*.

Keywords: selenopolybasite, new mineral species, polytypes, electron-microprobe data, reflectance data, X-ray diffraction data, De Lamar mine, Owyhee County, Idaho.

SOMMAIRE

La sélénopolybasite, de composition idéale [(Ag,Cu)₆(Sb,As)₂(S,Se)₇][Ag₉Cu(S,Se)₂Se₂], est une nouvelle espèce minérale découverte à la mine De Lamar, comté d'Owyhee, en Idaho, États-Unis. Elle se présente en grains noirs xénomorphes ou subidiomorphes atteignant 400 μm, étroitement associés à la naumannite, covellite, pyrite et calcite. La sélénopolybasite est opaque, avec un éclat métallique, et elle possède une rayure noire. Elle est cassante, sans fracture ou clivage évident. La microdureté de Vickers (VHN₁₀₀) est 131 kg/mm² (entre 125 et 141), correspondant à une dureté de Mohs de 3–3½. Nous n'avons pas pu mesurer la densité fautive de matériau. La densité calculée, fondée sur la formule empirique, est 6.548 g/cm³. En lumière polarisée réfléchie, la sélénopolybasite est gris pâle, faiblement à modérément biréfractante, et faiblement pleochroïque de gris à gris violacé bleuâtre. Avec les nicols croisés, elle est anisotrope, sans teintes de rotation caractéristiques et sans réflexions internes. Les valeurs de réflectance (*R*_{min} et *R*_{max}) mesurées aux quatre longueurs d'onde standard (COM) sont 32.8, 34.1 (471.1 nm), 31.0, 32.9 (548.3 nm), 30.2, 31.8 (586.6 nm), et 29.3, 30.0% (652.3 nm), respectivement. La sélénopolybasite est trigonale, groupe spatial *P*3̄m1,

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avec les paramètres réticulaires a 7.5950(4), c 12.0731(6) Å, V 603.12(5) Å³, c : a 1.5896, $Z = 1$. Les huit raies les plus intenses du spectre de diffraction (méthode des poudres) [d en Å(hkl)] sont: 3.1731(48)(201), 3.0183(84)(004), 2.8880(48)(022), 2.8880(100)(202), 2.5466(23)(023), 2.3629(34)(114), 2.2237(28)(024) et 1.8987(31)(220). Les résultats moyens de dix analyses à la microsonde électronique ont donné la formule chimique [(Ag_{5.67}Cu_{0.20}Bi_{0.01}Pb_{0.01}Zn_{0.01}Fe_{0.03})Σ_{5.93}(Sb_{1.86}As_{0.19})Σ_{2.05}(S_{6.68}Se_{0.34})Σ_{7.02}] [Ag₉Cu(S_{1.79}Se_{0.21})Σ_{2.00}Se₂], sur une base de 29 atomes et selon les résultats de l'affinement de la structure. Le nom choisi, sélénopolybasite, rappelle son statut comme analogue sélénifère de la polybasite. De plus, elle montre la maille élémentaire de type 111; son nom complet serait donc sélénopolybasite-*Tac*, l'analogue sélénifère de la polybasite-*Tac*.

Mots-clés: sélénopolybasite, nouvelle espèce minérale, polytypes, données de microsonde électronique, données de réflectance, données de diffraction X, mine De Lamar, comté d'Owyhee, Idaho.

INTRODUCTION

The minerals belonging to the pearceite–polybasite group, with the general formula (Ag,Cu)₁₆M₂S₁₁ with $M = \text{Sb, As}$, are relatively common in nature. Frondel (1963) divided this group of minerals into two series: pearceite–antimonpearceite, characterized by a “small” unit-cell (labeled 111) and a high Cu content, and polybasite–arsenpolybasite, with double-cell parameters (labeled 222) and a low Cu content. Later, an intermediate type of unit cell (labeled 221) was discovered by Harris *et al.* (1965), Edenharter *et al.* (1971) and Minčeva-Stefanova *et al.* (1979). From the chemical point of view, the members of both series are generally pure, containing only minor amounts of Bi, Pb, Zn, and Fe. Nonetheless, Harris *et al.* (1965) reported the occurrence of a sample of antimonpearceite from the San Carlos mine, Guanajuato (Mexico) containing up to 8.7 wt.% Se, and Barrett & Zolensky (1986) reported polybasite samples containing up to 7.8 wt.% of Se from the De Lamar mine, Owyhee County, Idaho (USA).

The crystal structures of all the members of the group (*i.e.*, pearceite, antimonpearceite, arsenpolybasite-221, arsenpolybasite-222, polybasite-221 and polybasite-222) have been recently determined (Bindi *et al.* 2006a, 2007a, Evain *et al.* 2006a). On the basis of information gained from the structural characterization, Bindi *et al.* (2007b) proposed new rules of nomenclature for this group of minerals. These authors considered these minerals as a family of polytypes and named all the members pearceite or polybasite. A hyphenated italic suffix indicating the crystal system and the cell-type symbol is added, if crystallographic data are available.

