

Strontio Piemontite, a new member of the epidote group, from Val Graveglia, Liguria, Italy

PAOLA BONAZZI*, SILVIO MENCHETTI* and ANDREA PALENZONA**

* C.N.R. Dipartimento di Scienze della Terra dell'Università, Via La Pira 4, I-50121 Firenze, Italy

** Istituto di Chimica Fisica dell'Università, Corso Europa 26, I-16132 Genova, Italy

Abstract: Strontio piemontite, a new member of the epidote group with simplified formula $\text{CaSr}(\text{Al}, \text{Mn}, \text{Fe})_3\text{Si}_3\text{O}_{11}\text{O}(\text{OH})$, occurs as small deep red prismatic crystals in the manganese ore deposit of Val Graveglia, Liguria, Italy. Physical properties, including the powder pattern, are similar to those of piemontite. Crystals are often twinned {100}. Crystal structure refinements performed on two separate crystals clearly show that the entry of Sr into the structure mainly occurs on the A(2) site (max. 70%) and leads to a significant increase of the A(2) polyhedron volume as well as the $c \cdot \sin\beta$ value.

Key-words: Strontio piemontite, epidote group, structure refinement, chemical analysis.

Introduction

Piemontite from Val Graveglia, Italy, was first reported by Cortesogno *et al.* (1979) in a paper dealing with manganese minerals from Liguria. The "piemontite" from the same occurrence described in the present study, however, should be considered as a new member of the epidote group. In fact the structural site A(2) is mainly occupied by Sr, which is a different chemical component from the Ca occurring in piemontite. The new mineral and the name have been approved by the New Minerals and Mineral Names IMA commission. The type material is preserved in the Museo di Mineralogia dell'Università di Firenze.

Occurrence, appearance and physical properties

The manganese mineralization at Val Graveglia is associated to the "Mt. Alpe Cherts" formation, overlying the ophiolitic rocks of Northern Apennines. The complex tectonic and metamorphic history of the ligurian-piedmont ocean produced a complex mineral association which, according

to Cortesogno & Venturelli (1978), can be ascribed to low-temperature metamorphic conditions (prehnite-pumpellyite facies). In addition to braunite, a wide variety of uncommon mineral species are present (Cortesogno *et al.* 1979).

The strontio piemontite from Val Graveglia was collected in the mining area of Molinello and Cassagna. Two samples, SRPM and SRPC, were selected for the present study: the standard properties refer to SRPM. The mineral appears generally as small prismatic crystals, elongated parallel to [010] (up to 0.5 mm), in veinlets about 3–4 mm thick, which cut black manganese ore deposit made up mainly of quartz and braunite. The veinlets also contain calcite, rhodonite, rhodochrosite, and ganophyllite. Physical properties are very similar to those of piemontite (colour deep red, streak purple-brown, lustre vitreous and transparent). Strontio piemontite shows a perfect {001} cleavage and hardness 6. The density value measured by heavy liquids ranges from 3.65(1) to 3.73(1) g/cm^3 , whereas the calculated value is 3.73 g/cm^3 .

Strontio piemontite is biaxial (+) and strongly pleochroic with X yellow-orange, Y violet and Z reddish violet. As regards the optical orientation, $Y = b$, while, because of experimental difficulties, the Z:c angle and the refraction indices were not

measured. The value of the refraction index calculated from the Gladstone-Dale relationship, is 1.763, using the empirical formula given below as well as the measured density and the constants given by Mandarino (1976). This calculated refraction index matches the value of \bar{n} (1.763) derived from the data published by Cortesogno *et al.* (1979) for the piemontite from Val Graveglia. Using this \bar{n} value, the $1-(Kp/Kc)$ parameter is 0.045, so the compatibility (Mandarino, 1981) is good.

Chemical composition

Strontio Piemontite was analysed using an ARL-SEM-Q electron microprobe with an operating voltage of 15 kV: analyses were carried out on several crystals. Results are given in Table 1.

Table 1. Chemical analyses of strontio Piemontite from Val Graveglia.

