Bassoite, SrV$_3$O$_7$·4H$_2$O, a new mineral from Molinello mine, Val Graveglia, eastern Liguria, Italy

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ABSTRACT

Bassoite, ideally SrV$_3$O$_7$·4H$_2$O, is a new mineral from the Molinello manganese mine, Val Graveglia, eastern Liguria, northern Apennines, Italy. It occurs as black euhedral to subhedral grains up to 400 μm across, closely associated with rhodonite, quartz and braunite. Bassoite is opaque with a sub-metallic lustre and a black streak. It is brittle and neither fracture nor cleavage was observed; the Vickers micro-hardness (VHN$_{100}$) is 150 kg/mm^2 (range 142−165; corresponding to a Mohs hardness of 4−4½). The calculated density is 2.940 g/cm^3 (on the basis of the empirical formula and X-ray single-crystal data). Bassoite is weakly bireflectant and very weakly pleochroic from grey to a dark green. Internal reflections are absent. The mineral is anisotropic, without characteristic rotation tints. Reflectance percentages (R_{min} and R_{max}) for the four standard COM wavelengths are 18.5%, 19.0% (471.1 nm); 17.2%, 17.8% (548.3 nm); 16.8%, 17.5% (586.6 nm) and 16.2%, 16.8% (652.3 nm), respectively.

Bassoite is monoclinic, space group $P2_1/m$, with unit-cell parameters: a = 5.313(3) Å, b = 10.495(3) Å, c = 8.568(4) Å, β = 91.14(5)°, V = 477.7(4) Å^3, a:b:c = 0.506:1:0.816, and Z = 2. The crystal structure was refined to R_1 = 0.0209 for 1148 reflections with F_o > 4σ(F_o) and it consists of layers of VO$_5$ pyramids (with vanadium in the tetravalent state) pointing up and down alternately with Sr between the layers (in nine-fold coordination). The nine most intense X-ray powder-diffraction lines [d in Å (I/I_0) (hkl)] are: 8.5663 (100) (001); 6.6363 (14) (011); 3.4399 (14) ($\bar{1}$21); 3.4049 (17) (121); 2.8339 (15) ($\bar{1}$22); 2.7949 (11) (122); 2.6550 (15) (200); 2.6237 (11) (040) and 1.8666 (15) (240). Electron microprobe analyses produce a chemical formula (Sr$_{0.97}$Ca$_{0.02}$Na$_{0.01}$)V$_{3.00}$O$_7$·4H$_2$O, on the basis of Σ(Sr+Ca+Na) = 1, taking the results of the structure refinement into account. The presence of water molecules was confirmed by micro-Raman spectroscopy. The name honours Riccardo Basso (b. 1947), full professor of Mineralogy and Crystallography at the University of Genova. The new mineral and mineral name have been approved by the Commission on New Minerals, Nomenclature and Classification, IMA (2011-028).

Introduction

In the Val Graveglia mines, Mn ores occur as braunite-bearing layered massive lenses and boudins near the stratigraphic base of the cherts of the 'Diaspri di M. Alpe' Formation, which overlies an ophiolitic basement (Cabella *et al.*, 1998). Mineralization is characterized by a

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braunite-quartz assemblage which equilibrated under prehnite−pumpellyite-facies conditions (Cortesogno *et al.*, 1979; Lucchetti *et al.*, 1990) during a tectono-metamorphic event that affected both the ophiolite and chert. Hydrothermal fluid circulation along later extensional fractures, at lower-grade metamorphic conditions, concentrated dispersed elements, such as As, Ba, Cu, Sr, and V, and precipitated a variety of uncommon minerals. Vanadium minerals such as saneroite, medaite, palenzonaite, gamagarite, volborthite, tangeite, reppiaite, and vanadomalayaite (Marchesini and Pagano, 2001) are common in this assemblage. Here we report the description and characterization of a new V^{4+}-bearing mineral from Val Graveglia, eastern Liguria, northern Apennines, Italy. The mineral, ideally $SrV_3O_7 \cdot 4H_2O$, is named after Riccardo Basso (b. 1947), full professor of mineralogy and crystallography at the University of Genova, Italy. Riccardo Basso has worked on the characterization of several new V-rich minerals from the Ligurian region and has determined the crystal structure of most of them (Basso *et al.*, 1994, 2003, 2005). The new mineral and mineral name have been approved by the Commission on New Minerals, Nomenclature and Classification, IMA (2011-028). Holotype material is deposited in the mineralogical collection of the Dipartimento per lo Studio del Territorio e delle sue Risorse, Università di Genova, Italy, under catalogue number M0480.