According to the approved rules of nomenclature, the new mineral studied here, having Sb in excess of As and two sulfur structural positions dominated by selenium, has been named selenopolybasite to indicate that it is the Se-dominant analogue of polybasite. Moreover, as it exhibits the 111 unit-cell type, the full name for the polytype is selenopolybasite-*Tac*, the Se-dominant analogue of polybasite-*Tac*. It is worthy of note that Barrett & Zolensky (1986) observed that the intermediate 221 unit-cell type is predominant for Se-rich polybasite from the De Lamar mine. Moreover, they found high Se contents associated with both the

111 and 221 unit-cell types, whereas the fully ordered 222 unit-cell type was only encountered for polybasite containing no Se. This means that the new mineral selenopolybasite can be found in nature into two different polytypes, *i.e.*, -*Tac* (this study) and -*T2ac* (Barrett & Zolensky 1986).

The new mineral and mineral name have been approved by the Commission on New Minerals, Nomenclature and Classification, IMA (2006–053). The type material is housed in the Mineralogical Collection of the Museo di Storia Naturale, Università di Firenze, Italy, under the catalogue number 2453/I.

OCCURRENCE AND PHYSICAL AND OPTICAL PROPERTIES

The new mineral species described herein is from the De Lamar mine, Owyhee County, Idaho, U.S.A., a well-known source of rare selenide minerals (Barrett & Zolensky 1986, Bindi & Cipriani 2004). The mineralization of the De Lamar mine is concentrated in northwest-trending siliceous veins in a rhyolite porphyry of middle Miocene age. Deposition of the primary minerals occurred at shallow depths from heated brines. Geological and metallogenic data concerning this mining district have been reported by Panze (1975).

The sample containing the new phase was not found *in situ*, but originates from the Mineralogical Collection of the Museo di Storia Naturale, Sezione di Mineralogia e Litologia, Università di Firenze, Italy, where it had been labeled as “pearceite, De Lamar mine, Owyhee County, Idaho, U.S.A.”.

Selenopolybasite is typically associated with naumannite and covellite to form subhedral to anhedral grains up to several hundred micrometers in size. The other minerals spatially associated with selenopolybasite are pyrite and calcite.

The mineral is opaque with a metallic luster; it possesses a black streak. It is brittle; neither fracture nor cleavage was observed. Unfortunately, the density could not be measured because of the small grain-size; the calculated density is 6.548 g/cm³ (on the basis of the empirical formula). Micro-indentation measurements carried out with a VHN load of 100 g gave a mean value of 131 kg/mm² (range 125–141), corresponding to a Mohs hardness of 3–3½.

In plane-polarized reflected light, selenopolybasite is light grey, weakly to moderately birefractant, and weakly pleochroic grey to a violet-blue grey. Between crossed polars, the mineral is anisotropic, without characteristic rotation-tints and internal reflections. Selenopolybasite is slightly more highly reflecting than polybasite.

Reflectance measurements were made in air with a MPM-200 Zeiss microphotometer equipped with a 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 (R_{\min} , R_{\max}) for the four standard COM wavelengths are 32.8, 34.1 (471.1 nm), 31.0, 32.9 (548.3 nm), 30.2, 31.8 (586.6 nm), and 29.3, 30.0% (652.3 nm), respectively.

CHEMICAL COMPOSITION

The chemical composition was determined using wavelength-dispersion analysis (WDS) by means of an JEOL JXA-8200 electron microprobe. Experimental details are given in Evain *et al.* (2006b), who reported the mineral as a Se-rich variety of antimonpearceite. The average chemical composition (10 analyses on different spots), together with ranges of element concentrations, are reported in Table 1. On the basis of 29 atoms and according to the results of the structure refinement (Evain *et al.* 2006b), the chemical formula can be written as $[(Ag_{5.67}Cu_{0.20}Bi_{0.01}Pb_{0.01}Zn_{0.01}Fe_{0.03})_{\Sigma 5.93}(Sb_{1.86}As_{0.19})_{\Sigma 2.05}(S_{6.68}Se_{0.34})_{\Sigma 7.02}][Ag_9Cu(S_{1.79}Se_{0.21})_{\Sigma 2.00}Se_2]$, ideally $[(Ag,Cu)_6(Sb,As)_2(S,Se)_7][Ag_9Cu(S,Se)_2Se_2]$.

X-RAY CRYSTALLOGRAPHY

The detailed description of the crystal structure of selenopolybasite-*Tac* [space group $P\bar{3}m1$; a 7.5950(4), c 12.0731(6) Å, V 603.12(5) Å³, $Z = 1$], as well the experimental details pertinent to data collection and

refinement, have been published by Evain *et al.* (2006b). In Table 2, we report the calculated X-ray powder pattern for selenopolybasite computed with the atom coordinates and the occupancy factors given in Evain *et al.* (2006b).