Oxide	wt %	range	probe standard
CaO	11.69	10.47–13.21	clinopyroxene
SrO	13.45	12.20–14.62	synth. anorthite
MgO	< 0.10	—	ilmenite
Al ₂ O ₃	17.56	17.00–18.05	spessartine
Fe ₂ O ₃	4.89	4.29– 5.66	clinopyroxene
Mn ₂ O ₃	12.93	12.32–13.32	spessartine
TiO ₂	< 0.10	—	amphibole
SiO ₂	34.27	33.97–34.48	spessartine
MnO	2.87*		
H ₂ O	1.72**		
total	99.38		

* MnO/Mn₂O₃ ratio was assumed on the basis of charge balance and site occupancy refinement.

** H₂O wt % was calculated to give one H per formula unit.

Manganese has been partitioned between MnO and Mn₂O₃ on the basis of the site occupancy refinement as well as charge balance criteria for the octahedra and the A polyhedra. H₂O was calculated to give one H per formula unit. With these assumptions the empirical formula (based on O = 13) can be written: (Ca_{0.79}Mn_{0.21}) (Sr_{0.68}Ca_{0.31}) (Al_{1.81}Mn_{0.86}Fe_{0.32})-Si₃O₁₁O(OH).

The ideal formula for the Sr end-member is: CaSr (Al, Mn³⁺, Fe³⁺)₃Si₃O₁₁O(OH).

Crystallography

The indexed powder pattern is given in Table 2. It was obtained with a Guinier camera using CuK α radiation and Si as internal standard. Indexing was performed on the basis of the single crystal data and comparing the observed intensities with those calculated from the refined structure. The pattern is very similar to that of piemontite. The unit cell parameters, determined from powder data by means of a least-squares method, are: $a = 8.862(2)$, $b = 5.682(1)$, $c = 10.191(4)$ Å, $\beta = 114.70(1)^\circ$.

Intensity data were collected on two crystals, coming from SRPM and SRPC respectively. Both crystals are tiny (SRPC: $0.03 \times 0.06 \times 0.10$ mm³; SRPM: $0.06 \times 0.06 \times 0.10$ mm³) and the latter was found to be twinned with (010) as twin plane. Fig. 1 reports the reflection population due to the whole twinned crystal, drawn in the a^*c^* reciprocal lattice plane. The intensity data can be sorted into two categories; the first contains the well-sep-

Table 2. X-Ray powder pattern of strontio Piemontite from Val Graveglia; d-spacings in Å units.

l/h_0	$d_{\text{meas.}}$	$d_{\text{calc.}}$	h	k	l
20	5.031	5.0211	-1	0	2
10	4.019	4.0255	2	0	0
10	3.971	3.9677	-2	0	2
50	3.493	3.4938	-2	1	1
100	2.916	2.9142	-1	1	3
50	2.836	2.8411	0	2	0
10	2.713	2.7120	0	1	3
40	2.678	2.6792	1	2	0
50	2.601	2.6007	-3	1	1
10	2.553	2.5547	2	0	2
5	2.470	2.4727	-1	2	2
25	2.421	2.4214	0	2	2
20	2.399	2.3980	-3	1	3
10	2.308	2.3099	-2	2	2
30	2.165	2.1634	-4	0	1
20	2.132	2.1335	2	2	1
40	2.117	2.1161	-2	2	3
10	2.092	2.0903	0	2	3
10	1.899	1.8997	2	2	2
30	1.881	1.8813	-2	2	4
10	1.702	1.7020	-4	1	5
15	1.654	1.6540	-1	3	3
30	1.626	1.6265	-4	2	4
50	1.590	1.5898	-3	3	1
10	1.554	1.5539	4	1	2
30	1.421	1.4205	0	4	0

Unit cell parameters: $a = 8.862(2)$ $b = 5.682(1)$
 $c = 10.191(4)$ $\beta = 114.70(1)$

arated reflections ($l = 2, 5, 9, 13$) and the second groups more or less overlapping reflections. From the intensities of non-superimposed reflections,

the relative volumes of the two members of the twin were computed; the resulting A/B ratio is about 1.9. Many uncertainties, however, occur in determining the intensities of the partially overlapped reflections. Intensity data were corrected for absorption by means of the semiempirical

