

# Ba-rich celestine: new data and crystal structure refinement

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## Abstract

A Ba-rich celestine ( $\text{Sr}_{0.87}\text{Ba}_{0.13}\text{SO}_4$ ) filling cavities of volcanoclastic rocks from Montecchio Maggiore (Vicenza, Italy) was studied. The role of the Ba content in the mineral was determined using X-ray powder data, single crystal X-ray refinement, thermal and chemical analyses. The unit cell parameters (obtained by single crystal diffraction) are  $a = 8.408$ ,  $b = 5.372$ ,  $c = 6.897$  Å, and the refinement in the space group  $Pnma$  ( $Z = 4$ ) gives the final  $R$  value of 0.039. The average (Sr,Ba)–oxygen bond length is 2.842 Å and agrees with an occupancy of Sr 87% and Ba 13%. Individual bond lengths (Sr,Ba)–O and bond strength calculations confirm that all twelve interactions are significant and define an irregular array around the cation.

KEYWORDS: celestine, barium, crystal structure refinement, Vicenza, Italy.

## Introduction

THE strontium–barium sulphate system (celestine–baryte) has been extensively studied. It is known that a solid-solution series is formed over the entire compositional range (Bostrom *et al.*, 1968; Browner, 1973) and that the unit cell edges vary non-linearly with composition (Bostrom *et al.* 1968; Burkhard, 1973; Goldish, 1989). Furthermore, a statistical study on naturally-occurring samples shows that the composition of the great majority of mixed celestine–baryte crystals is close to that of the end members, and ranges between  $\text{Ba}_{1.0}\text{—Sr}_{0.1}\text{Ba}_{0.9}$  and between  $\text{Sr}_{1.0}\text{—Sr}_{0.9}\text{Ba}_{0.1}$  (Hanor, 1968; Bouhler, 1985).

The end-member celestine structure type was first determined by James and Wood (1925) and later refined by Garske and Peacor (1965), Hawthorne and Ferguson (1975) and Miyake *et al.* (1978), but the role of Ba in naturally occurring samples has not been thoroughly investigated. Here we present the mineralogical and structural details of a natural Ba-rich celestine (Ba = 0.13 atoms per formula unit).

## Occurrence, properties and composition

The occurrence of celestine in basalts and in volcanoclastic sedimentary rocks outcropping near Montecchio Maggiore, Vicenza, north-eastern Italy, has already been reported (Billows, 1920; Boscardin and Sovilla, 1988). The mineral fills rock cavities and

occurs as euhedral to subhedral crystals, as crystal fragments and as granular aggregates. It is white or light blue in colour and closely associated with analcite, natrolite, celadonite and apophyllite. Recently, a number of samples of celestine have been found in a slope-cutting carried out in basaltic lava, near the town. It occurs rarely as single crystals (Fig. 1a), almost always as aggregates of subparallel lamellae from colourless to snow-white, which decussate in an irregular manner to fill the rock cavities (Fig. 1b).

The crystal density, measured at room temperature by the Berman method (1939) is  $4.046(3)$  g/cm<sup>3</sup> and agrees with a composition of  $\text{Sr}_{0.87}\text{Ba}_{0.13}\text{SO}_4$ .

Backscattered electron imaging on several crystal fragments (using a Philips SEM XL-40 equipped with energy dispersive electron microprobe EDS-EDAX 9900) did not reveal Sr or Ba zoning. The quantitative chemical data gathered by a wavelength dispersive ARL-SEMQ electron microprobe (operating voltage of 15 kV, 15 nA sample current, 5 µm electron beam diameter;  $\Phi(\rho Z)$  correction procedures; after Pouchou and Pichoir, 1985), on the same crystal used for the structure refinement, are reported in Table 1.

Thermogravimetric analysis (SEIKO 5200 apparatus; start temperature: 20°C; limit temperature: 1300°C; program rate: 10°C/min; Ar gas, flow rate: 30 ml/min) revealed only one weight loss, linked to a broad derivative maximum at 1200°C which is produced by  $\text{SO}_3$  loss.

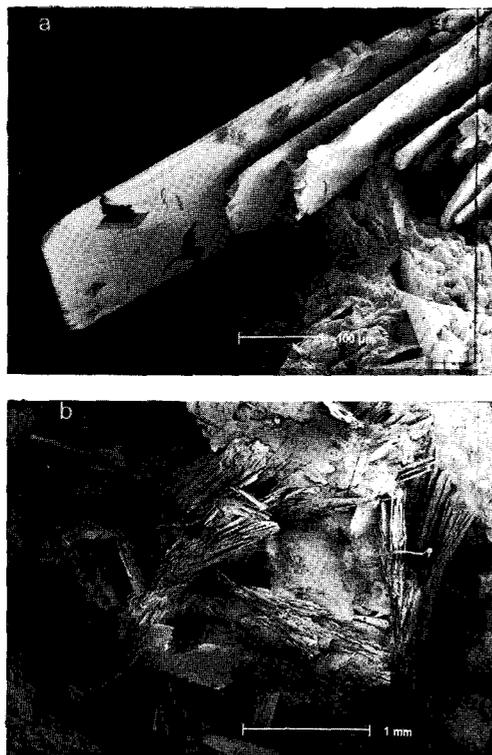


FIG. 1. Scanning electron micrographs showing: a) Barite celestine crystals and b) the crystal nets. The photographs were taken using a Philips SEM XL-40 scanning electron microscope.

