Fassinaite, $Pb_2^{2+}(S_2O_3)(CO_3)$, the first mineral with coexisting thiosulphate and carbonate groups: description and crystal structure

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ABSTRACT

Fassinaite, ideally $Pb_2^{2+}(S_2O_3)(CO_3)$, is a new mineral from the Trentini mine, Mount Naro, Vicenza Province, Veneto, Italy (holotype locality). It is also reported from the Erasmus adit, Schwarzleo District, Leogang, Salzburg, Austria and the Friedrich-Christian mine, Schapbach, Black Forest, Baden-Württemberg, Germany (cotype localities). At the Italian type locality it occurs as acicular [010], colourless crystals up to 200 μm long, closely associated with galena, quartz and anglesite. At the Austrian cotype locality it is associated with cerussite, rare sulphur and very rare phosgenite. At the German cotype locality anglesite is the only associated phase. Fassinaite crystals commonly have flat chisel-shaped terminations. They are transparent with vitreous to adamantine lustre and a white streak. Fassinaite is brittle with an irregular fracture and no discernible cleavage; the estimated Mohs hardness is 1½−2. The calculated density for the type material is 6.084 g cm^{-3} (on the basis of the empirical formula), whereas the X-ray density is 5.947 g cm^{-3}. In common with other natural lead thiosulphates (i.e. sidpietersite and steverustite) fassinaite has intense internal reflections, which do not allow satisfactory optical data to be collected; the crystals are length-slow and have very high birefringence. The mineral is not fluorescent.

Fassinaite is orthorhombic, space group *Pnma*, with unit-cell parameters (for the holotype material) $a = 16.320(2)$, $b = 8.7616(6)$, $c = 4.5809(7)$ Å, $V = 655.0(1)$ Å^3, $a:b:c = 1.863:1:0.523$, $Z = 4$. Single-crystal structural studies were carried out on crystals from all three localities: $R_1(F)$ values range between 0.0353 and 0.0596. The structure consists of rod-like arrangements of Pb-centred polyhedra that extend along the [010] direction. These 'rods' are linked, alternately, by $(CO_3)^{2-}$ and $(S_2O_3)^{2-}$ groups. The $(S_2O_3)^{2-}$ groups point alternately left and right (in a projection on [001] with [010] set vertical) if the apex occupied by the S^{2-} in the thiosulphate group is defined to be the atom giving the direction. The lead atoms are nine-coordinated by seven oxygen atoms and two sulphur (S^{2-}) atoms. The eight strongest X-ray powder-diffraction lines [*d* in Å (*I/I₀*) (*hkl*)] are: 4.410 (39) (101), 4.381 (59) (020), 4.080 (62) (400), 3.504 (75) (301), 3.108 (100) (121), 2.986 (82) (420), 2.952 (49) (221) and 2.736 (60) (321). Electron-microprobe analyses produce an empirical formula $Pb_{2.01(1)}(S_{1.82(2)}O_3)CO_3$ (on the basis of six oxygen atoms). The presence of both carbonate and thiosulphate groups was corroborated by Raman spectra, which are discussed in detail. Fassinaite is named after Bruno Fassina (b. 1943), an Italian mineral collector who discovered the mineral in 2009.

Introduction

THIOSULPHATES were identified as weathering products by Braithwaite *et al.* (1993) who

described their occurrence as intermediate phases in the oxidative weathering of BaS to $BaSO_4$ in slags derived from the smelting of sulphide ores in Yorkshire and Derbyshire, UK. The compounds present in this assemblage include two barium thiosulphates, a barium sulphite and a hydrated barium aluminium hydroxy-trisulphide. A full structural characterization was not reported by Braithwaite *et al.* (1993), but the crystal structure of one of the compounds, $Ba_2F_2(S_2O_3)$, which was found in well formed crystals at the Surrender Mill in Yorkshire, was recently reported by Kampf (2009). Stracher *et al.* (2009) reported an occurrence of $(NH_4)_2(S_2O_3)$ from a burning coal dump in the Witbank coalfield (South Africa). Thiosulphates of Pb, Fe, Zn, Cu and possibly Au were reported as minute grains in fine-grained ore samples containing sphalerite, galena, pyrite-'melnikovite' and gold from various localities (Kucha, 1988; Kucha and Stumpfl, 1992; Kucha *et al.*, 1989, 1995*a,b*, 1996) but they have not been characterized as minerals.

The only thiosulphate-bearing minerals formed in natural environments, and for this reason accepted as valid mineral species by the International Mineralogical Association, are sidpietersite, $Pb_4^{2+}(S_2O_3)O_2(OH)_2$ (Roberts *et al.*, 1999; Cooper and Hawthorne, 1999) and sliever-ustite, $Pb_5^{2+}(OH)_5[Cu^+(S_2O_3)_3](H_2O)_2$ (Cooper *et al.*, 2009). Two other approved minerals are reported to contain the thiosulphate group: bazhenovite, $CaS_5 \cdot CaS_2O_3 \cdot 6Ca(OH)_2 \cdot 20H_2O$, which occurs in burning dumps in the Chelyabinsk coal basin, South Urals, Russia (Chesnokov *et al.*, 1987); and viaeneite, $(Fe,Pb)_4S_8O$, which is found in Pb-Zn ore from Engis, Belgium (Kucha *et al.*, 1996). Bindi *et al.* (2005) studied a sample of bazhenovite provided by Boris Chesnokov (i.e. type material) but did not detect the thiosulphate group by structural or spectroscopic analysis, however they conceded that the bazhenovite type material might be slightly different in its chemistry from the specific sample studied by Chesnokov *et al.* (1987). Viaeneite (Kucha *et al.*, 1996) was poorly characterized because of the small amount of material available and its low quality. The presence of thiosulphate in viaeneite remains to be confirmed.

