

Rosiaite, PbSb_2O_6 , a new mineral from the Cetine mine, Siena, Italy

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Abstract: Rosiaite occurs at the Cetine di Cotorniano mine, formerly named Rosia mine, associated with valentinite, tripuhyite, bindheimite and a phase corresponding to the synthetic $\beta\text{-Sb}_2\text{O}_4$ polymorph of cervantite. Rosiaite, appearing generally as aggregates of minute tabular {0001} crystals with hexagonal outline, is colourless to pale yellow, transparent, optically uniaxial negative and nonpleochroic with $\omega = 2.092(2)$ and $\epsilon = 1.920(10)$. Microprobe analyses reveal a good compositional homogeneity and a quasi-ideal composition. The strongest lines in the powder pattern are $d_{101} = 3.49 \text{ \AA}$ and $d_{110} = 2.648 \text{ \AA}$. The crystal structure, described in the space group $P\bar{3}1m$ with $a = 5.295(1) \text{ \AA}$, $c = 5.372(1) \text{ \AA}$ and $Z = 1$, has been refined to $R = 0.033$, confirming the new mineral to be the natural analogue of synthetic PbSb_2O_6 studied previously. The approximately hexagonal close-packed structure of rosiaite shows a pattern of occupied octahedral sites identical to that of synthetic compounds such as Li_2ZrF_6 , Li_2NbOF_5 and several double hexaoxides, containing Sb or As.

Key-words: rosiaite, new mineral, physical and chemical data, powder pattern, structure refinement.

Introduction

Rosiaite, PbSb_2O_6 , is a new mineral found in the Cetine mine, central Tuscany, Italy. It is the natural phase corresponding to the synthetic compound PbSb_2O_6 known for many years (Magneli, 1941).

The name of the new mineral is after the village of Rosia, near to the Cetine di Cotorniano mine, formerly named Rosia mine. Both mineral and its name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (ref. 95-021). Type material is preserved at the Dipartimento di Scienze della Terra, Sezione di Mineralogia, Università di Genova, Italy.

Recently rosiaite has been recognized also in material coming from the abandoned Tafone mine, Grosseto, Tuscany, Italy.

Occurrence

The Cetine mine, eastern flank of the Colline Metallifere, province of Siena, Italy, was active from 1878 for antimony exploitation; the active mining was finally terminated in 1948.

The mineralization, previously described by many authors (Pelloux, 1901; Lotti, 1910; Dessau, 1952; Sabelli & Brizzi, 1984), occurs in brecciated dolomitic limestones developed in evaporitic deposits of Triassic age known as

"Calcare Cavernoso". The "Calcare Cavernoso" overlies a quartzitic phyllitic basement, Paleozoic to Triassic in age, and in turn is tectonically overlain by shales and argillaceous limestones. Hydrothermal fluids, originating from magmatic Pliocene-Pleistocene intrusions, were active along fault systems; the circulating fluids strongly silicified the "Calcare Cavernoso" and deposited the mineralization, mainly consisting of stibnite as disseminated small pods (Sabelli & Brizzi, 1984).

The Cetine mine is a well known site for mineral collectors and mineralogists, because of the presence of numerous rare minerals and new species, such as onoratoite (Belluomini *et al.*, 1968), cetineite (Sabelli & Vezzalini, 1987), coquandite (Sabelli *et al.*, 1992), rosenbergite (Olmli *et al.*, 1993) and brizziite (Olmli & Sabelli, 1994).

Rosiaite, to the best of our knowledge, is the first Pb mineral found in the antimony deposit of the Cetine mine. It occurs in little cavities of a rock fragment found in the debris derived from mining operations, associated with valentinite, Sb_2O_3 , tripuhyite, $FeSb_2O_3$, bindheimite, $Pb_2Sb_2O_6(O,OH)$, and a phase corresponding to the synthetic β - Sb_2O_4 polymorph of cervantite, at present under study. Rosiaite generally occurs as aggregates, not exceeding 2 mm in size, of minute crystals up to 0.3 mm in size.

