

Brizziite, NaSbO₃, a new mineral from the Cetine mine (Tuscany, Italy): description and crystal structure

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Abstract: Brizziite is a new sodium antimonate mineral from the Cetine mine, Tuscany, Italy. It occurs as dense aggregates of platy {001} hexagonal crystals. Associated minerals are stibiconite and mopungite. The crystals, which are polysynthetically twinned, are colourless and transparent, with pearly lustre. Electron microprobe analyses give Na₂O 15.98 and Sb₂O₅ 83.28 wt.%, corresponding to the formula NaSbO₃. Optically, brizziite is uniaxial (-) with $\epsilon = 1.631(1)$, $\omega = 1.84$, birefringence 0.21(1); VHN₁₅ microhardness 57; $D_{\text{meas}} = 4.8(2)$ g/cm³; $D_{\text{calc}} = 4.95$ g/cm³. The unit cell is rhombohedral (hexagonal) $a = 5.301(1)$, $c = 15.932(4)$ Å, space group $R\bar{3}$ and $Z = 6$. The strongest lines in the X-ray Gandolfi pattern are (d_{obs} , l , hkl) 5.30(53)(003), 3.00(55)(104), 2.650(67)(006,110), 2.365(69)(113), 1.874(100)(116), 1.471(69)(119,303). The IR spectrum is given also. The mineral is named for the mineral collector G. Brizzi (1936-1992). The crystal structure was refined to an R index of 0.025, using a set of 334 observed (6σ) reflections ($R = 0.043$ for all 385 collected reflections). The structure consists of the ilmenite-type octahedral arrangement; layers of distorted edge-sharing Na octahedra alternate with layers of edge-sharing Sb⁺⁵ octahedra along [001]. The layers are connected to one another by octahedral face-sharing.

Key-words: brizziite, new mineral, sodium antimonate, crystal structure, Cetine mine (Italy).

Introduction

The existence of two crystalline forms of NaSbO₃ has been known for many years (Schrewelius, 1938). The high-pressure form is cubic whereas the form occurring at one atmosphere has the rhombohedral ilmenite structure (Hong *et al.*, 1974). Dr. G. Brizzi, while collecting minerals at the Cetine mine, found a few specimens of an unknown mineral, which he brought to our attention. This mineral has the same powder diffraction pattern and chemical composition as the ilmenite-type NaSbO₃ compound.

We are pleased to name this mineral brizziite, in honour of Dr. Giancarlo Brizzi (1936-1992) in recognition of his contribution to the mineralogy of Tuscany and particularly to the Cetine mine.

The new mineral was approved by the I.M.A. Commission on New Minerals and Mineral Names. Holotype material is preserved at the Museum of Natural History of the University of Florence under catalogue number 2037/RI.

A single-crystal structure refinement of brizziite was made for comparison to the related structures of the ilmenite group minerals.

Occurrence

The Cetine mine is located approximately 20 km southwest of Siena, on the far eastern flank of the Colline Metallifere. It is an antimony deposit described (Dessau, 1952) as an epigenetic mineralization related to a late phase of the Pliocene-Pleistocene Apennine magmatism. At its base, the local geological succession comprises

quartzitic/phyllitic terrains of the so-called Tuscan basement, which are Paleozoic to Triassic in age. These are overlain by a weathered Triassic evaporite formation known as "Calcare Cavernoso". At the Cetine mine, the ore consists of stibnite in small pods disseminated within this strongly silicified limestone. The area is a well-known site for mineralogists and mineral collectors, because of the presence of numerous rare minerals, mainly sulphates and oxidation products of stibnite, and because of the occurrence of new species, such as onoratoite, cetineite, coquandite, and rosenbergite.

Brizziite occurs as encrustations, mainly with stibiconite, in waste material and slag derived from mining operations, near the locality of the cetineite occurrence (Sabelli & Vezzalini, 1987). Although samples of the oxide-sulfide cetineite often are associated with antimony drops due to smelting activity, brizziite shows no traces of Sb drops. Brizziite appears to be related to deep weathering, as indicated by the presence of stibiconite, $Sb^{+3}Sb_2^{+5}O_6(OH)$, and mopungite, $NaSb^{+5}(OH)_6$.

The encrustations of brizziite, light pink or yellow in colour, are microscopic aggregates of platy crystals and, more rarely, thin tabular crystals (Fig. 1).