Occurrence and physical properties

The sample containing the new mineral bassoite, $SrV_3O_7 \cdot 4H_2O$, was collected at the Molinello mine, Val Graveglia, eastern Liguria, northern Apennines, Italy. The sample mainly consists of bassoite with associated rhodonite, quartz and braunite (Fig. 1). Bassoite occurs as euhedral to subhedral grains which are homogeneous and not intergrown with other minerals. The maximum grain size is about 400 μm.

Bassoite is black in colour and has a black streak. It is opaque with a sub-metallic lustre and it is brittle without fracture or cleavage. The density could not be determined experimentally because of the small grain size. The calculated density is 2.940 g/cm^3 (on the basis of the empirical formula and X-ray single-crystal data). The micro-indentation measurements, carried out with a VHN load of 100 g, gave a mean value of 150 kg/mm^2 (range: 142−165), corresponding to a Mohs hardness of 4 to 4½.

In plane-polarized incident light, bassoite is weakly bireflectant and very weakly pleochroic with colour varying from grey to dark green. With crossed polars, bassoite is anisotropic, without characteristic rotation tints. Internal reflections are absent and there is no evidence of growth zoning.

Reflectance measurements were performed in air using a Zeiss MPM-200 microphotometer equipped with an MSP-20 system processor on a Zeiss Axioplan ore microscope. The filament temperature was approximately 3350 K. An interference filter was used to select the four wavelengths for measurement (471.1, 548.3, 586.6 and 652.3 nm). Measurements were obtained from an area 0.1 mm in diameter for the specimen and a SiC standard under the same conditions. Reflectance percentages (R_{min} and R_{max}) are 18.5%, 19.0% (471.1 nm); 17.2%, 17.8% (548.3 nm); 16.8%, 17.5% (586.6 nm) and 16.2%, 16.8% (652.3 nm), respectively.

X-ray crystallography and crystal-structure determination

Several crystals of bassoite were selected from the type specimen (Fig. 1) and examined using a Bruker MACH3 single-crystal diffractometer with graphite-monochromated Mo-$K\alpha$ radiation. The unit-cell dimensions were determined by least-squares refinement of the setting angles of 25 high-θ reflections ($12º < \theta_{Mo-K\alpha} < 18º$). This procedure gave nearly identical unit-cell dimensions for all of the crystals that were investigated. As the crystals produced nearly identical results, we decided to collect data using the crystal that produced the best quality diffraction data only. The data was collected using an Oxford Diffraction Xcalibur 3 diffractometer, fitted with
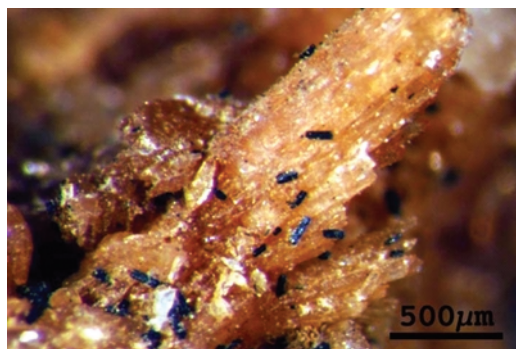

FIG. 1. Black bassoite crystals on rhodonite.

a Sapphire 2 CCD detector (see Table 1 for details). Intensity integration and standard Lorentz-polarization corrections were performed using the *CrysAlis RED* (Oxford Diffraction, 2006) software package. The empirical absorption correction was determined by the *ABSPACK* program, which is also part of the *CrysAlis RED* suite (Oxford Diffraction, 2006). The agreement among equivalent reflections for the data set expressed as R_{int} decreased from 0.1335 before the absorption correction was applied to 0.0690 after correction. Statistical tests on the distribution of |E| values ($|E^2-1| = 0.863$), which indicated the presence of an inversion centre, together with the observed systematic absences, led unequivocally to the choice of the space group $P2_1/m$.

The positions of most of the atoms (all of the metals and two O-positions) were determined from the three-dimensional Patterson synthesis (Sheldrick, 2008). A least-squares refinement using these heavy-atom positions and isotropic temperature factors yielded an R factor of 0.1018. Three-dimensional difference Fourier synthesis yielded the positions of the remaining oxygen atoms. The full-matrix least-squares program *SHELXL-97* (Sheldrick, 2008) was used for the refinement of the structure. All atom sites were found to be fully occupied. Neutral scattering curves for Sr, V and O, taken from *The International Tables for X-ray Crystallography*, volume IV (Ibers and Hamilton, 1974) were used. In the last stage of the analysis, with the anisotropic atomic displacement parameters assigned to all atoms and with no constraints, the residual value settled at $R_1 = 0.0209$ for 491 observed reflections $[F_o > 4\sigma(F_o)]$ and 77 parameters and at $R_1 = 0.0238$

TABLE 1. Crystallographic data and refinement parameters for bassoite.

