Demicheleite-(Cl), BiSCl, a new mineral from La Fossa crater, Vulcano, Aeolian Islands, Italy

FRANCESCO DEMARTIN, CARLO MARIA GRAMACCIOLI,* AND ITALO CAMPOSTRINI

Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università degli Studi di Milano, via Venezian 21, I-20133 Milano, Italy

ABSTRACT

Demicheleite-(Cl), ideally BiSCl, is the chlorine analog of demicheleite-(Br) and is closely related to this species that occurs in the same locality. The mineral is the first natural bismuth sulfochloride discovered so far in a natural environment, and it is identical with the corresponding and already known synthetic compound. It was found in an active medium-temperature intracrater fumarole at La Fossa crater, Vulcano Island, Aeolian archipelago, Sicily, Italy. The mineral occurs as acicular to stout translucent crystals up to 0.25 mm long in an altered pyroclastic breccia, together with demicheleite-(Br), bismoclite, bismuthinite, godovikovite, panichiite, and three new minerals pending the IMA approval (IMA 2008-015, IMA 2008-039, and IMA 2008-057). The mineral is orthorhombic, space group *Pnam*, with $a = 7.7933(10)$, $b = 9.9293(12)$, and $c = 3.9880(4)$ Å, $V = 308.60(4)$ Å^3 (from X-ray powder data), $Z = 4$. The crystal habit is prismatic with {110} as the dominant form, terminated by minor faces of another prism {011}, a pinacoid {010}, and a bipyramid {111}. The color is dark red to black; the luster submetallic. It is non-fluorescent. The tenacity is brittle. The cleavage and fracture were not observed. The calculated density is 5.934 g/cm^3.

The chemical analysis obtained by WDS electron microprobe gave (wt%) Bi 72.74, Cl 11.42, Br 3.13, S 11.74, Se 0.01 wt%, total 99.04, corresponding to the empirical formula (based on 3 apfu): $Bi_{0.97}(Cl_{0.90}Br_{0.11})_{\Sigma1.01}S_{1.02}$.

The crystal structure has been refined to a final R index of 0.0218 and contains Bi in sevenfold coordination inside a monocapped trigonal prism. By base sharing, these polyhedra form rows extending along [001]. The rows are connected with symmetry-related rows by sharing S-S edges of the pyramidal caps; these pairs of rows are linked to the others by sharing Cl/Br atoms. The distribution of bond lengths is close to that of the synthetic counterparts BiSCl and BiSBr, with Bi-S distances of 2.601(2) and 2.709(1) Å, and Bi-Cl/Br distances of 2.937(1) and 3.388(1) Å.

The strongest 6 lines in the X-ray powder diffraction pattern [d_{obs}(Å) (*I*) (*hkl*)] are: 2.896 (100) (121), 4.174 (45) (120), 2.684 (42) (211), 2.784 (33) (201), 1.725 (30) (411), 2.543 (27) (031).

Both the mineral and the mineral name have been approved by the Commission on New Minerals, Nomenclature and Classification of the IMA (no. 2008-020).

Keywords: Demicheleite-(Cl), demicheleite-(Br), new mineral species, bismuth, sulfochlorides, crystal structure, Vulcano Island, Aeolian Islands, Italy

INTRODUCTION

The fumaroles at La Fossa crater, Vulcano, Aeolian Islands, have long been the object of mineralogical investigation, and even in the last few years a considerable number of new species have been discovered (see Campostrini et al. 2008; Demartin et al. 2008a, 2008b, 2008c, 2009, and references therein).

Here we report the discovery of another new mineral, demicheleite-(Cl), BiSCl. It is the natural equivalent of bismuth sulfide chloride, a substance belonging to a well-known group of synthetic thioalogenides, which have drawn much attention in recent years because of their optical, photoconducting, and ferroelectric properties (Voutsas and Rentzeperis 1980, 1984, and references therein). The bromian equivalent, BiSBr or demicheleite-(Br), was also discovered in the same environment (Demartin et al. 2008c). A closely related substance BiS(I,Cl,Br)

was observed as a component of volcanic sublimates collected in quartz tubes in the fumaroles at Mutnovski, Kamchatka (Zelenski and Bortnikova 2005).