X-ray crystallography

The X-ray powder diffraction pattern of brizziite, given in Table 1, was obtained using of a

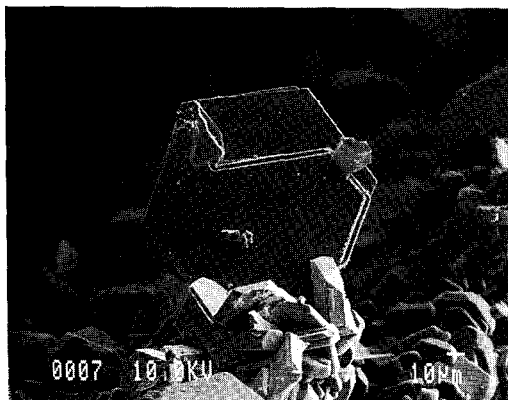


Fig. 1. Electron micrograph of well-defined crystals of brizziite showing hexagonal outline.

Table 1. X-ray powder diffraction data for brizziite.

$2\theta_{exp}$ (°)	I/I_0	d_{exp} (Å)	hkl	$\Delta 2\theta$ * (°)
16.73	53	5.30	003	+0.037
20.22	41	4.39	101	+0.092
22.43	38	3.96	012	+0.080
29.74	50	3.00	104	+0.047
33.82	67	2.650	[006 +0.067 110 +0.004	
34.32	14	2.613	015	+0.066
38.04	69	2.365	113	+0.103
44.33	16	2.043	107	-0.094
45.71	34	1.985	024	+0.099
48.59	100	1.874	116	+0.063
51.69	12	1.768	009	+0.060
53.21	14	1.721	211	+0.122
54.16	12	1.693	122	+0.072
57.03	14	1.615	027	+0.055
58.06	34	1.589	214	+0.089
60.60	38	1.528	300	+0.104
61.62	36	1.505	1,0,10	+0.005
63.20	69	1.471	[119 +0.044 303 -0.034	
67.85	19	1.381	[0,1,11 +0.002 217 -0.074	
70.90	21	1.329	0,0,12	-0.088
71.16	38	1.325	[306 +0.060 220 +0.023	
72.10	19	1.310	0,2,10	-0.069
73.76	22	1.285	223	+0.090
75.57	9	1.258	312	-0.060
79.04	10	1.211	134	+0.110
81.21	47	1.185	[1,0,13 -0.029 226 +0.112	
82.07	26	1.174	2,1,10	-0.053
83.49	19	1.158	309	-0.009
93.18	24	1.061	[0,0,15 +0.113 229 -0.027	
100.63	34	1.002	140	+0.015
101.53	15	.995	1,3,10	-0.083
103.03	22	.985	143	-0.052
110.60	36	.938	[2,2,12 +0.056 146 -0.057	
121.47	22	.884	[330 -0.034 1,3,13 -0.156	
124.22	44	.872	[0,3,15 +0.094 149 -0.076	

* $\Delta 2\theta = 2\theta_{exp} - 2\theta_{calc}$

Gandolfi camera (114.6 mm diameter) and $\text{CuK}\alpha$ radiation. Indexing involved the use of intensities collected for the structural study. The data are in agreement with those of Coffeen (1956) and Holzer & McCarthy (1991) on synthetic material. Unit cell data of brizziite, derived from the powder data by least-squares, is rhombohedral (hexagonal) with $a = 5.301(1)$, $c = 15.932(4)$ Å, $V = 387.7$ Å³, $Z = 6$ formula units. Single-crystal data show systematic extinctions of the type hkl with $-h+k+l = 3n$. On this basis and by analogy with ilmenite, the space group $R\bar{3}$ was determined.

Chemical, physical, and optical properties

Brizziite was analyzed with a Jeol JXA-8600 electron microprobe at 10 kV accelerating voltage and 5 nA beam current (Faraday cup). Albite and senarmonite were used as standards for Na and Sb, respectively. Elements other than Na and Sb were not detected by energy-dispersion spectra. The raw data were corrected by the Bence & Albee method (1968). 40 analyses were performed on 3 different grains. The Na_2O content ranges from 15.42 to 16.54 with an average of 15.98 wt.% and Sb_2O_5 from 82.05 to 84.75 with an average of 83.28 wt.%. On the basis of three oxygens, the formula is exactly NaSbO_3 .