Here we report the description and characterization of the first mineral with coexisting $(S_2O_3)^{2-}$ and $(CO_3)^{2-}$ groups in its crystal structure. The mineral, ideally $Pb_2^{2+}(S_2O_3)(CO_3)$, is named after the Italian mineral collector Bruno Fassina (b. 1943), who discovered it at the Trentini mine in 2009. The crystal structure of material from the cotype localities in Salzburg and the Black Forest was briefly reported in a conference contribution (Kolitsch, 2010). The new mineral and mineral name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association; IMA2011-048. Holotype material is deposited in the mineral collection of the Museum of Mineralogy of the Department of Geosciences at the University of Padova, Italy, under catalogue number MMP M10008. Cotype specimens from Salzburg and the Black Forest are deposited in the mineral collection of the Naturhistorisches Museum of Wien, under catalogue numbers N 9055 (four micromounts and the crystal used for structure determination) and N 9056 (crystal used for structure determination; the micromount-sized specimen from the Black Forest is in the collection of Mr Stephan Wolfsried, Waiblingen, Germany), respectively.

Occurrence and physical properties

The holotype specimen of fassinaite was collected in the underground adit of the Trentini mine, Mount Naro, Vicenza Province, Veneto, Italy. The mine is located in the Vicentine Alps metal-bearing district and has been exploited for lead, zinc and silver since ancient times. From a genetic point of view, the mineralization is linked to Mid-Triassic calc-alkaline magmatism. Hydrothermal fluids related to volcanism deposited sulphides, baryte and Fe- and Mn-bearing minerals at the boundary between Ladinic volcanites and limestone of the Mount Spitz Formation. Supergene minerals including sulphates, carbonates and arsenates of Zn, Pb and Cu are very common (Maini *et al.*, 2000). Fassinaite was found as radiating aggregates of acicular, colourless crystals up to 200 µm long (Fig. 1), closely associated with galena, quartz and anglesite.

Fassinaite was also found at the Erasmus adit, Schwarzleo District, Leogang, Salzburg, Austria and at the Friedrich-Christian mine, Schapbach, Black Forest, Baden-Württemberg, Germany. At the Erasmus adit, it was found in material collected from a small dump by Mr Rolf Poeverlein of Traunstein, Germany. The dump, which is probably of late medieval date (R. Poeverlein, pers. comm., 2009), consists of cobbed sulphide ore (in blocks smaller than about

FIG. 1. Fassinaite crystals from the type locality at Trentini mine, Mount Naro, Vicenza Province, Veneto, Italy. The width of the picture is 1.6 mm.

10−15 cm) which was set aside by the miners for crushing, roasting and smelting. Additional specimens (not considered to be cotype material) were found on a dump from the Herren adit, also in the Schwarzleo District, but they are much rarer. The mineralogy of the ancient and famous Leogang mining district is complex. It was described in detail by Paar (1987) and Poeverlein and Hochleitner (1987). The polymetallic primary Ag, Pb, Zn, Cu, Ni, Co, Hg, As and Sb ores were exposed to low-grade metamorphism (Lengauer, 1987).

The Austrian fassinaite occurs as sprays of colourless, prismatic crystals, up to 0.4 mm long. It is found in fractures in massive galena; on cerussite and anglesite; and on grey-black schist ('Wildschöner Schiefer'). Associated minerals include rare sulphur and very rare phosgenite. The specimens were collected in 2007−2009.

Fassinaite was found as small sprays of prismatic crystals (<0.2 mm) on a single micromount-sized specimen from the Friedrich-Christian mine, Schapbach, Black Forest, Baden-Württemberg, Germany. The mine worked hydrothermal veins containing Pb-Zn ore and was described in detail by Lippolt *et al.* (1986), Walenta (1992) and Markl (1996).

At all of the localities described here, fassinaite is transparent with a vitreous to adamantine lustre and a white streak. It is brittle with an irregular fracture and no discernible cleavage. The Mohs hardness is estimated to be 1½−2.

The crystals are acicular to prismatic [010], with a flattened diamond-shaped cross-section.

The Austrian crystals are sufficiently well developed to allow determination of some of the crystal forms: the prism {101} is large and dominant, with a flat chisel-shaped {*hk*0} termination, possibly {110}. Small faces which are possibly {011} are rarely present. Further forms are minute and difficult to measure as they are commonly rounded. On casual inspection, fassinaite crystals are easily mistaken for anglesite, but anglesite does not have such steep crystal terminations. It is likely that fassinaite occurs in other Pb-Zn deposits, but has been overlooked.