Crystal data

Ideal formula	$SrV_3O_7 \cdot 4H_2O$
Crystal system	monoclinic
Space group	$P2_1/m$
Unit-cell parameters a, b, c (Å)	5.313(3), 10.495(3), 8.568(4)
β (°)	91.14(5)
Unit-cell volume (Å^3)	477.7(4)
Z	2
Crystal size (mm)	$0.024 \times 0.031 \times 0.039$

Data collection

Diffractometer	Oxford Diffraction Excalibur 3 (CCD)
Temperature (K)	298(3)
Radiation, wavelength (Å)	Mo-$K\alpha$, 0.71073
θ range for data collection (°)	3.15 - 29.46
h, k, l ranges	±7, ±13, ±11
Axis, frames, width (°), time per frame (s)	ω, 789, 0.60, 110
Total reflections collected	4592
Unique reflections (R_{int})	1148 (0.069)
Unique reflections $F_o > 4\sigma(F_o)$	491
Data completeness to θ_{max} (%)	98.9
Absorption correction method	multiscan (*ABSPACK*)

Structure refinement

Refinement method	Full-matrix least-squares on F^2
Weighting scheme	$1/\sigma^2(F)$
Data/restraints/parameters	1148/0/77
R_1 [$F > 4\sigma(F)$]	0.0209
R_1 all	0.0238
Largest difference, peak and hole (e$^-$/Å^3)	0.52, -0.82

$R_{int} = (n/n - 1)^{1/2}[F_o^2 - F_o \text{ (mean)}^2]/\Sigma F_o^2$
$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$
Where n is the number of reflections and p is the number of refined parameters.

TABLE 2. Atoms, multiplicity and Wyckoff position, fractional atom coordinates (Å), and equivalent isotropic displacement parameters (Å²) for bassoite.

Atom	Wyckoff	x	y	z	U_{iso}
Sr	2e	0.25846(9)	¼	0.23638(7)	0.0372(2)
V1	2e	0.74697(16)	¼	−0.04422(11)	0.0309(3)
V2	4f	0.24763(11)	0.01931(6)	−0.07309(7)	0.0268(2)
O1	4f	−0.0100(4)	0.1155(2)	0.0288(3)	0.0290(8)
O2	4f	0.5171(4)	0.1169(2)	0.0315(3)	0.0296(8)
O3	4f	0.7670(4)	−0.0478(2)	0.2567(2)	0.0255(8)
O4	2e	0.7379(5)	¼	0.7720(4)	0.0268(12)
O5W	4f	0.2615(4)	0.0169(2)	0.3526(3)	0.0388(9)
O6W	2e	0.2058(8)	¼	0.5372(6)	0.085(2)
O7W	2e	0.7461(7)	¼	0.3506(5)	0.0737(19)

for all 1148 independent reflections. Inspection of the difference Fourier map revealed that maximum positive and negative peaks were 0.52 and −0.82 e⁻/Å³, respectively. Experimental details and R indices are given in Table 1. Fractional atom coordinates and anisotropic-displacement parameters are provided in Tables 2 and 3, respectively. Bond distances are reported in Table 4. The calculated X-ray powder pattern for bassoite computed with *XPOW* (Downs *et al.*, 1993) using the atomic coordinates and the occupancy factors reported in Table 2 is reported in Table 5. Structure factors are deposited with the Principal Editor of Mineralogical Magazine at http://www.minersoc. org/pages/e_journals/dep_mat.html.

Chemical composition

A preliminary chemical analysis using energy-dispersive spectrometry (EDS), on the crystal fragment used for the structural study, did not indicate the presence of elements (Z > 9) other than Sr, V, O and very minor Ca and Na (Fig. 2). The chemical composition was determined by wavelength-dispersive spectrometry (WDS) using a JEOL JXA-8200 electron microprobe on the same crystal fragment used for the structural study. Major and minor elements were determined at 15 kV accelerating voltage and 30 nA beam current, with 20 s as counting time and a 1 μm beam diameter. For the WDS analyses, Sr-$K\alpha$, Ca-$K\alpha$, Na-$K\alpha$ and V-$K\alpha$ lines were used. The crystal fragment was found to be homogeneous within analytical uncertainty (7 analyses on different spots). The H_2O content was calculated by stoichiometry from the results of the crystal-structure analysis; its presence was confirmed by Raman spectroscopy (see below). Analytical data are presented in Table 6.