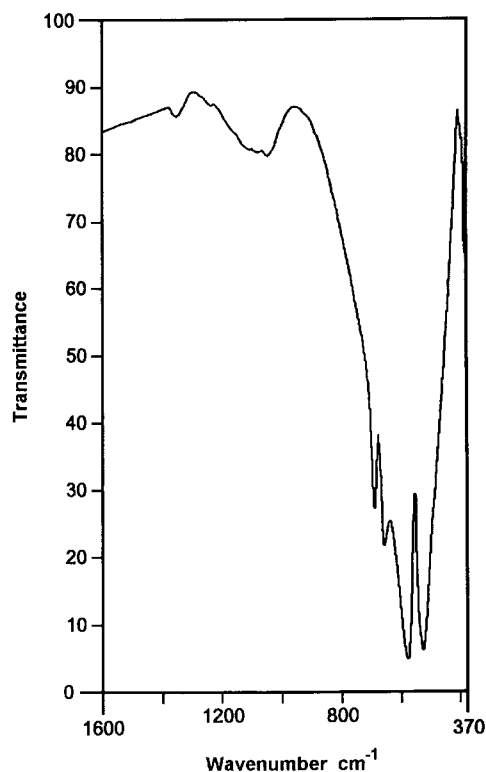


Fig. 2. Infrared absorption spectrum of brizziite in the region $1600\text{--}370$ cm^{-1} .

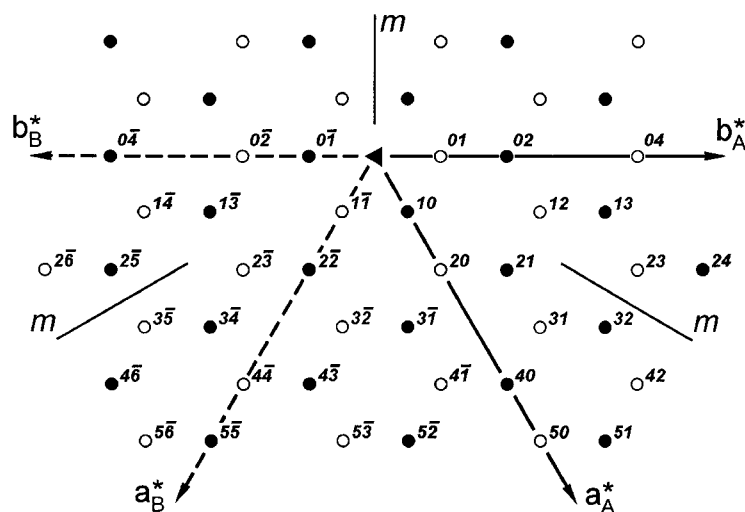


Fig. 3. A reciprocal lattice net of twinned brizziite. Solid and open circles represent reflections belonging to the A and B individuals, respectively. Numbering refers to the h and k Miller indices of reflections with $l = 3n + 1$ of the A individual. The letter m indicates the mirror plane (100) which is the operator symmetry responsible for the twinning.

An infrared absorption spectrum was recorded on a Perkin Elmer FTIR 1760X spectrophotometer in the range 4000-370 cm^{-1} using a KBr micropellet. No significant peaks in the 4000-1600 cm^{-1} region were observed. The absorptions at 683, 648, 570, 518 cm^{-1} (Fig. 2) are in good agreement with the corresponding absorptions at 675, 637, 579, 527 cm^{-1} given by Siebert (1959) for synthetic NaSbO_3 .

The tabular {001} crystals are colourless and transparent, and have a pearly lustre, a white streak, and perfect {001} cleavage. They are flexible and have a hardness of VHN = 57 (average of 10 determinations with 15g indenter: range 41-70). The observed density, determined by the pycnometer method, is 4.8(2) g/cm^3 ; the calculated value is 4.95 g/cm^3 . The mineral does not fluoresce under long- or short-wave ultraviolet light.

Optically, brizziite is uniaxial negative, with a birefringence of 0.21(1) (rotary compensator). The refractive indices are: $\epsilon = 1.631(1)$ (white light) and $\omega = 1.84$ (calculated). The Gladstone-Dale relationship gives $K_p = 0.1556$ and $K_c = 0.159$, with an "excellent" compatibility index $1 - (K_p/K_c) = 0.21$ (Mandarino, 1981).

TG, DTG and DTA curves show no changes up to 1100°C and the X-ray powder diffraction pattern of the thermally treated material is identical to the pattern of the mineral.

The maximum size of the brizziite crystals is 0.2 mm. They are polysynthetically twinned, with {100} as twin plane.