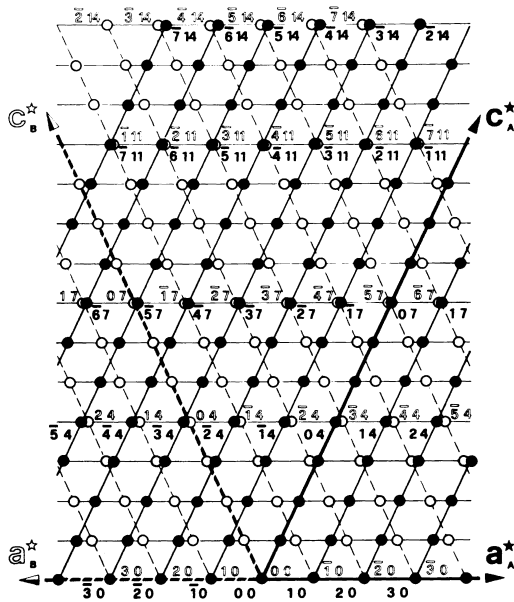


Fig. 1. An a^*c^* layer of the reciprocal lattice of a twinned strontio piemontite crystal. The open circled lattice belongs to the A member and the black-dotted lattice to the B member of the twin.

Table 3. Crystal data and experimental details.

	SRPM	SRPC
Crystal system		Monoclinic
space group		$P2_1/m$
Cell parameters	$a = 8.849(2)$ $b = 5.671(2)$ $c = 10.203(2)$ $\beta = 114.63(2)$ $V = 465.4(2)$	$a = 8.870(2)$ $b = 5.681(1)$ $c = 10.209(2)$ $\beta = 114.88(2)$ $V = 466.7(2)$
Apparatus	Enraf Nonius CAD4	Enraf Nonius CAD4
Wavelength	MoK α (0.71069 Å)	MoK α (0.71069 Å)
theta-range (°)	2–30	2–28
Scan mode	ω	ω
Scan width (°)	2.0	2.0
Scan speed (°/s)	0.039	0.046
No. of independent reflections	1246	1069
No. of reflections with $F_o > n\sigma(F_o)$	724	658
R (%)	$n = 8$ 5.0	$n = 8$ 3.5

Table 4. Atomic positional parameters and equivalent isotropic temperature factors (Å^2) with their standard deviations.

SRPM				SRPC					
	x	y	z	$U_{eq.}$	x	y	z	$U_{eq.}$	
A(1)	0.7604(4)	0.7500(0)	0.1559(4)	0.0118(10)	A(1)	0.7606(4)	0.7500(0)	0.1559(3)	0.0142(11)
A(2)	0.5949(2)	0.7500(0)	0.4238(2)	0.0116(7)	A(2)	0.5954(2)	0.7500(0)	0.4233(2)	0.0152(8)
Si(1)	0.3407(5)	0.7500(0)	0.0403(5)	0.0075(13)	Si(1)	0.3403(5)	0.7500(0)	0.0420(4)	0.0083(12)
Si(2)	0.6852(5)	0.2500(0)	0.2771(4)	0.0069(13)	Si(2)	0.6849(5)	0.2500(0)	0.2783(4)	0.0097(13)
Si(3)	0.1808(5)	0.7500(0)	0.3154(5)	0.0059(14)	Si(2)	0.1811(5)	0.7500(0)	0.3156(4)	0.0099(14)
M(1)	0.0000(0)	0.0000(0)	0.0000(0)	0.0085(14)	M(1)	0.0000(0)	0.0000(0)	0.0000(0)	0.0104(13)
M(2)	0.0000(0)	0.0000(0)	0.5000(0)	0.0069(13)	M(2)	0.0000(0)	0.0000(0)	0.5000(0)	0.0100(13)
M(3)	0.2945(3)	0.2500(0)	0.2189(3)	0.0065(8)	M(3)	0.2940(3)	0.2500(0)	0.2198(2)	0.0097(8)
O(1)	0.2335(8)	0.9905(13)	0.0344(7)	0.0112(15)	O(1)	0.2340(8)	0.9901(14)	0.0354(7)	0.0148(25)
O(2)	0.3003(9)	0.9763(14)	0.3494(8)	0.0116(16)	O(2)	0.3013(7)	0.9782(13)	0.3511(6)	0.0097(24)
O(3)	0.7957(9)	0.0151(14)	0.3401(8)	0.0107(15)	O(3)	0.7954(8)	0.0155(13)	0.3421(7)	0.0119(21)
O(4)	0.0569(13)	0.2500(0)	0.1307(12)	0.0102(22)	O(4)	0.0580(11)	0.2500(0)	0.1312(10)	0.0070(35)
O(5)	0.0386(12)	0.7500(0)	0.1452(11)	0.0078(21)	O(5)	0.0407(11)	0.7500(0)	0.1460(11)	0.0109(37)
O(6)	0.0673(12)	0.7500(0)	0.4077(12)	0.0097(20)	O(6)	0.0650(11)	0.7500(0)	0.4032(11)	0.0126(38)
O(7)	0.5166(13)	0.7500(0)	0.1712(12)	0.0136(22)	O(7)	0.5145(13)	0.7500(0)	0.1743(11)	0.0195(40)
O(8)	0.5247(13)	0.2500(0)	0.3130(13)	0.0134(23)	O(8)	0.5234(12)	0.2500(0)	0.3118(11)	0.0151(38)
O(9)	0.6280(17)	0.2500(0)	0.1024(16)	0.0229(32)	O(9)	0.6292(13)	0.2500(0)	0.1024(12)	0.0190(43)
O(10)	0.0829(13)	0.2500(0)	0.4314(12)	0.0116(24)	O(10)	0.0823(11)	0.2500(0)	0.4309(11)	0.0111(37)
					H	0.0350(15)	0.2500(0)	0.3350(15)	0.0540(45)