Physical properties and chemical composition

Rosiaite crystals show tabular habit with hexagonal outline (Fig. 1). The morphology is char-

acterized by a dominant pinacoid $\{0001\}$ associated with subordinated forms: hexagonal dipyramid $\{10\bar{1}1\}$, hexagonal prism $\{10\bar{1}0\}$ and a not indexed scalenohedron. The crystals are colourless to pale yellow, transparent, with resinous lustre and white streak; no cleavage is present, only a possible $\{0001\}$ parting has been observed. The mineral is brittle with conchoidal fracture. Due to the small size of the crystals, it was impossible to measure density and hardness. The calculated density is 6.96 g/cm^3 . The mineral does not fluoresce under short- and long-wave ultraviolet light. Optically, rosiaite is non-pleochroic, uniaxial negative, with $\omega = 2.092(2)$ and $\epsilon = 1.920(10)$, for 589 nm at 25°C using Cargille's liquids.

The chemical composition of rosiaite was determined by an electron microprobe (PHILIPS SEM 515 electron microscope equipped with EDAX PV9100 spectrometer) in energy dispersive mode, with an accelerating voltage of 15 kV and a beam current of about 2.10 nA.

Spot analyses show neither significant variations nor compositional zoning in single crystals. Microprobe analysis, average of 3 measurements, gives PbO 40.88 (ranging from 40.65 to 41.18) and Sb_2O_5 58.67 (ranging from 58.46 to 58.82) wt%, corresponding to the empirical formula $Pb_{1.008}Sb_{1.997}O_6$, calculated on the basis of six oxygen atoms.

X-ray powder diffraction

The powder pattern was obtained by a Guinier STOE camera using graphite-monochromatized

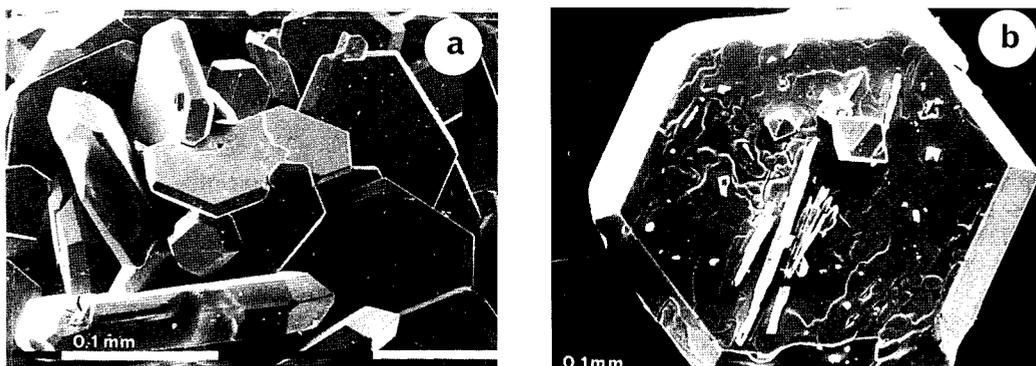


Fig. 1. SEM images showing: (a) aggregate of rosiaite crystals, (b) octahedra of bindheimite and acicular crystals of valentinite overgrown on a hexagonal tablet of rosiaite.

Table 1. X-ray powder-diffraction data for rosiaite (d in Å).

h	k	l	Calculated d	I	Measured d	I	h	k	l	Calculated d	I	Measured d	I
0	0	1	5.372	4	5.37	VVW	2	1	1	1.650	13	1.651	W
1	0	0	4.586	3	4.60	VVW	2	1	$\bar{1}$	1.650	9		
1	0	1	3.488	100	3.49	VS	3	0	0	1.529	11	1.531	W
0	0	2	2.686	10	2.688	VW	2	0	3	1.411	8	1.412	VVW
1	1	0	2.648	35	2.648	M	3	0	2	1.329	9	1.330	VW
1	1	1	2.375	2	2.376	VVW	2	2	0	1.324	5	1.325	VW
1	1	$\bar{1}$	2.375	1			2	1	3	1.245	5	1.246	VW
1	0	2	2.318	2	2.319	VVW	2	1	$\bar{3}$	1.245	6		
2	0	0	2.293	2	2.293	VVW	3	1	1	1.238	4	1.239	VW
2	0	1	2.109	22	2.110	W	3	1	$\bar{1}$	1.238	6		
1	1	2	1.886	22	1.887	W	1	1	4	1.198	3	1.198	VVW
1	1	$\bar{2}$	1.886	16			1	1	$\bar{4}$	1.198	5		
1	0	3	1.668	11	1.671	VW	2	2	2	1.187	4	1.188	VW
							2	2	$\bar{4}$	1.187	5		

CuK α radiation and silicon as an internal standard. The relative intensities of the reflections were estimated visually and the indices were inferred from the pattern calculated by the LAZY PULVERIX program (Yvon *et al.*, 1977), using as

input data the structural model resulting from the X-ray single-crystal analysis. In Table 1 calculated and measured diffraction data are compared. The cell parameters refined from powder data are $a = 5.301(1)$ Å and $c = 5.375(1)$ Å.