Crystal structure refinement and discussion

All attempts to find untwinned crystals were unsuccessful. A small twinned hexagonal platelet of 0.15 mm diameter was selected for intensity data collection, using an Enraf Nonius CAD-4 diffractometer. 1237 reflections with θ less than 35° for graphite-monochromatized $\text{MoK}\alpha$ radiation were measured using the ω - θ scan technique. From a total of 385 independent data, 334 were considered observed reflections on the basis of $F_o > 6\sigma(F_o)$. The R -factors from the counting statistics (after merging) were 0.030 and 0.098 for the observed and for all reflections, respectively. Semi-empirical absorption (North *et al.*, 1968) and L_p corrections were applied. Neutral atomic scattering factors were taken from the In-

ternational Tables for X-ray Crystallography (1974). Real and imaginary parts of the anomalous dispersion corrections were also included.

Fig. 3 shows the reflection population of the twinned crystal, for the reciprocal lattice nets with $l = 3n + 1$. Nets with $l = 3n + 2$ show a similar reflection population, but solid circles substitute for open ones and *vice versa*. In contrast, the lattice points of nets with $l = 3n$ occupy the positions which are unoccupied in the scheme of Fig. 3. The effect of the twinning is to superimpose the reflections of the type $l = 3n$, all re-

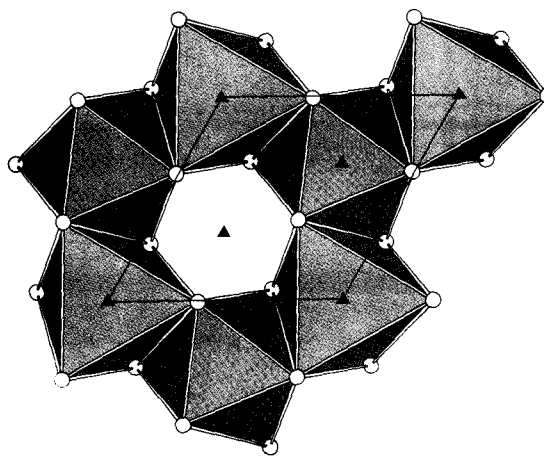
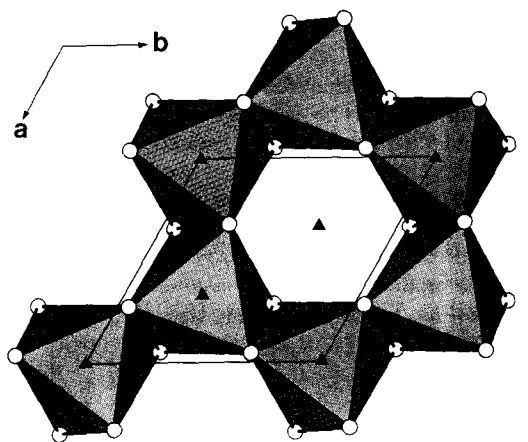


Fig. 4. Two adjacent sheets, viewed along [001], of edge-sharing Sb-octahedra (top) and Na-octahedra (bottom).

Table 2. Fractional atomic coordinates, anisotropic thermal parameters, bond distances, and angles.

	x	y	z	B_{eq}	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na	0	0	.6391(2)	1.15	134(5)	134	12(1)	67	0	0
Sb	0	0	.83904(3)	.39	34(1)	34	6(1)	17	0	0
O	.0461(5)	.3236(5)	.7638(2)	.56	78(9)	62(9)	4(1)	29(8)	-4(3)	-1(2)

Bond distances (Å)			Bond angles (°)			
Na-O	2.557(4)		O-Na-O	65.9(1)	O-Sb-O	79.2(1)
Na-O	2.320(3)		O-Na-O	92.6(1)	O-Sb-O	87.8(1)
			O-Na-O	98.7(1)	O-Sb-O	95.7(1)
Sb-O	2.005(2)		O-Na-O	99.0(1)	O-Sb-O	98.5(1)
Sb-O	1.973(2)		O-Na-O	157.0(1)	O-Sb-O	165.3(1)