On the basis of (Sr + Ca + Na) = 1, the formula of bassoite is $(Sr_{0.97}Ca_{0.02}Na_{0.01})V_{3.00}O_7 \cdot 4H_2O$. The simplified formula is $SrV_3O_7 \cdot 4H_2O$, which

TABLE 3. Anisotropic displacement parameters of the atoms in bassoite.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sr	0.0370(3)	0.0375(3)	0.0370(4)	0	0.0005(3)	0
V1	0.0311(5)	0.0314(6)	0.0303(6)	0	0.0010(4)	0
V2	0.0267(3)	0.0277(4)	0.0261(4)	0.0003(3)	0.0010(3)	0.0001(3)
O1	0.0289(13)	0.0294(15)	0.0286(16)	−0.0024(12)	−0.0018(11)	−0.0014(11)
O2	0.0298(13)	0.0299(15)	0.0289(16)	−0.0006(12)	−0.0009(11)	−0.0001(11)
O3	0.0266(13)	0.0271(13)	0.0229(15)	−0.0011(11)	0.0018(10)	0.0013(11)
O4	0.0282(18)	0.028(2)	0.024(2)	0	−0.0012(15)	0
O5W	0.0395(15)	0.0442(16)	0.0326(17)	0.0012(14)	0.0004(12)	−0.0013(13)
O6W	0.073(3)	0.068(3)	0.113(5)	0	0.002(3)	0
O7W	0.076(3)	0.078(3)	0.067(4)	0	0.002(3)	0

Table 4. Interatomic distances (Å) for bassoite.

Sr−O1	2.663(2)	O1−O1^{viii}	2.477(3)
Sr−O1^i	2.663(2)	O1−O1^i	2.823(3)
Sr−O2	2.649(2)	O1−O2^{ii}	2.513(3)
Sr−O2^i	2.649(2)	O1−O2	2.800(3)
Sr−O5	2.641(2)	O1−O3^{ii}	2.871(3)
Sr−O5^i	2.641(2)	O1−O3^{iii}	2.877(3)
Sr−O6	2.598(5)	O1−O4^{ix}	2.917(3)
Sr−O7^{ii}	2.911(4)		
Sr−O7	2.751(4)		
		O2−O2^{iii}	2.518(3)
		O2−O2^i	2.794(3)
V1−O1^v	2.004(2)	O2−O3	2.893(3)
V1−O1^{vi}	2.004(2)	O2−O3^{iii}	2.958(3)
V1−O2	1.974(2)	O2−O4^{vii}	2.894(4)
V1−O2^i	1.974(2)		
V1−O4^{vii}	1.575(3)		
V1−V2^{iii}	2.9997(7)		
V1−V2^{iv}	2.9997(7)	O3−O5	2.905(3)
		O3−O5^v	2.820(3)
		O3−O6^x	2.763(4)
V2−O1	1.924(2)		
V2−O1^{viii}	1.939(2)	O4−O5^x	2.998(3)
V2−O2	1.962(2)	O4−O5^{xi}	2.998(3)
V2−O2^{iii}	1.928(2)		
V2−O3^{iii}	1.601(2)		
V2−V2^{viii}	2.9643(8)	O5−O6	2.931(4)
V2−V2^{iii}	2.9648(8)	O6−O7^{ii}	2.892(6)

Symmetry codes are: (*i*) *x*,1/2−*y*,*z*; (*ii*) −1+*x*,*y*,*z*; (*iii*) 1−*x*,−*y*,−*z*; (*iv*) 1−*x*,1/2+*y*,−*z*; (*v*) 1+*x*,*y*,*z*; (*vi*) 1+*x*,1/2−*y*,*z*; (*vii*) *x*,*y*,−1+*z*; (*viii*) −*x*,−*y*,−*z*; (*ix*) −1+*x*,*y*,−1+*z*; (*x*) 1−*x*,−*y*,1−*z*; (*xi*) 1−*x*,1/2+*y*,1−*z*.

requires SrO 24.41, VO_2 58.61, H_2O 16.98, total 100.00 wt.%.

Raman investigation

Raman spectra were collected using a Renishaw RM2000 micro-Raman apparatus, coupled with a diode laser source emitting at 785 nm. The sample was irradiated using the $50 \times$ microscope objective on a Leica DMLM microscope. The beam power was ~3 mW and the laser spot size was adjusted to between 1 and 3 µm. The Raman data were collected by an air-cooled CCD detector. The acquisition time for each measurement was 20 s. All spectra were calibrated with respect to a silicon wafer at 520 cm^{-1}. Unpolarized spectra in the region 1250−2000 cm^{-1} and 3000−4000 cm^{-1} are shown in Fig. 3. The peak at 1645 cm^{-1} in Fig. 3*a* is ascribed to H_2O bending whereas the peaks at 3407 and 3534 cm^{-1} in Fig. 3*b* are produced by OH stretching.

Description of the structure and discussion

The crystal structure of bassoite (Fig. 4) consists of layers parallel to {001} consisting of edge-sharing $V^{4+}O_5$ square pyramids, with the Sr between the layers in nine-fold coordination.