The density could not be measured due to the small grain size. The calculated density of the type material is 6.084 g cm^{-3} (on the basis of the empirical formula) and the X-ray density is 5.947 g cm^{-3}. In common with other natural lead thiosulphates (i.e. sidpietersite and steverustite), fassinaite has intense internal reflections, which hamper reflectance measurements; we were unable to gather full optical data. The prisms are length-slow with straight extinction and very high birefringence. The mean calculated refractive index n is 2.13. No twinning was observed. Fassinaite is not fluorescent under either short- or long-wavelength ultraviolet light.

X-ray crystallography and crystal-structure determination

Several crystals of fassinaite from the Trentini mine (Fig. 1) were selected and examined by means of a STOE-STADI IV CCD single-crystal diffractometer using graphite-monochromatized

Mo-$K\alpha$ radiation (see Table 1 for details). A careful analysis of the data collected from a suitable crystal led unequivocally to the choice of the space group *Pnma* (only the procedure used for the structure determination the crystal from the Trentini mine, designated FAS-01, is reported here). The positions of most of the atoms (all the metals, S^{6+}, S^{2-} and two O-positions) was determined from a three-dimensional Patterson synthesis (Sheldrick, 2008). A least-squares refinement using these heavy atom positions and isotropic temperature factors yielded an R_1 factor of 0.097. Three-dimensional difference Fourier synthesis yielded the position of the carbon atom and the remaining oxygen atoms. The full-matrix least-squares program *SHELXL-97* (Sheldrick, 2008) was used for the refinement of the structure. The occupancies of all atom sites were allowed to vary and all sites were found to be fully occupied. Neutral scattering curves for Pb, S, C and O, taken from *The International Tables of X-ray Crystallography*, volume IV (Ibers and Hamilton, 1974) were used. At the last refinement stage, with anisotropic atomic displacement parameters for all atoms and no constraints, the residual value for FAS-01 settled at $R_1(F) = 0.0596$ for 702 observed reflections [$F_o > 4\sigma(F_o)$] and 58 parameters and at $R_1(F) = 0.1091$ for all 1008 independent reflections. The other two crystals measured (using a Nonius KappaCCD diffractometer), FAS-02 (from Salzburg) and FAS-03 (from the Black Forest), were refined using the same procedure, and produced slightly lower residuals (Table 1).

Experimental details and *R* indices for the three crystals are given in Table 1. Fractional atom coordinates and anisotropic displacement parameters are listed in Tables 2 and 3, respectively. Selected bond distances are reported in Table 4. The calculated X-ray powder pattern for fassinaite, computed from the FAS-01 structure model, is listed in Table 5. Structure factors for FAS-01, FAS-02 and FAS-03 are deposited with the Principal Editor of Mineralogical Magazine at http://www.minersoc.org/pages/e_journals/dep_mat.html.

Chemical composition

One of the single crystals investigated by X-ray diffraction (FAS-01) was analysed using a CAMECA-CAMEBAX electron microprobe operating in wavelength-dispersive (WDS) mode at an accelerating voltage of 15 kV and a beam

TABLE 1. Crystallographic data and refinement parameters for fassinaite.

	FAS-01	FAS-02	FAS-03
Crystal data			
Chemical formula	$Pb_2^{2+}(S_2O_3)(CO_3)$	$Pb_2^{2+}(S_2O_3)(CO_3)$	$Pb_2^{2+}(S_2O_3)(CO_3)$
Locality	Trentini mine	Salzburg	Black Forest
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	*Pnma*	*Pnma*	*Pnma*
Unit-cell parameters a, b, c (Å)	16.320(2), 8.7616(6), 4.5809(7)	16.343(3), 8.760(2), 4.592(1)	16.326(3), 8.773(2), 4.583(1)
Unit-cell volume (Å^3)	655.0(1)	657.4(2)	656.4(2)
Z	4	4	4
Crystal size (mm)	0.02 × 0.02 × 0.05	0.02 × 0.03 × 0.14	0.03 × 0.03 × 0.07

Data collection

	STOE-STADI IV CCD	Nonius KappaCCD	Nonius KappaCCD
Diffractometer	STOE-STADI IV CCD	Nonius KappaCCD	Nonius KappaCCD
Temperature (K)	298(3)	293(3)	293(3)
Radiation, wavelength (Å)	Mo-$K\alpha$, 0.71073	Mo-$K\alpha$, 0.71073	Mo-$K\alpha$, 0.71073
Crystal-detector dist. (mm)	50	30	30
Rotation axes, width (°)	φ, ω, 1	φ, ω, 1	φ, ω, 1
Total no. of frames	1380	932	484
Collection time per degree (s)	150	340	100
θ range for data collection (°)	1.00–30.00	1.00–30.00	1.00–30.00
h, k, l ranges	$-21\to+22$, $-5\to+12$, ±6	±22, ±12, ±6	±22, ±12, ±6
Total reflections collected	6436	1938*	1937*
Unique reflections (R_{int})	1008 (0.1253)	1016 (0.0249)	1018 (0.0341)
Unique reflections $F > 4\sigma(F)$	702	877	770
Absorption correction method	multi-scan (Otwinoski $et\ al.$, 2003)	multi-scan (Otwinoski $et\ al.$, 2003)	multi-scan (Otwinoski $et\ al.$, 2003)