The mineral is named in close analogy with demicheleite-(Br) after Vincenzo de Michele (b. 1936). The bromian term was first called "demicheleite" with no suffix; after approval of the present mineral (no. 2008-020) the IMA Commission on New Minerals, Nomenclature and Classification agreed to call the two minerals demicheleite-(Br) and demicheleite-(Cl), respectively. The holotype is deposited (no. 2008-3) in the Reference Collection of Dipartimento di Chimica Strutturale e Stereochimica Inorganica of Università degli Studi di Milano.

OCCURRENCE AND PHYSICAL PROPERTIES

The new mineral demicheleite-(Cl) occurs in a medium-temperature (250 °C) intracrater fumarole, as acicular to stout dark red to black translucent crystals up to 0.25 mm long on

* E-mail: carlo.gramaccioli@unimi.it

altered pyroclastic breccia, together with demicheleite-(Br), bismoclite, bismuthinite, IMA 2008-015, unusual ammonium-bearing species such as godovikovite $(NH_4)Al(SO_4)_2$, panichiite $(NH_4)_2SnCl_6$ (Demartin et al. 2009), IMA 2008-039 $(NH_4)_3PbCl_5$, IMA-2008-057 $(NH_4)_4NaAl_2(SO_4)_4Cl(OH)_2$, and other minerals currently under investigation. Pseudomorphs of demicheleite-(Cl) after distinct crystals of bismoclite have also been observed. The crystal habit is prismatic {110}, terminated by minor faces of another prism {011}, a bipyramid {111}, and the {010} pinacoid (see Figs. 1 and 2); these indices have been inferred by comparison with computer-generated drawings. The streak is brown; the luster submetallic; it is non-fluorescent. The tenacity is brittle, and cleavage and fracture were not observed. The calculated density is 5.934 g/cm^3 (from the empirical formula reported below and the unit-cell data). The indices of refraction are too high and the crystals are too sensitive to chemical agents to use the oil-immersion method.

CHEMICAL DATA

Chemical analyses were carried out by means of a JEOL JXA 8200 electron microprobe (WDS mode, 15 kV, 5×10^{-9}A, 10 μm beam diameter). The mean analytical results are reported in Table

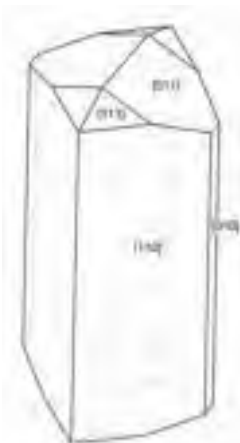**FIGURE 1.** Scanning electron microscope (SEM) image (BSE) of demicheleite-(Cl).

FIGURE 2. Idealized drawing of a demicheleite-(Cl) crystal.

1. The empirical formula (based on 3 apfu) is $Bi_{0.97}(Cl_{0.90}Br_{0.11})_{\Sigma 1.01}$ $S_{1.02}$; the simplified formula is BiSCl, which requires: Bi 75.58, S 11.60, Cl 12.82, total 100.00 wt%. Although the Cl content clearly exceeds that of Br, the natural sample here studied contains 13% Br (in atoms), and is an intermediate between BiSCl and the isostructural (and most likely isomorphous) sulfide bromide, BiSBr (Voutsas and Rentzeperis 1980, 1984). This Cl,Br content is in good agreement with the result of the crystal structure refinement (see below).