The VO_5 pyramids are the basic structural units in bassoite. There are two distinct vanadium positions, V1 and V2. The $V2O_5$ pyramids, with apices pointing up and down alternately, form
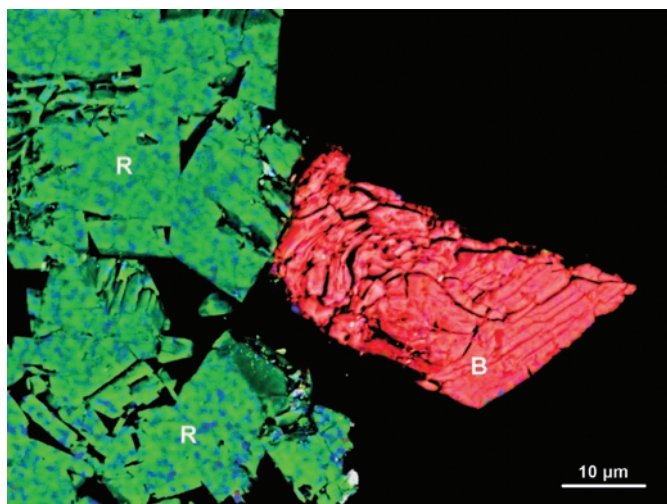

Fig. 2. Elemental X-ray maps of bassoite (B) with rhodonite (R). The red colour refers to vanadium whereas the blue and green colours refer to Mn and Si, respectively.

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

I_{calc}	d_{calc}	h	k	l	I_{calc}	d_{calc}	h	k	l
100.00	**8.5663**	**0**	**0**	**1**	1.52	2.0613	−2	3	1
14.08	**6.6363**	**0**	**1**	**1**	1.42	2.0534	−1	3	3
2.59	4.7395	1	1	0	2.20	2.0462	2	3	1
1.42	4.5552	−1	0	1	1.32	2.0310	1	3	3
1.76	4.4747	1	0	1	2.63	1.9828	0	2	4
2.87	4.4747	0	2	1	2.14	1.9521	1	5	0
2.05	4.1786	−1	1	1	2.35	1.9308	−2	1	3
3.34	4.1162	1	1	1	2.10	1.8941	2	1	3
13.89	**3.4399**	**−1**	**2**	**1**	**14.96**	**1.8666**	**2**	**4**	**0**
17.37	**3.4049**	**1**	**2**	**1**	1.10	1.8465	1	2	4
4.07	3.3182	0	2	2	3.25	1.8291	−2	4	1
5.08	3.2387	0	3	1	2.10	1.8235	−1	4	3
6.15	3.2062	−1	1	2	1.87	1.8185	2	4	1
5.44	3.1501	1	1	2	1.77	1.8078	1	4	3
1.27	2.9217	1	3	0	1.76	1.6912	0	5	3
3.45	2.8554	0	0	3	1.05	1.6523	−3	2	1
15.10	**2.8339**	**−1**	**2**	**2**	1.84	1.6406	3	2	1
11.48	**2.7949**	**1**	**2**	**2**	1.06	1.6031	−2	2	4
2.01	2.7745	−1	3	1	1.46	1.5750	2	2	4
2.00	2.7560	1	3	1	2.06	1.5722	−3	2	2
3.10	2.7553	0	1	3	3.92	1.5654	−1	2	5
14.81	**2.6560**	**2**	**0**	**0**	1.26	1.5522	−1	6	2
11.33	**2.6237**	**0**	**4**	**0**	3.94	1.5489	1	2	5
2.99	2.5362	−1	0	3	1.92	1.3280	4	0	0
2.57	2.4945	1	0	3	1.06	1.3119	0	8	0
1.65	2.4653	−1	1	3	1.23	1.2102	−3	2	5
1.47	2.4269	1	1	3	1.27	1.1876	3	2	5
1.95	2.4260	−1	3	2	1.03	1.1849	4	4	0
1.70	2.4014	1	3	2					
1.08	2.2736	−1	4	1					
1.26	2.2634	1	4	1					
1.14	2.2373	0	4	2					
3.56	2.2121	0	3	3					
1.82	2.1416	0	0	4					

The calculated X-ray powder pattern was computed on the basis of a = 5.313(3) Å, b = 10.495(3) Å, c = 8.568(4) Å, β = 91.14(5)º, and with the atomic coordinates reported in Table 2.

TABLE 6. Electron microprobe data for bassoite.