Structure refinement

	STOE-STADI IV CCD	Nonius KappaCCD	Nonius KappaCCD
Refinement method	F^2	F^2	F^2
Data/restraints/parameters	702/0/58	877/0/59	770/0/59
Extinct. coefficient		0.0008(2)	0.0007(2)
R_1 [$F > 4\sigma(F)$]	0.0596	0.0424	0.0353
R_1 all	0.1091	0.0535	0.0566
wR_2 all	0.1240	0.0978	0.0815
Goodness-of-fit on F^2	0.993	1.194	1.082
Largest diff. peak and hole (e$^-$/Å³)	2.91, −4.50	3.06, −1.51	2.69, −2.61

* after averaging of multiply measured single reflections;

$R_{int} = (n/n - 1)^{1/2}[F_o^2 - F_o\ (\text{mean})^2]/\Sigma F_o^2$

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$;

$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$;

$GooF = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$

where n is the number of reflections and p is the number of refined parameters.

current of 15 nA with an ~1 μm beam diameter and with 10 s counting times on the peak and 5 s for total background. The WDS data were converted into oxide wt.% using the PAP correction program (Pouchou and Pichoir, 1985). The crystal is chemically homogeneous (on the basis of 11 microprobe analyses). The composition and further analytical details are listed in Table 6. Carbon was not analysed because of the small amount of sample that was available; it was calculated by stoichiometry.

On the basis of six oxygen atoms, the empirical formula for fassinaite is $Pb_{2.01(1)}(S_{1.82(2)}O_3)CO_3$. The simplified formula, in which the S content is partitioned into S^{6+} and S^{2-} in a 1:1 ratio on the basis of structural considerations, is $Pb_2^{2+}(S_2^{6+}O_3S^{2-})(CO_3)$, which requires PbO 76.11, SO 16.39, CO_2 7.50, total 100.00 wt.% (with sulphur expressed as SO for clarity).

The SEM-EDS analyses of samples from the two cotype localities showed only Pb, S, C and O; the Pb:S ratio of 1:1 was confirmed.

Raman spectroscopy

Raman spectra of fassinaite from the type locality were collected using a dispersive Horiba LabRAM−HR spectrometer interfaced to an Olympus BX41 optical microscope. The system was equipped with a diffraction grating with 1800 lines per millimetre and a Peltier-cooled charge-coupled detector. Spectra were excited using a 632.8 nm He-Ne laser with the power reduced to 0.8 mW at the sample surface. An Olympus 50 × objective was used. The system was calibrated using Ne lamp emissions and the Rayleigh line; resolution was 0.8 cm^{-1}. Eight replicate measurements were done on three crystals, changing their

TABLE 2. Atoms, multiplicities and Wyckoff sites, fractional atom coordinates and equivalent isotropic displacement parameters for the selected fassinaite crystals.

Atom	Wyckoff	x/a	y/b	z/c	U_{iso} (Å^2)
FAS-01					
Pb	$8d$	0.13583(4)	0.48701(7)	0.5842(2)	0.0213(3)
S1	$4c$	0.0031(4)	¼	0.069(1)	0.014(1)
C	$4c$	0.713(1)	¼	0.387(7)	0.019(6)
O1	$4c$	0.062(1)	¼	0.828(4)	0.021(4)
O2	$8d$	0.2757(8)	0.623(1)	0.501(3)	0.021(3)
O3	$8d$	0.0139(7)	0.111(1)	0.251(3)	0.021(3)
O4	$4c$	0.187(1)	¼	0.388(5)	0.023(4)
S2	$4c$	0.8850(4)	¼	0.929(2)	0.020(1)
FAS-02					
Pb	$8d$	0.13571(2)	0.48680(4)	0.5838(1)	0.0199(2)
S1	$4c$	0.0026(2)	¼	0.0718(7)	0.0130(6)
C	$4c$	0.7125(8)	¼	0.375(3)	0.014(3)
O1	$4c$	0.0598(6)	¼	0.826(2)	0.019(2)
O2	$8d$	0.2755(4)	0.6219(8)	0.501(2)	0.024(2)
O3	$8d$	0.0139(4)	0.1126(7)	0.248(2)	0.019(1)
O4	$4c$	0.1858(6)	¼	0.387(2)	0.022(2)
S2	$4c$	0.8853(2)	¼	0.9277(9)	0.0184(7)
FAS-03					
Pb	$8d$	0.13597(2)	0.48701(4)	0.58424(9)	0.0205(2)
S1	$4c$	0.0030(2)	¼	0.0734(7)	0.0155(6)
C	$4c$	0.7115(7)	¼	0.373(3)	0.017(3)
O1	$4c$	0.0604(5)	¼	0.827(2)	0.021(2)
O2	$8d$	0.2758(4)	0.6203(7)	0.502(2)	0.027(2)
O3	$8d$	0.0138(3)	0.1110(6)	0.252(2)	0.019(1)
O4	$4c$	0.1872(6)	¼	0.394(2)	0.028(2)
S2	$4c$	0.8853(2)	¼	0.9276(8)	0.0197(6)

TABLE 3. Anisotropic displacement parameters for the atoms in fassinaite.