method of North *et al.* (1968). Structure refinement performed using the SHELX program (Sheldrick, 1976) led to a final *R* values of 3.5% (SRPC) and 5.0% (SRPM) for all the observed reflections. Other details of the experimental work are given in Table 3. Atom parameters are given in Table 4, while Table 5 shows the interatomic distances.

Crystal chemical formulae obtained from structure refinements of SRPC and SRPM are:

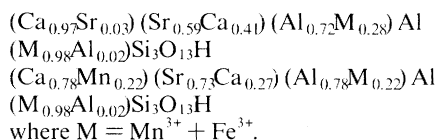


Table 5. Selected interatomic distances (Å) and volumes of coordination polyhedra (Å³).

		SRPM	SRPC			SRPM	SRPC	
A(2)	—0(7)	2.374(12)	2.333(11)	A(1)	—0(7)	2.227(13)	2.268(13)	
	—0(10, vi)	2.608(10)	2.609 (9)		—0(3, i)	2.324 (9)	2.343 (8)	
	—0(2, vii)	2.614 (8)	2.599 (7)		—0(3, ii)	2.324 (9)	2.343 (8)	
	—0(2, viii)	2.614 (8)	2.599 (7)		—0(1, iii)	2.455 (8)	2.465 (8)	
	—0(2)	2.715 (8)	2.722 (7)		—0(1, iv)	2.455 (8)	2.465 (8)	
	—0(2, ix)	2.715 (8)	2.722 (7)		—0(5, v)	2.509(12)	2.529(12)	
	—0(3, i)	2.722 (9)	2.710 (8)		—0(6, v)	2.857 (9)	2.816 (8)	
	—0(3, ii)	2.722 (4)	2.710 (3)		—0(9, i)	3.029 (5)	3.031 (4)	
	—0(8, i)	3.019 (4)	3.027 (3)		—0(9)	3.029 (5)	3.031 (4)	
	—0(8)	3.019 (4)	3.027 (3)					
	mean volume	2.712 35.3	2.706 35.0		mean volume	2.578 27.1	2.588 27.4	
M(2)	—0(10)	1.862 (9)	1.866 (9)	M(1)	—0(4)	1.866 (7)	1.870 (6)	
	—0(10, xiv)	1.862 (9)	1.866 (6)		—0(4, xi)	1.866 (7)	1.870 (6)	
	—0(3, xv)	1.865 (6)	1.854 (6)		—0(1, xii)	1.947 (7)	1.952 (7)	
	—0(3, xvi)	1.865 (6)	1.854 (6)		—0(1, xiii)	1.947 (7)	1.952 (7)	
	—0(6, xii)	1.928 (9)	1.951 (9)		—0(5, xii)	1.975 (8)	1.979 (8)	
	—0(6, xiv)	1.928 (9)	1.951 (9)		—0(5, xi)	1.975 (8)	1.979 (8)	
mean volume	1.885 8.8	1.890 8.9	mean volume	1.929 9.5	1.934 9.6			
Si(1)	—0(7)	1.573(10)	1.567(9)	M(3)	—0(8)	1.855(10)	1.848(10)	
	—0(9, x)	1.591(15)	1.607(14)		—0(4)	1.911(11)	1.899 (9)	
	—0(1)	1.648 (8)	1.643 (8)		—0(2, xii)	2.031 (8)	2.028 (7)	
	—0(1, ix)	1.648 (8)	1.643 (8)		—0(2, ix)	2.031 (8)	2.028 (7)	
mean volume	1.615 2.2	1.615 2.2	mean volume	2.061 11.2	2.058 11.2			
Si(3)	—0(2)	1.606 (8)	1.620 (7)	Si(2)	—0(8)	1.608(15)	1.607(13)	
	—0(2, ix)	1.606 (8)	1.620 (7)		—0(3)	1.618 (8)	1.619 (7)	
	—0(6)	1.638(15)	1.623(14)		—0(3, ii)	1.618 (8)	1.619 (7)	
	—0(5)	1.667(10)	1.654 (9)		—0(9)	1.637(15)	1.650(13)	
mean volume	1.629 2.2	1.629 2.2	mean volume	1.620 2.2	1.624 2.2			