Constituent	Wt.%	Range	Stand. Dev.	Probe standard
SrO	23.66	23.40−23.81	0.15	Strontianite
CaO	0.27	0.20−0.31	0.04	Calcite
Na_2O	0.07	0.05−0.14	0.02	Albite
VO_2	58.56	58.01−58.71	0.19	Vanadium metal
H_2O*	16.99			
Total	99.55			

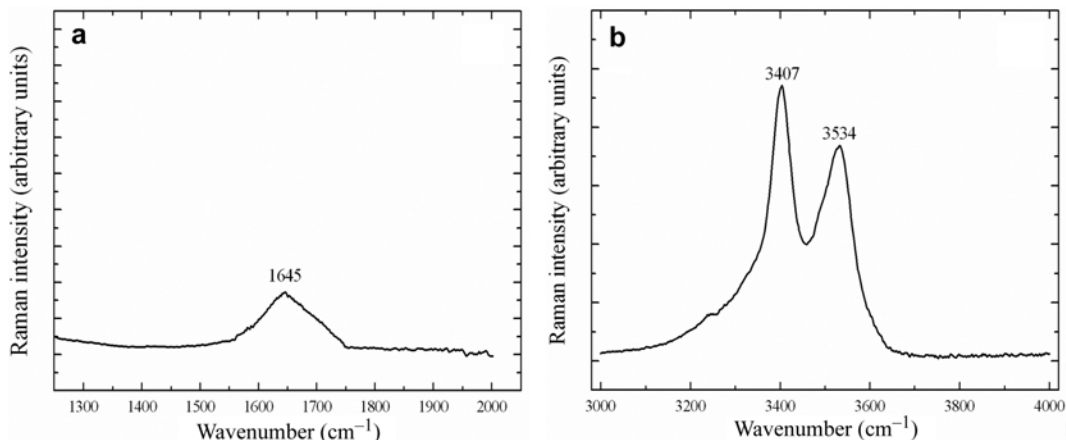* from crystal structure stoichiometry.

FIG. 3. Unpolarized micro-Raman spectra of bassoite in: (*a*) the $1250-2000$ cm^{-1} region and (*b*) the $3000-4000$ cm^{-1} region.

infinite edge-sharing ribbons parallel to [100], whereas the V1O$_5$ pyramids link these chains by edge-sharing parallel to [010] (Fig. 5). The mean bond distances for the VO$_5$ pyramids (1.906 and 1.871 Å for V1 and V2, respectively) is in excellent agreement with those observed in synthetic AV$_3$O$_7$ (A = Ca, Sr) V^{4+}-oxovanadates (Prinz *et al.*, 2007). The slight difference in the size of the two VO$_5$ pyramids is related to the fact that whereas V1 shares only two edges, V2 shares three edges of the base. As a consequence, the V2 pyramid has a smaller base area and a longer apical distance.

The Sr^{2+} cations are located between the layers and are coordinated by nine O atoms. There are seven shorter distances (from 2.598 Å to 2.663 Å)
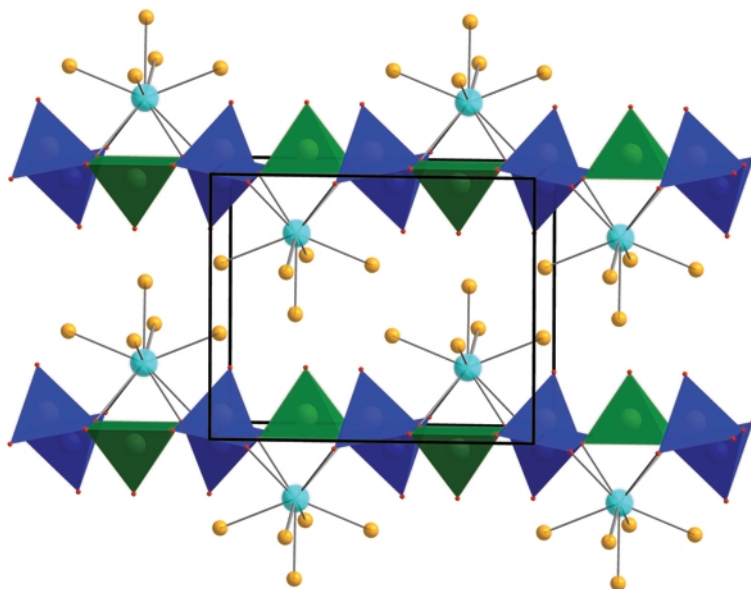