X-RAY DATA AND REFINEMENT OF THE STRUCTURE

X-ray powder-diffraction data were obtained using a Gandolfi camera 114.6 mm in diameter, with Cu$K\alpha$ radiation (Table 2). A least-squares fit of these data provided the following orthorhombic unit-cell parameters: $a = 7.7933(10)$, $b = 9.9293(12)$, $c = 3.9880(4)$ Å, and $V = 308.60(4)$ Å^3. A comparison between these data and those of the corresponding synthetic compounds BiSBr and BiSCl (Voutsas and Rentzeperis 1980, 1984) is reported in Table 3.

Single-crystal diffraction data were collected from a crystal fragment (0.090 × 0.011 × 0.006 mm) with Mo$K\alpha$ radiation (λ = 0.71073 Å), using a Bruker Apex II diffractometer equipped with a 2K CCD detector. A 1 min frame-time and 0.3° frame width

TABLE 1. Chemical composition of demicheleite-(Cl)

Constituent	wt%	apfu	Range	Standard deviation	Probe standard
Bi	72.74	0.97	72.13–73.66	0.4	Bi$_2$Se$_3$
Cl	11.42	0.90	10.71–11.97	0.4	phosgenite
Br	3.13	0.11	2.39–4.30	0.7	TlBr
S	11.74	1.02	11.60–11.95	0.1	FeS$_2$
Se	0.01	0.00	0–0.07	0.1	Bi$_2$Se$_3$
Total	99.04	3			

TABLE 2. X-ray powder-diffraction data for demicheleite-(Cl)

	Demicheleite-(Cl) BiSCl		Synthetic BiSCl* (Voutsas and Rentzeperis 1980)		
I/I_o†	d_{obs} (Å)	d_{calc} (Å)‡	I/I_o	d_{calc} (Å)	hkl
8	6.116	6.130	100	6.124	110
17	4.951	4.965	1	4.996	020
45	4.174	4.187	90	4.199	120
16	3.609	3.627	52	3.613	210
			51	3.710	011
100	2.896	2.888	87	2.895	121
33	2.784	2.787	47	2.782	201
42	2.684	2.683	12	2.680	211
27	2.543	2.547	32	2.558	031
10	2.482	2.482	36	2.498	040
16	2.421	2.421	41	2.429	131
8	2.299	2.302	10	2.295	320
			1	2.163	231
3	2.130	2.126	6	2.120	311
23	2.044	2.043	13	2.041	330
25	1.992	1.994	19	1.998	002
			32	1.990	321
20	1.853	1.854	17	1.855	022
10	1.801	1.800			122
7	1.771	1.769			250
30	1.725	1.724	16	1.718	411
8	1.672	1.671			222
10	1.637	1.637			341
12	1.561	1.562	15	1.561	312
6	1.533	1.533			440

* For the synthetic compound, the reported values have been calculated using Voutsas and Rentzeperis's (1980) single-crystal structural data.
† Determined densitometrically from a Gandolfi camera film.
‡ Calculated from the unit cell: $a = 7.7933(10)$ Å, $b = 9.9293(12)$ Å, $c = 3.9880(4)$ Å, obtained from least-squares refinement from the above data using the program UNITCELL (Holland and Redfern 1997).

TABLE 3. Unit-cell parameters for demicheleite minerals and synthetic BiSBr and BiSCl (single-crystal data)

	Demicheleite-(Cl) BiSCl	Demicheleite-(Br) BiSBr	BiSCl*	BiSBr†
a (Å)	7.802(1)	8.0424(9)	7.7508(16)	8.1666(9)
b (Å)	9.930(1)	9.8511(11)	9.9920(5)	9.8532(9)
c (Å)	3.9905(6)	4.0328(5)	3.9955(5)	4.0492(6)
V (Å³)	309.16(8)	319.50(6)	309.44(8)	325.83(7)

* From Voutsas and Rentzeperis (1980).
† From Voutsas and Rentzeperis (1984).