Atom	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{23} (Å^2)	U_{13} (Å^2)	U_{12} (Å^2)
FAS-01						
Pb	0.0178(4)	0.0197(4)	0.0265(4)	−0.0009(3)	−0.0015(3)	−0.0010(3)
S1	0.015(3)	0.019(3)	0.008(3)	0	−0.009(3)	0
C	0.01(1)	0.02(1)	0.03(2)	0	−0.01(1)	0
O1	0.004(8)	0.04(1)	0.02(1)	0	0.008(7)	0
O2	0.023(7)	0.028(7)	0.012(7)	−0.011(5)	0.012(5)	−0.019(6)
O3	0.020(6)	0.021(6)	0.023(7)	−0.002(6)	−0.008(7)	0.001(5)
O4	0.03(1)	0.020(9)	0.02(1)	0	−0.01(1)	0
S2	0.013(3)	0.025(3)	0.020(3)	0	−0.003(3)	0
FAS-02						
Pb	0.0169(3)	0.0188(3)	0.0239(3)	−0.0004(1)	−0.0011(1)	−0.0011(1)
S1	0.010(1)	0.017(1)	0.012(1)	0	−0.004(1)	0
C	0.010(6)	0.020(6)	0.012(6)	0	−0.005(5)	0
O1	0.012(5)	0.033(5)	0.011(5)	0	0.004(4)	0
O2	0.022(3)	0.026(4)	0.023(4)	−0.013(3)	0.008(3)	−0.006(3)
O3	0.016(3)	0.023(3)	0.017(3)	0.005(3)	−0.005(3)	−0.002(2)
O4	0.025(5)	0.024(5)	0.017(5)	0	0.014(5)	0
S2	0.011(1)	0.024(2)	0.020(2)	0	−0.002(1)	0
FAS-03						
Pb	0.0186(2)	0.0187(2)	0.0242(2)	−0.0007(1)	−0.0011(1)	−0.0011(1)
S1	0.013(1)	0.014(1)	0.019(2)	0	−0.001(1)	0
C	0.013(5)	0.018(5)	0.020(7)	0	0.006(5)	0
O1	0.016(4)	0.027(5)	0.019(5)	0	0.007(4)	0
O2	0.023(3)	0.027(3)	0.032(4)	−0.012(3)	0.009(3)	−0.006(3)
O3	0.019(3)	0.015(3)	0.022(3)	0.002(3)	−0.004(3)	−0.005(2)
O4	0.037(5)	0.030(5)	0.018(5)	0	0.011(5)	0
S2	0.017(1)	0.021(1)	0.021(2)	0	−0.004(1)	0

orientation under the microscope to minimize potential polarization effects and to check for potential µm-scale heterogeneity. No noticeable laser-induced luminescence was observed. As expected from the structure determination (see above), no bands due to C−H, O−H or H_2O were observed. A representative spectrum is shown in Fig. 2; other spectra have different band intensities due to different crystal orientations.

Raman spectra of fassinaite from the Austrian cotype locality were measured on several randomly oriented crystals with a Renishaw RM 1000 confocal laser micro-Raman spectrometer using an excitation wavelength of 632.8 nm in the range 100−4000 cm^{-1}. They are in good agreement with those described above; again, the band intensities vary depending on the crystal orientations.

The high quality of all the measured spectra allows detailed band assignments to be made (the values given below all refer to the Horiba LabRAM−HR spectra). In common with sidpie-tersite (Roberts *et al.*, 1999; IR spectra), the large majority of the bands observed for fassinaite are characteristic of the thiosulphate group (Meuwsen and Heinze, 1952; Gabelica, 1979, 1980); the strong ν(SS) stretching mode is located at 438 cm^{-1}, and the stretching modes ν_{sym}(SO) and ν_{asym}(SO) are at 983 cm^{-1} (weak to strong, depending on orientation) and 1137 cm^{-1} (very weak, broad), respectively. The symmetric deformation mode δ_{sym}(SO) produces a very strong band at 637 cm^{-1}. This band has a shoulder at 629 cm^{-1} (indicating minor degeneracy) and a tiny satellite at 661 cm^{-1}; the latter may, however, also belong to a split ν_4(CO) band (see below). The asymmetric deformation mode δ_{asym}(SO) produces a split band at 549 and 520 cm^{-1}. The rotation mode ρ(SO$_3$) appears to produce the split band at 358 and 342 cm^{-1}.

The presence of the CO$_3$ group (cf. Griffith, 1970; Downs, 2006) is shown by the strong symmetric stretching band (ν$_1$) at 1061 cm^{-1}; this

TABLE 4. The main interatomic distances for the selected fassinaite crystals.