FIG. 4. A projection of the bassoite structure along [100] (slightly canted). The Sr atoms are shown as light blue spheres, O atoms of VO$_5$ pyramids as small red spheres and O atoms of water molecules as light orange spheres. The V1O$_5$ and V2O$_5$ pyramids are green and blue, respectively. The unit cell is outlined.
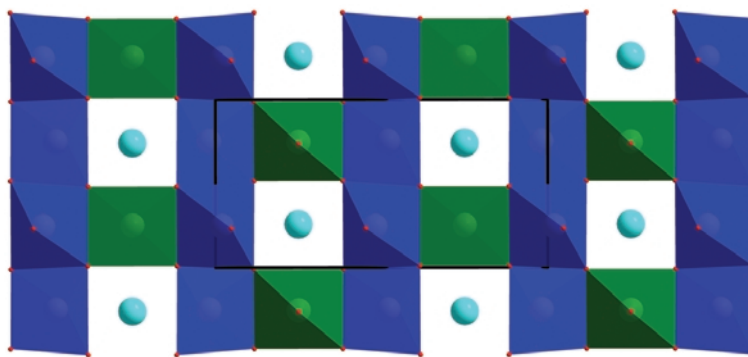
FIG. 5. A projection of a portion of the bassoite structure along [001] to show the topology of the V_3O_7 layer. The Sr atoms are shown as light blue spheres, O atoms of VO_5 pyramids as small red spheres. The $V1O_5$ and $V2O_5$ pyramids are green and blue, respectively. The unit cell is outlined.

and two longer ones (2.751 Å and 2.911 Å; Table 4). This Sr coordination is quite different from that observed in the orthorhombic crystal structure of anhydrous SrV_3O_7 (Prinz *et al.*, 2007), where the Sr−O distances can be grouped into three distance ranges: two rather long Sr−O1 distances of 2.975 Å, two short Sr−O2 distances of 2.483 Å and four equivalent intermediate Sr−O3 distances of 2.565 Å.

An interesting structural feature is observed if we consider the tilt angle (δ) between the basal planes of the $V1O_5$ and $V2O_5$ pyramids (Fig. 6). This parameter was first introduced by Bouloux and Galy (1973) in their study of V^{4+}-bearing oxovanadates. The tilt angle gives an useful estimation of the degree of buckling of the V_3O_7 layers. In comparing the room-temperature crystal structures of CaV_3O_7 and SrV_3O_7, Prinz *et al.* (2007) noticed a difference in the tilt angles [12.89(9)º and 9.3(2)º, respectively], and attributed it to the different sizes of the two alkaline-earth cations. Indeed, as already postulated by Bouloux and Galy (1973), the larger size of the Sr^{2+} cation leads to a less pronounced buckling of the V_3O_7 layers as compared with that in the Ca compound. The measured tilt angle δ of 10.0(3)º in bassoite is relatively small, which is in good agreement with the findings of the earlier workers.

Although hydrogen atoms were not located in the difference Fourier maps, bond-valence calculations (Table 7) clearly indicate that the oxygen atoms O5, O6 and O7 belong to water molecules. The presence of H_2O was also confirmed by Raman spectroscopy (see above). To study a possible hydrogen-bonding system for the

bassoite structure, the O...O distances suitable for hydrogen bonds were examined. There are only four independent O...O contacts which are not polyhedral edges. They are the following: $d[O5^v...O3] = 2.820(3)$ Å; $d[O5...O3] = 2.905(3)$ Å; $d[O5^{x,xii}...O4] = 2.998(3)$ Å and $d[O6^x...O3] = 2.763(4)$ Å. As O5, O6 and O7 belong to water molecules, it seems likely that O3 acts as an acceptor of hydrogen bonds from both
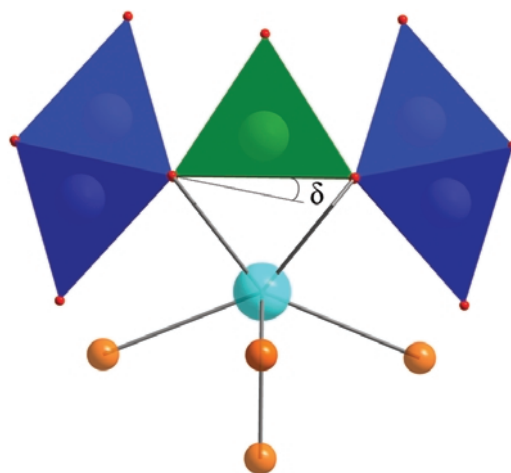

FIG. 6. A portion of the bassoite structure along [100] to show the tilt angle (δ) between the basal planes of the $V1O_5$ and $V2O_5$ pyramids of the V_3O_7 layer (see text). The Sr atoms are shown as light blue spheres, O atoms of VO_5 pyramids as small red spheres and O atoms of water molecules as light orange spheres. The $V1O_5$ and $V2O_5$ pyramids are green and blue, respectively.

TABLE 7. Bond-valence (v.u.) arrangement for bassoite.