TABLE 4. Single-crystal data and refinement parameters for demicheleite-(Cl)

Crystal system	orthorhombic
Space group	*Pnam* (no.62)
a (Å)	7.802(1)
b (Å)	9.930(1)
c (Å)	3.9905(6)
V (Å³)	309.16(8)
Z	4
Radiation	Mo$K\alpha$
μ (cm^{-1})*	582.4
D_{calc} (g/cm³)*	5.934
Measured reflections	3650
Independent reflections	674
Observed reflections [$I > 2\sigma(I)$]	547
Parameters refined	22
Final R and $wR2$	0.0218, 0.0356
S	0.879

Notes: $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0107k)^2$ where $k = (F_o^2 + 2F_c^2)/3$; $S = \{\Sigma[w(F_o^2 - F_c^2)]/(n-p)\}^{1/2}$ where n is the number of reflections and p is the number of refined parameters.
* Obtained using the empirical formula.

TABLE 5. Atomic coordinates and displacement parameters for demicheleite-(Cl) [$U_{eq}/U_{ij} \times 10^4$]

Atom	X/a	Y/b	Z/c	U_{eq}		
Bi	0.13874(3)	0.13250(3)	1/4	187(1)		
Cl/Br	0.5176(2)	0.8115(2)	1/4	247(5)		
S	0.8226(2)	0.0495(2)	1/4	143(3)		

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Bi	202(1)	196(1)	162(1)	0	0	−26(1)
Cl/Br	247(9)	276(9)	218(8)	0	0	−38(6)
S	162(9)	134(7)	132(7)	0	0	14(6)

Note: The anisotropic displacement factor exponent takes the form:
$-2\pi^2[U_{11}h^2(a^*)^2 + ... + 2U_{12}hka^*b^* + ...]; U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$.

TABLE 6. Interatomic distances (Å)*

	Demicheleite-(Cl)	Synthetic BiSBr† Voutsas and Rentzeperis (1984)	Synthetic BiSCl Voutsas and Rentzeperis (1980)
Bi-S	2.601(2)	2.607	2.605(2)
Bi-S (2×)	2.709(1)	2.721	2.711(1)
Bi-S	3.468(2)		
Bi-Cl/Br (2×)	2.937(2)	3.038	2.927(2)
Bi-Cl/Br (2×)	3.388(2)	3.539	3.367(2)
S-S (2×)	3.551(2)	3.556	3.549(3)
S-S (2×) = c	3.991(1)	4.049	3.996(1)
S-Cl/Br (2×)	3.353(2)	3.450	3.360(3)
S-Cl/Br (2×)	3.596(2)	3.596	3.492(3)
S-Cl/Br (2×)	3.894(2)	3.990	3.873(3)
Cl/Br-Cl/Br (2×)	3.991(1)	4.049	3.996(1)
Cl/Br-Cl/Br (2×)	4.088(2)	4.340	4.041(4)

* Below 4.1 Å; the distances not reported by Voutsas and Rentzeperis (1980, 1984) do not belong to the coordination polyhedron around Bi. The unit-cell parameters here used are those obtained from single-crystal measurements.
† No e.s.d. values are reported for these data.

were used. A total of 3650 reflections, corresponding to a complete scanning of the reciprocal lattice up to $2\theta_{max} = 67.3°$, were measured; of these 674 were unique. The unit-cell dimensions obtained from the single crystal were refined by least-squares analysis of 1179 reflections with $I > 5\sigma(I)$; their values are given in Table 4, together with other details concerning the data collection and refinement. The data were reduced using the Bruker program SAINT, and corrected for Lorentz, polarization, and background. An absorption correction was applied (minimum transmission factor 0.418) using the SADABS program (Sheldrick 2000). The non-standard setting for space group no. 62, *Pnam*, was adopted to facilitate comparison with the structure of demicheleite-(Br). The structure was refined starting from the corresponding atomic positions in demicheleite-(Br) using the SHELXL97 program (Sheldrick 1997) implemented in the WinGX suite (Farrugia 1999); the occupation parameter for the halide site was also refined and the result [Cl = 0.87(2), Br = 0.13(2)] is in close agreement with the chemical analysis (see Table 1). The final coordinates and displacement parameters of the atoms are reported in Table 5. The final R is 0.0218 for 547 observed reflections [$I > 2\sigma(I)$]. Selected interatomic distances are reported in Table 6.