symmetry key: none x,y,z; i) x, 1+y,z; ii) x, 1/2−y,z; iii) 1−x, −1/2+y, −z; iv) 1−x, 2−y, −z; v) 1+x,y,z; vi) 1−x, 1/2+y, 1−z; vii) 1−x, −1/2+y, 1−z; viii) 1−x, 2−y, 1−z; ix) x, 3/2−y,z; x) 1−x, 1/2+y, −z; xi) −x, −1/2+y, −z; xii) x, −1+y,z; xiii) −x, 1−y, −z; xiv) −x, −1/2+y, 1−z; xv) −1+x,y,z; xvi) 1−x, −y, 1−z.

The structural arrangement is quite similar to that of monoclinic epidotes and the mean octahedral M—O distances well agree with the proposed cation distribution in M(1), M(2) and M(3). However the high content of Sr leads to some interesting comparisons with samples having little or no Sr (Dollase, 1969; Catti *et al.*, 1989; Bonazzi & Menchetti, 1989). The substitution $\text{Sr} \rightleftharpoons \text{Ca}$ which takes place in the 10-coordinated A(2) site, causes an increase in the A(2)—O mean distance and the polyhedral volume. This lengthening is not isotropic, affecting mainly the shorter distances, in particular A(2)—O(7). The A(1) site is not affected by significant $\text{Sr} \rightleftharpoons \text{Ca}$ substitution. However, little geometrical variation is induced by the entry of Sr into the adjacent A(2) site. In fact, with increasing Sr, O(7) goes away from A(2) and, to save the charge balance, approaches A(1). Therefore, the A(1)—O(7) distance decreases with increasing Sr and, since O(7) moves along the c

$\sin\beta$ direction, its z/c coordinate is well correlated to the Sr content in A(2), as shown in Fig. 2. The shortening of the A(1)—O(7) distance is greater in the crystal from SRPM because of the entry of Mn^{2+} into the A(1) site. It is clear that the unit cell volume expands with the entry of Sr, mainly because of an increase of the $c \cdot \sin\beta$ value.

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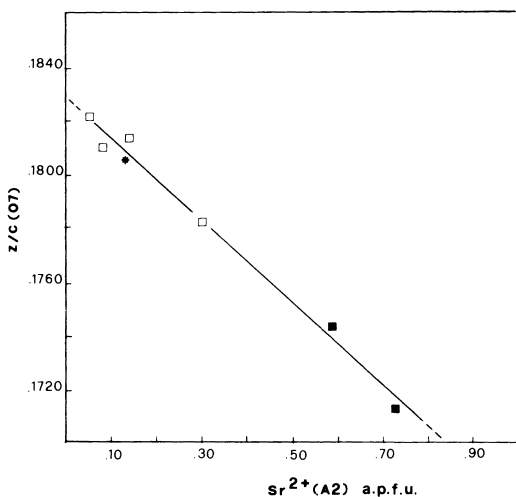


Fig. 2. Linear relation between the z/c coordinate of O(7) and the Sr content in A(2). The best straight line fitting is $y = 0.1828 - 0.01532x$, with $r = -0.993$. (filled squares = this work; star = Dollase, 1969; empty squares = Catti *et al.*, 1989).