	Sr	V1	V2	ΣO
O1	$0.229^{\times 2}{\downarrow}^{\times 1\rightarrow}$	$0.55^{\times 2}{\downarrow}^{\times 1\rightarrow}$	$0.658{\downarrow}^{\times 1\rightarrow}$ $0.685{\downarrow}^{\times 1\rightarrow}$	2.121
O2	$0.238^{\times 2}{\downarrow}^{\times 1\rightarrow}$	$0.59^{\times 2}{\downarrow}^{\times 1\rightarrow}$	$0.618{\downarrow}^{\times 1\rightarrow}$ $0.678{\downarrow}^{\times 1\rightarrow}$	2.132
O3			$1.640{\downarrow}^{\times 1\rightarrow}$	1.640
O4		$1.759{\downarrow}^{\times 1\rightarrow}$		1.759
O5	$0.243^{\times 2}{\downarrow}^{\times 1\rightarrow}$			0.243
O6	$0.273{\downarrow}^{\times 1\rightarrow}$			0.273
O7	$0.117{\downarrow}^{\times 1\rightarrow}$ $0.181{\downarrow}^{\times 1\rightarrow}$			0.298
	1.991	4.059	4.279	

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

O5 and O6 whereas O4 acts as an acceptor of hydrogen bonds from two O5 atoms. Thus, the following hydrogen-bonding model can be assumed: O5 → O3, O6 → O3, and O5 → O4. The situation is much more complicated for O7 where the O...O distance is longer and not to a polyhedral edge (i.e. d[O7...O3] = 3.213(3) Å). Considering the proposed hydrogen-bonding system and by adding the contributions of the H atoms to donor and acceptor oxygens, satisfactory oxygen bond-valence sums can be obtained. However, a more detailed analysis of the hydrogen-bonding system in bassoite must await the availability of either more suitable crystals or the application of different, non-conventional techniques.

Acknowledgements

References

Basso, R., Lucchetti, G., Zefiro, L. and Palenzona, A. (1994) Vanadomalayaite, CaVOSiO₄, a new mineral vanadium analog of titanite and malayaite. *Neues Jahrbuch für Mineralogie Monatshefte*, 489−498.

Basso, R., Lucchetti, G., Martinelli, A. and Palenzona, A. (2003) Cavoite, CaV₃O₇, a new mineral from the Gambatesa mine, northern Apennines, Italy. *European Journal of Mineralogy*, **15**, 181−184.

Basso, R., Cabella, R., Lucchetti, G., Martinelli, A. and Palenzona, A. (2005) Vanadiocarpholite, Mn²⁺V³⁺Al(Si₂O₆)(OH)₄, a new mineral from the Molinello mine, northern Apennines, Italy. *European Journal of Mineralogy*, **17**, 501−507.

Bouloux, J.-C. and Galy, J. (1973) Les hypovanadates *M*V₃O₇ (*M* = Ca, Sr, Cd). Structure cristalline de CaV₃O₇. *Acta Crystallographica*, **B29**, 269−275.

Brese, N.E. and O'Keeffe, M. (1991) Bond-valence parameters for solids. *Acta Crystallographica*, **B47**, 192−197.

Cabella, R., Lucchetti, G. and Marescotti P. (1998) Mn-ores from Eastern Ligurian ophiolitic sequences ("Diaspri di Monte Alpe" Formation, Northern Apennines, Italy). *Trends in Mineralogy*, **2**, 1−17.

Cortesogno, L., Lucchetti, G. and Penco, A.M. (1979) Le mineralizzazioni a manganese nei diaspri delle ofioliti liguri: mineralogia e genesi. *Rendiconti S.I.M.P. (Società Italiana di Mineralogia e Petrologia)*, **35**, 151−197.

Downs, R.T., Bartelmehs, K.L., Gibbs, G.V. and Boisen, M.B., Jr. (1993) Interactive software for calculating and displaying X-ray or neutron powder diffractometer patterns of crystalline materials. *American Mineralogist*, **78**, 1104−1107.

Ibers, J.A. and Hamilton, W.C. (editors) (1974) *International Tables for X-ray Crystallography*, volume 4. Kynock Press, Birmingham, UK, 366 pp.

Lucchetti, G., Cabella, R. and Cortesogno, L. (1990)

Pumpellyite and coexisting minerals in different low grade metamorphic facies of Liguria, Italy. *Journal of Metamorphic Geology*, **8**, 539−550.

Marchesini, M. and Pagano, R. (2001) The Val Graveglia manganese district, Liguria, Italy. *The Mineralogical Record*, **32**, 349−379.

Oxford Diffraction (2006) *CrysAlis RED (Version 1.171.31.2) and ABSPACK in CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, Oxfordshire, UK.

Prinz, S., Sparta, K.M. and Roth, G. (2007) Temperature dependence of the AV_3O_7 (A = Ca, Sr) structure. *Acta Crystallographica*, **B63**, 836−842.

Sheldrick, G.M. (2008) A short history of *SHELX. Acta Crystallographica*, **A64**, 112−122.