Table 2. Crystal structure data for rosiaite.

Formula used for refinement	PbSb ₂ O ₆
Space group	$P\bar{3}1m$
Z	1
a (Å)	5.295(1)
c (Å)	5.372(1)
V (Å ³)	130.4
μ (MoK α , mm ⁻¹)	42.77
Reflections measured ($-7 \leq h \leq 7$, $-7 \leq k \leq 7$, $-7 \leq l \leq 7$)	1508
Unique reflections	153
Observed reflections ($I > 3\sigma_I$)	151
R (observed)	0.033
R (all)	0.033
Extinction parameter ($\times 10^{-3}$)	1.2(3)

Table 3. Atomic coordinates and equivalent isotropic temperature factors (\AA^2) for rosiaite.

Atom	x/a	y/b	z/c	Beq
Pb	0.0	0.0	0.0	1.33
Sb	1/3	2/3	0.5	0.95
O	0.3770(16)	0.0	0.2965(22)	1.36

Table 4. Interatomic distances (\AA) and angles ($^\circ$) in rosiaite.

	$M-O$ distance		O-O distance	O-M-O angle
<u>PbO_6 octahedron</u>				
6 Pb-O	2.554(9)	6 O-O'	3.457(15)	85.21(36)
		6 -O''	3.759(20)	94.79(36)
Average	2.554		3.608	90.0
<u>SbO_6 octahedron</u>				
6 Sb-O	1.989(7)	3 O-O'	2.545(21)	79.56(46)
		6 -O''	2.878(6)	92.68(40)
		3 -O'''	2.960(19)	96.18(57)
Average	1.989		2.815	90.28

Refinement of the crystal structure

A near hexagonal tablet, measuring 0.20 x 0.11 x 0.04 mm, was used for the X-ray single-crystal analysis. The data collection was performed by means of an ENRAF-NONIUS CAD-4 automatic diffractometer. The cell parameters were determined

and refined using 25 reflections within the angular range $24 < \theta < 28^\circ$. The diffraction intensities were measured up to $\theta = 30^\circ$, using graphite-monochromatized $MoK\alpha$ radiation and operating in the $\omega - \theta$ scan mode. An absorption correction was applied using the ψ scan method (North *et al.*, 1968).

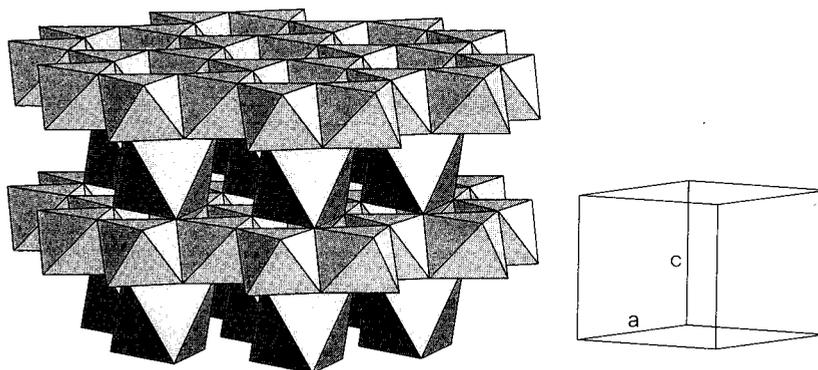


Fig. 2. Layers of edge-sharing SbO_6 octahedra alternating with layers of isolated PbO_6 octahedra in the rosiaite structure; the Pb atoms are positioned midway along [001] between the centers of SbO_6 octahedra rings.

The crystal structure was refined in the space group $P\bar{3}1m$ starting with the coordinates resulting from the structural analysis of the corresponding synthetic compound (Hill, 1987). Eight cycles of least squares refinement were carried out by a modified version of the ORFLS program (Busing *et al.*, 1962), using the scattering factors for neutral atoms from the International Tables for X-ray Crystallography, vol. IV (1974). Total site occupancy was fixed for all atoms; scale factor, secondary extinction coefficient, oxygen coordinates and temperature factors were simultaneously derived. The anisotropic temperature

factors were introduced after the fourth cycle. Tables 2, 3 and 4 summarize experimental details and results of the crystal structure refinement. These results confirm rosiaite to be the natural analogue of the synthetic $PbSb_2O_6$ studied by Magneli (1941) and Hill (1987).