	FAS-01 (Å)	FAS-02 (Å)	FAS-03 (Å)
Pb−O4	2.42(1)	2.406(5)	2.405(5)
−O2	2.58(1)	2.585(7)	2.575(6)
−O2	2.60(1)	2.601(7)	2.593(6)
−O1	2.65(1)	2.661(6)	2.661(5)
−O3	2.65(1)	2.664(6)	2.654(6)
−O3	2.78(1)	2.791(6)	2.780(5)
−O2	3.18(1)	3.190(8)	3.174(7)
−S2	3.22(1)	3.235(3)	3.232(3)
−S2	3.31(1)	3.309(3)	3.308(3)
<Pb−φ>	2.82	2.827	2.820
S1−O1	1.46(2)	1.46(2)	1.469(9)
−O3	1.48(1)	1.462(7)	1.478(6)
−O3	1.48(1)	1.462(7)	1.478(6)
−S2	2.031(8)	2.029(4)	2.035(4)
<S−φ>	1.613	1.603	1.615
C−O2	1.24(2)	1.273(9)	1.289(8)
−O2	1.24(2)	1.273(9)	1.289(8)
−O4	1.33(3)	1.28(2)	1.29(1)
<C−O>	1.27	1.275	1.289

TABLE 5. Calculated X-ray powder diffraction data for fassinaite.

I_{calc}	d_{calc}	h	k	l
5.53	5.9714	2	1	0
38.57	4.4104	1	0	1
58.78	**4.3808**	**0**	**2**	**0**
61.77	**4.0800**	**4**	**0**	**0**
37.49	3.9945	2	0	1
6.55	3.8597	2	2	0
75.16	**3.5040**	**3**	**0**	**1**
4.30	3.2535	3	1	1
100.00	**3.1081**	**1**	**2**	**1**
81.89	**2.9857**	**4**	**2**	**0**
48.97	**2.9517**	**2**	**2**	**1**
4.76	2.8777	4	1	1
5.58	2.7497	2	3	0
60.09	**2.7364**	**3**	**2**	**1**
7.81	2.7200	6	0	0
11.64	2.6582	5	0	1
4.55	2.5013	4	2	1
10.34	2.3388	6	0	1
5.35	2.3108	6	2	0
7.00	2.2905	0	0	2
11.47	2.2726	5	2	1

TABLE 5 (*contd.*).

I_{calc}	d_{calc}	h	k	l
18.39	2.2682	1	0	2
20.15	2.1904	0	4	0
7.92	2.1110	3	0	2
20.53	2.0778	7	0	1
13.88	2.0632	6	2	1
14.16	2.0400	8	0	0
4.14	2.0298	0	2	2
21.71	2.0142	1	2	2
6.14	1.9973	4	0	2
8.70	1.9618	1	4	1
24.69	1.9299	4	4	0
9.45	1.9206	2	4	1
9.17	1.9017	3	2	2
33.72	1.8773	7	2	1
14.23	1.8749	5	0	2
24.71	1.8574	3	4	1
12.79	1.8493	8	2	0
8.88	1.8173	4	2	2
17.86	1.7237	5	2	2
9.38	1.5756	1	4	2
5.64	1.5293	10	2	0
4.51	1.5200	3	4	2
8.04	1.5075	7	4	1
7.53	1.5009	2	0	3
6.15	1.4928	8	4	0
9.12	1.4244	5	4	2
6.25	1.4217	9	0	2
17.86	1.4199	2	2	3
5.02	1.4115	11	0	1
5.47	1.3863	1	6	1
5.37	1.3749	4	6	0
7.95	1.3523	9	2	2
4.29	1.3479	3	6	1
8.26	1.3434	11	2	1
4.38	1.3315	6	0	3
8.35	1.2740	6	2	3
5.91	1.2381	2	4	3
4.81	1.1947	7	6	1
5.57	1.1925	9	4	2
6.00	1.1865	11	4	1
4.78	1.1378	6	4	3
4.60	1.0466	2	6	3

The strongest reflections are given in bold. Only reflections with $I_{calc} > 4$ are listed.
The X-ray powder diffraction pattern was computed on the basis of a = 16.320(2), b = 8.7616(6), c = 4.5809(7) and with the atom coordinates and occupancies reported in Table 2 (unit-cell values and atom coordinates for FAS-01).

TABLE 6. Electron microprobe data for fassinaite (crystal FAS-01).

Oxides	Wt.%	Spectrum line	Standard
PbO	77.1(4)	$K\alpha$	PbS
SO$_3$	12.0(1)	$K\alpha$	PbS
CO$_2$*	7.60(4)		
S^{2-}	4.83(1)		
O = S^{2-}	−2.41(2)		
Total	99.2(4)		

* CO$_2$ was calculated for each single analysis by stoichiometry.

band is degenerate since in some crystal orientations an additional weak band is also present at 1082 cm^{-1}. A very weak band at 845 cm^{-1} is probably caused by the out-of-plane bend (v_2), which is theoretically inactive in Raman spectra, but is often visible due to a lowered site symmetry of the CO$_3$ group (as in fassinaite). The asymmetric stretching vibration (v_3) is responsible for the very weak broad bands at 1444 and 1322 cm^{-1} (the latter may, however, also be explained by a combination band, 983 + 438 cm^{-1}). The in-plane bend (v_4) causes the very weak band at 722 cm^{-1}.