RESULTS AND DISCUSSION

The crystal structure of demicheleite-(Cl) is closely similar to that of demicheleite-(Br) (see Figs. 3 and 4 in Demartin et al. 2008c). Following the criterion reported by Voutsas and Rentzeperis (1980, 1984) for selecting the bond distances, the bismuth atom is seven coordinated by three S atoms at distances 2.601(2)–2.709(1) Å and four Cl/Br atoms at distances 2.937(2)–3.388(2) Å; the corresponding polyhedron can be described as a distorted trigonal monocapped prism (see Fig. 4 in Demartin et al. 2008c) having a height equal to the unit-cell parameter c. The vertices of the triangular bases are occupied by two Cl atoms and one S atom; those of one lateral face are occupied by four Cl atoms, whereas at the vertices of the other two faces are two S and two Cl atoms for each face. One of the latter faces is almost square and is capped by an S atom. By sharing the triangular bases, the polyhedra form polymeric rows extended along [001]; these rows are joined to symmetry-related rows by sharing S-S edges of the pyramidal caps of the constituent polyhedra, thereby forming infinite double chains of composition $[Bi_2S_4(Cl/Br)_8]_n$. These pairs of rows are linked to the others by sharing Cl/Br atoms. These aggregations result in planes made exclusively either of S or Cl/Br atoms.

Regarding the deviation of solid solutions of BiSCl and BiSBr from ideality, see the discussion in Demartin et al. (2008c).

CONCLUDING REMARKS

The discovery of the chlorine-rich equivalent of demicheleite-(Br) increases the number of natural sulfohalides, most of which are Ag or Hg minerals, as for instance cordeoite (Foord et al. 1974), lavrientievite $Hg_3S_2Cl_2$, arzakite $Hg_3S_2(Br,Cl)_2$ (Vasil'ev et al. 1984), perrouite $Hg_5Ag_4S_5(Cl,I,Br)_4$ (Sarp et al. 1987), and capgaronnite HgAgS(Cl,Br,I) (Mason et al. 1992).

Sulfochlorides of Bi and Pb (such as $Bi_{19}Cl_3S_{27}$ and Pb_4SCl_6) formed at temperatures from 300 to 500 °C in quartz tubes inserted into the outlet of fumaroles at La Fossa crater, Vulcano, have already been observed by Garavelli et al. (1997, 2005). According to these authors (see also the long list of references reported in these works), the deposition of such sulfohalides is due to reaction of $PbCl_2$ (cotunnite) with H_2S or galena. Similar

reactions occur in the formation of bismuth sulfochlorides from $BiCl_3$ and H_2S. All these observations underline the chemical complexity of such volcanic environments, which are currently an object of active interest.

As for demicheleite-(Br), another mineral found at La Fossa crater (Demartin et al. 2008c), the present mineral is also notably Br-rich. At the same locality, a significant enrichment in Br was already noted by Coradossi et al. (1996) for samples of ammonium chloride. Furthermore, a selective enrichment in Br for other minerals was also noted by Garavelli et al. (2005) for chlorine-rich sulfosalts such as vurroite $Pb_{20}Sn_2(Bi,As)_{22}S_{54}Cl_6$, and a notable enrichment was observed by Roberts et al. (2006) for lafossaite Tl(Cl,Br). A similar effect was also noted for volcanic sublimates from other localities, such as Mutnovski volcano, Kamchatka (Zelenski and Bortnikova 2005).

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