According to the description given by the above authors, the structure of rosiaite is based on an approximately hexagonal close-packed array of oxygen atoms. The polyhedral framework consists of gibbsite-like layers, with 2/3 of the octahedral interstices occupied by Sb, alternating with layers where 1/3 of the octahedral

Table 5. Synthetic MSb_2O_6 and natural MM'_2O_6 compounds related to rosiaite.

Name	Chemical formula	Space group or crystal system	References
Synthetic	$CuSb_2O_6$	$P2_1/c$	SR 8, 153; PDF
	$\beta\text{-MnSb}_2O_6$	$P3$	SR 54A, 152
	$\gamma\text{-MnSb}_2O_6$	$P321$	SR 56A, 128; PDF
	$BaSb_2O_6$	$P\bar{3}1m$	SR 8, 157; PDF
	$PbSb_2O_6$	$P\bar{3}1m$	SR 54A, 152; PDF
	$SrSb_2O_6$	$P\bar{3}1m$	SR 8, 157
	$HgSb_2O_6$	$P\bar{3}1m$	SR 8, 157
	$CaSb_2O_6$	$P\bar{3}1m$	SR 8, 157; PDF
	$CdSb_2O_6$	$P\bar{3}1m$	SR 8, 157; 55A, 153; PDF
	$ZnSb_2O_6$	$P4/mnm$	SR 8, 153; PDF
	$FeSb_2O_6$	tet.	SR 8, 155; PDF
	$CoSb_2O_6$	$P4/mnm$	SR 8, 155; 56A, 128; PDF
	$NiSb_2O_6$	tet.	SR 8, 155; PDF
	$MgSb_2O_6$	tet.	SR 8, 155; PDF
Ludlockite	$(Fe,Pb)As_2O_6$	tric.	C, FM, NN, PDF
Foordite	$(Sn,Pb)(Nb,Ta)_2O_6$	mon.	C, FM, NN, PDF
Thoreaulite	$SnTa_2O_6$	mon.	C, FM, NN, PDF
Columbite group			
aeschynite subgroup		orth.	PDF
columbite subgroup		orth.	PDF
Tantalite	$(Fe,Mn)(Ta,Nb)_2O_6$	orth.	C, FM, NN, PDF
Changbaiite	$PbNb_2O_6$	trig.	C, FM, NN, PDF
Ferrotapiolite group			FM
or		tet.	
Rutile group			
trirutile subgroup			PDF

C = Clark (1993), FM = Fleischer & Mandarino (1991), NN = Nickel & Nichols (1991), PDF = Powder Diffraction File, SR = Structure Reports.

interstices, located above and below the vacant holes of the Sb layers, are occupied by Pb (Fig. 2). The deviation of the arrangement of oxygen atoms from the ideal close packing is related to the strongly different sizes of PbO_6 and SbO_6 octahedra.

Synthetic MSb_2O_6 and natural compounds with the same atomic ratios of rosiaite are reported in Table 5. From the structural point of view, synthetic or natural complex halides and oxides, containing two kinds of cations occupying one-half of the octahedral sites in close-packed structures, show different patterns of octahedral sites occupied. The four recognized kinds of approximately hexagonal close-packed structures for these MM'_2X_6 compounds are reported by Wells (1975): trirutile-, columbite-, Li_2ZrF_6 - and Na_2SiF_6 -type structures. As suggested by Hill (1987), in the structure of $MM'_2\text{O}_6$ compounds the segregation of M from M' cations into separate layers is favoured by a strong difference between the respective cationic radii. Rosiaite, some MSb_2O_6 and MAS_2O_6 compounds (Hill, 1987) as well as Li_2NbOF_5 (Galy *et al.*, 1969) and Li_2NbF_6 (de Bournoville *et al.*, 1986) show a Li_2ZrF_6 structure type (Brunton, 1973), with distinct M and M' layers. The other synthetic MSb_2O_6 , with $M = \text{Cu}, \text{Mn}, \text{Zn}, \text{Fe}, \text{Co}, \text{Ni}$ and Mg , and the known minerals referenced in Table 5 show different structures characterized by mixed $M M'$ layers.

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