REMARKS ON NOMENCLATURE AND STABILITY OF POLYTYPES

To propose new rules of nomenclature for the minerals belonging to the pearceite-polybasite group, Bindi *et al.* (2007b) studied thirty-one samples from different localities, with variable chemical composition, and showing the 111, 221, and 222 unit-cell types. These authors observed that the members having the 111 unit-cell type show a Cu content in the range 7.92–14.03 wt.% of the element, whereas those having the 221 or 222 unit-cell type show a range of 2.88–6.98%. Thus, the findings by Bindi *et al.* (2007b) corroborated the ideas of Hall (1967) that the variation of Cu content might be the driving force in stabilizing the various unit-cells. On this basis, Evain *et al.* (2006a) proposed a pattern of possible mechanisms regulating the stabilization of unit-cell types. Starting from the hypothetical stoichiometric and fully ordered $Ag_{15}CuSb_2S_{11}$ polybasite-222 structure, with a low $C2/c$ monoclinic symmetry and a large 222 supercell, the disorder introduced by the substitution of Cu for Ag increases the long-range-order symmetry, with a cell reduction along the c axis yielding the 221 supercell in the trigonal system. A further increase of the substitution gives rise to a halving of the cell along the a and b axes and the pearceite-111 structure, $P\bar{3}m1$ space group.

One should note, however, that two samples of polybasite-*Tac* (*i.e.*, 17004/80 and 2453/I) studied by Bindi *et al.* (2007b) show a copper content of 3.46 and 3.19%, respectively, although with unit-cell type 111.

TABLE 1. ELECTRON-MICROPROBE DATA, ATOM PROPORTIONS WITH THEIR STANDARD DEVIATIONS (σ) FOR SELENOPOLYBASITE-*Tac*

	wt.%	range	atom proportions	σ
Ag	66.17	65.21 – 67.39	14.67	0.14
Cu	3.19	2.88 – 3.81	1.20	0.07
Bi	0.09	0.09 – 0.16	0.01	0.01
Pb	0.09	0.02 – 0.20	0.01	0.01
Zn	0.03	0.00 – 0.09	0.01	0.01
Fe	0.07	0.00 – 0.12	0.03	0.01
Sb	9.47	9.00 – 9.89	1.86	0.09
As	0.60	0.23 – 0.99	0.19	0.02
S	11.36	10.88 – 11.56	8.47	0.08
Se	8.42	8.01 – 8.77	2.55	0.06
Total	99.49	99.11 – 100.26		

TABLE 2. CALCULATED X-RAY POWDER-DIFFRACTION DATA FOR SELENOPOLYBASITE-*Tac*

l	d_{calc} (Å)	h	k	l	l	d_{calc} (Å)	h	k	l
19.89	6.5775	1	0	0	5.96	2.1572	0	3	1
9.28	3.7975	1	1	0	14.48	2.1572	3	0	1
8.45	3.6225	1	1	1	18.57	2.0376	1	1	5
9.22	3.2887	2	0	0	10.52	1.9463	2	0	5
9.92	3.2144	1	1	2	12.81	1.9253	0	3	3
8.12	3.1731	0	2	1	31.47	1.8987	2	2	0
47.54	3.1731	2	0	1	18.56	1.8757	2	2	1
83.81	3.0183	0	0	4	15.06	1.7172	2	2	3
48.24	2.8880	0	2	2	18.86	1.7164	2	0	6
100.0	2.8880	2	0	2	6.36	1.6072	2	2	4
22.52	2.5466	0	2	3	14.32	1.5866	0	4	2
10.91	2.5466	2	0	3	7.68	1.5866	4	0	2
7.99	2.4350	2	1	1	6.11	1.5091	0	0	8
33.61	2.3629	1	1	4	8.51	1.4926	2	2	5
27.63	2.2237	0	2	4	5.66	1.4440	4	0	4
8.32	2.2237	2	0	4	6.45	1.2733	0	4	6
13.04	2.1925	3	0	0	5.34	1.2175	4	2	2

Note: The calculated X-ray powder pattern was computed with the atom coordinates and the occupancy factors reported in Evain *et al.* (2006b).

Moreover, the low copper content is associated with a relatively high content of selenium (2.03 and 8.42 wt.%, respectively). Hence, it seems that the Se-for-S substitution induces further structural disorder, thus increasing the long-range-order symmetry and giving rise to a folding of the cell along the three axes (111 unit-cell type). For this reason, it appears reasonable to suppose that the fully ordered polytypes of the mineral selenopolybasite (*i.e.*, $-M2a2b2c$) is unlikely to occur in nature. This hypothesis corroborates the ideas of Barrett & Zolensky (1986) that the presence of Se in polybasite inhibits full ordering to the 222 unit-cell type.

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