The very weak band at 1690 cm^{-1} is either an overtone of the v_2(CO$_3$) mode or a combination band (1061 + 661 or 637 cm^{-1}). The remaining bands are mostly unassigned; those at low wavenumbers are probably produced by lattice modes, they include: 602, 250, ~203 (possibly CO$_3$), 180 (possibly Pb−O), ~118 and 75 cm^{-1}.

Description of the structure and discussion

The crystal structure of Pb$_2^{2+}$(S$_2$O$_3$)(CO$_3$) is not related to that of any known synthetic or natural thiosulphate. It consists of rod-like arrangements of Pb-centred polyhedra that extend along the [010] direction (Fig. 3). These 'rods' are linked, alternately, by (CO$_3$)$^{2-}$ and (S$_2$O$_3$)$^{2-}$ groups. The (S$_2$O$_3$)$^{2-}$ groups point alternately left and right in the orientation illustrated in Fig. 3 if the apex occupied by S^{2-} in the thiosulphate group is defined as the direction vector (Fig. 3). The Pb atoms are nine-coordinated by seven oxygen atoms and two sulphur (S^{2-}) atoms (Table 4 and Fig. 4); the latter are only weakly bonded to the Pb atoms. In the thiosulphate group, the central sulphur (S^{6+}) atom is linked to three oxygen atoms at a mean distance in the range 1.46−1.48 Å and to a sulphur (S^{2-}) atom at 2.03−2.04 Å, the four anions forming a distorted tetrahedron. The mean bond length for the thiosulphate group is in the range 1.60−1.62 Å, which is in excellent agreement with the values obtained for synthetic Ba$_2$F$_2$(S$_2$O$_3$) (Kampf, 2009) and for sidpietersite (Cooper and Hawthorne, 1999) and steverustite (Cooper *et*
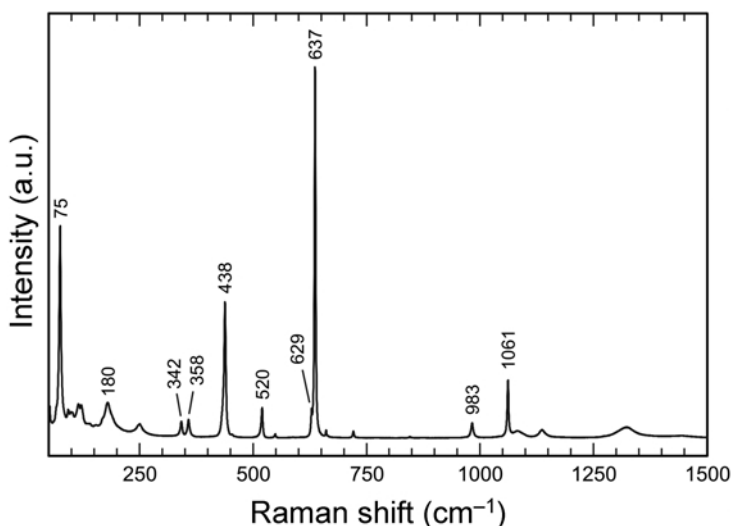

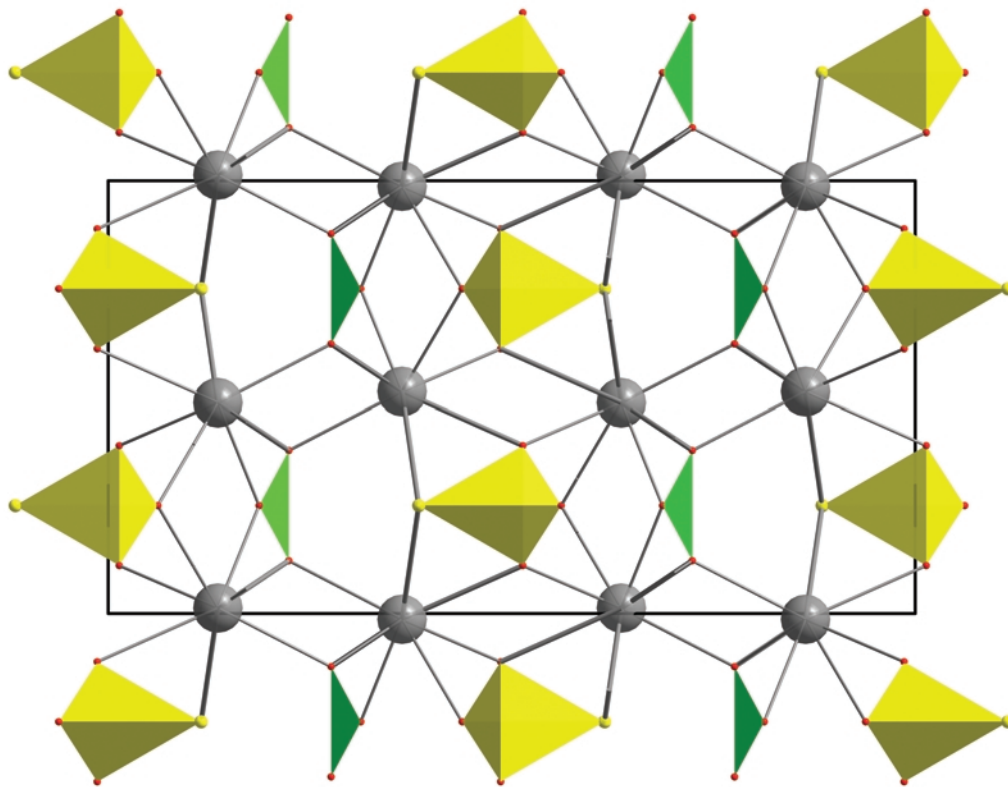FIG. 2. An unpolarized micro-Raman spectrum of type fassinaite.