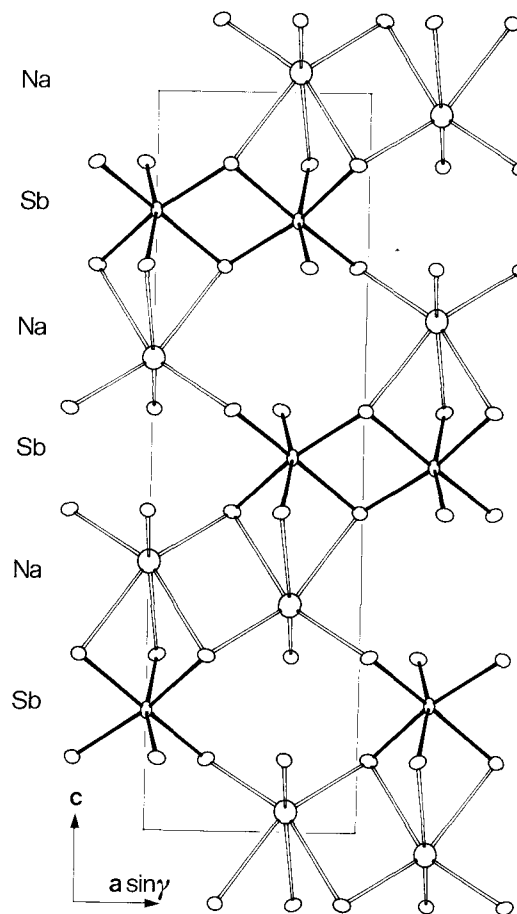
Anisotropic temperature factors ($\times 10^4$) are in the form $\exp(-\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)$.
 $B_{eq} (\text{Å}^2) = 4/3(\Sigma_i \Sigma_j \beta_{ij} a_i a_j)$.
 Bond distances and angles are repeated by the three-fold axis.

maining ones constitute two well-separated sets of data. From the reciprocal lattice net of Fig. 3 it is evident that the hkl points of the A component (solid circles) are related to the khl points of the B component (open circles) by the (100) mirror plane, which is the twin operator.

From the mean ratio of the intensities of the pairs of separated reflections (with $l \neq 3n$), the volumes of the individuals A and B were easily computed. The volume ratio ($A/B = 5.52$) allowed the composite intensities of the overlapped reflections (with $l = 3n$) to be divided into the intensities of the two twin components. Thus, a homogeneous set of "untwinned" reflections was obtained.

The structures of synthetic ilmenite, FeTiO_3 , (Wechsler & Prewitt, 1984) and synthetic geikielite, MgTiO_3 , (Wechsler & Von Dreele, 1989) were used as the starting point for the location of Sb, Na, and O atoms in brizziite. The program employed for least-squares refinement was a modified version of ORFLS (Busing *et al.*, 1962). The refinement with isotropic temperature factors converged to a R index ($R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$) of 0.063. A weight $w = 1/\sigma^2(F_o)$ was given to the observed reflections (zero weight for "unobserved" ones).

Fig. 5. The [010] projection of the structure showing the connection of alternating Na and Sb octahedral sheets. Ellipsoids are scaled at the 70% probability level).



The anisotropic refinement lowered the R index to 0.025 for the observed reflections ($R = 0.043$ for all data). Final atomic parameters, together with bond distances and angles, are given in Table 2. A list of observed and calculated structure factors may be obtained on request from the authors or through the E.J.M. Editorial Office.

The structure of brizziite is similar to those of the ilmenite group minerals and consists of gibbsite-type octahedral sheets, perpendicular to the c -axis (Fig. 4). The bond distances of the Na octahedron (Table 2) fall in the 2.25-2.78 Å range, which is consistent with six-fold coordinated Na atom (International Tables for X-ray Crystallography, 1962). The bond angles (e.g., 65.9°, 157°) indicate that the Na polyhedron is distorted. The Sb octahedron is less distorted, with angle variations from 79.2° to 165.3°. The mean Sb-O bond distance (1.989 Å) is short relative to the mean of 2.008 Å in melanostibite, where 50 % Fe is in this site (Moore, 1968). Other Sb-O mean values in Sb⁵⁺ octahedra are comparable: 1.992 Å for Sb₂O₅ (Jansen, 1979), 1.965 and 1.986 Å for bahianite (Moore & Araki, 1976), 1.987 Å for α -Sb₂O₄ (Thornton, 1977).

Each Na and Sb octahedron shares edges with three symmetry-related octahedra to form Na and Sb layers respectively. Each octahedron also shares a face with another octahedron of an adjacent layer, but the opposite face is unshared (Fig. 5). Thus, pairs of Na and Sb octahedra alternate with octahedral holes along the c -axis. There are six alternating Na and Sb sheets in the unit-cell, to form a hexagonal close-packed framework.

As concerns the structural elements which produce twinning, it is evident how the (100) twin operator is the *pseudo*-symmetry plane that affects both Na and Sb polyhedra (Fig. 4).

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