FIG. 3. Projection of the fassinaite structure along [001]. Grey circles are Pb atoms, yellow tetrahedra are thiosulphate groups and light green triangles are carbonate groups. The unit cell is outlined.

al., 2009). In the carbonate group there are two C$-$O bonds at 1.24$-$1.29 Å and one at 1.28$-$1.33 Å (Table 4).

Bond valence sums calculated from the curves of Brese and O'Keeffe (1991) are given in Table 7. An interesting feature of the bond valence sums for the central S^{6+} atoms in the thiosulphate groups was pointed out by Cooper and Hawthorne (1999). These authors concluded that there is a problem with the S$^{6+}-$S^{2-} bond-valence curve reported by Brese and O'Keeffe (1991), which leads to an underestimation with respect to the ideal value of 6.00 v.u. [5.78 v.u. in sidpietersite (Cooper and Hawthorne, 1999); 5.67, 5.79, 5.81 v.u. in steverustite (Cooper *et al.*, 2009); 5.72 v.u. in Ba$_2$F$_2$(S^{6+}O$_3$S^{2-}) (Kampf, 2009)]. For fassinaite we obtained values in the range 5.56$-$5.74 v.u. (Table 7). These are consistent with those in other thiosulphates and, as noted by Cooper and Hawthorne (1999), this suggests that revision of the S$^{6+}-$S^{2-}
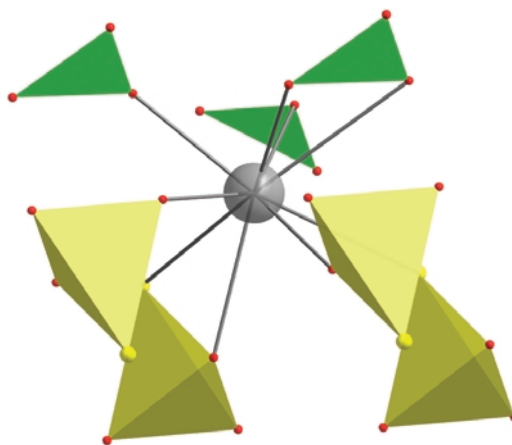

FIG. 4. Coordination environment of the Pb atoms in fassinaite. Grey circles are Pb atoms, yellow tetrahedra are thiosulphate groups and light green triangles indicate carbonate groups.

TABLE 7. Bond valence (v.u.) analysis for fassinaite crystals.*

	FAS-01	FAS-02	FAS-03
Pb	1.96	1.94	1.97
S1	5.59	5.74	5.56
C	4.18	4.09	3.94
O1	2.02	2.02	1.98
O2	2.11	1.97	1.93
O3	1.87	1.94	1.87
O4	2.06	2.25	2.21
S2	1.66	1.65	1.63

* calculated from the bond-valence curves of Brese and O'Keeffe (1991)

bond-valence curve of Brese and O'Keeffe (1991) would be useful.

Cooper *et al.* (2009) undertook a careful review of the structural aspects of several $(S_2O_3)^{2-}$-bearing compounds. Their results led them to divide thiosulphates into two groups based upon the coordination of the large cation (X) adjacent to the S^{2-} atom. Group 1 contains compounds where the X cation [X = H {H_2O, NH_3, NH_4}, Na, K, Co, Ni, Ag, Cd, Ba, La, Pb] may bond to one or more S^{2-} atoms, in addition to one or more O or N atoms. Group 2 contains compounds where the X cation [X = Cu, Ag, Au] links the S^{2-} atoms of two to four thiosulphate groups exclusively. In such a classification, fassinaite belongs to group 1. A more detailed classification of thiosulphates, taking into account the difference between monodentate, bidentate and chelate configurations, was proposed by Gabelica (1980). In this classification, fassinaite belongs to the group in which the thiosulphate anion acts as a chelating ligand to a metal cation (Pb^{2+} in this case).

Finally, some remarks concerning the conditions of formation for fassinaite can be made. The matrix of all of the specimens (from the three different localities) consists of a mixture of fine-grained minerals with a predominance of galena. Fassinaite is commonly associated with anglesite and less commonly with cerussite. Fassinaite forms as a result of the supergene alteration of galena. It seems likely that thiosulphate formation occurred at an intermediate stage in the oxidation process as the assemblages moved toward complete oxidation (with the formation of the common and stable phases anglesite and cerussite). Since the thiosulphate anion is stable only in neutral or alkaline solutions, fassinaite probably formed in such conditions. The presence of carbonate in the chemical formula can be explained by a suitable CO_2 fugacity during the formation of the mineral. The presence of minor cerussite in the material from Salzburg reflects an increasing carbonate concentration in the environment in which the mineral was crystallizing.

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