### X-ray crystallography

*X-ray powder diffraction.* X-ray powder diffraction data sets were collected using an automated Philips diffractometer, Cu-K $\alpha$  Ni-filtered radiation with PbNO<sub>3</sub> as an internal standard.

The unit cell parameters based on orthorhombic indexing (space group *Pnma*) are:  $a = 8.414(3)$ ,  $b = 5.369(2)$ ,  $c = 6.909(3)$  Å, and were derived from  $d$ -spacing by a least squares refinement program (Alberti, 1976). Goldish (1989) emphasized that synthetic solid solution unit cell parameters show deviations from Vegard's Law, concerning mostly the  $c$  parameter, and he therefore suggests that the SrSO<sub>4</sub> molar fraction can be derived from the equation  $d_{(211)} = 3.1023 - 0.1317 \times S$ , (where  $S$  is the SrSO<sub>4</sub> mole fraction). Our data agree with the composition Sr<sub>0.88</sub>Ba<sub>0.12</sub>SO<sub>4</sub>, which in turn agrees very well with the one determined by chemical analysis.

TABLE I. Representative electron microprobe analysis and chemical formula of Ba-rich celestine from Montecchio Maggiore (Vicenza, Italy)

Chemical data (oxide wt.%)		Atoms per formula unit	
SrO	47.41	Sr	0.87
BaO	10.49	Ba	0.13
SO <sub>3</sub>	42.11	S	1.00
Sum	100.01		

*Collection of X-ray single-crystal data and structure refinement.* For intensity data collection a plate crystal measuring 0.17 [100]  $\times$  0.04 [010]  $\times$  0.11 [001] mm was mounted on a Siemens P4 rotating anode automated four-circle diffractometer (Mo-K $\alpha$  graphite monochromatized radiation operating at 45 kV, 140 mA), equipped with XSCANS software (Siemens, 1993). Cell dimensions were refined using the  $2\theta$  values for 30 centred reflections with  $25 \leq 2\theta \leq 45$ . Intensities for reflections  $\pm h+k+l$  were collected to a maximum value of 70° using the  $\omega$  scan mode, with a scan width of 1.6° and corrected for background, Lorentz, polarization and absorption effects. Intensity data of symmetrically equivalent reflections were averaged. Three standard reflections measured every 1 h showed less than 1.0% variation in intensity.

Structure refinement was carried out using 596 unique reflections ( $I \geq 3\sigma(I)$ ,  $R_{int} = 0.025$ ) with the SHELX76 and SHELX-S86 programs (Sheldrick, 1976, 1986), starting from the atomic parameters given by Pasero and Davoli (1987) for isostructural hashemite in the centrosymmetric space group *Pnma*. The final agreement factors were  $R = 0.039$  and  $wR = 0.037$ . The structure refinement in the non-centrosymmetric space group *Pn2<sub>1</sub>a* produced neither an improvement in the  $R$  agreement value nor a significant departure of the atoms from the position on the mirror plane. The e.s.d.'s on bond distances and angles were computed using the program ORFFE (Busing *et al.*, 1962). The atomic scattering factors for neutral atoms were taken from the *International Tables for X-ray Crystallography* (Ibers and Hamilton, 1974). Fractional atomic coordinates, isotropic and anisotropic thermal factors are reported in Table 2, selected bond distances and angles are reported in Table 3. The observed and calculated structure factor list is available on request.

Thermal factors are generally lower than those previously reported for the two end-members SrSO<sub>4</sub> and BaSO<sub>4</sub>. This feature could be ascribed to experimental conditions. Furthermore, they confirm

TABLE 2. Single-crystal data; lattice constants, atom coordinates and displacement factors ( $\text{\AA}^2$ ) of Ba-rich celestine from Montecchio Maggiore (Vicenza, Italy)

Cell parameters ( $\text{\AA}$ )						
<i>a</i>	8.408(2)					
<i>b</i>	5.372(1)					
<i>c</i>	6.897(2)					
Atomic coordinates and isotropic thermal factors.						
Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$B_{\text{eq}}$		
M	0.1836(1)	0.25	0.1585(1)	0.66(1)		
S	0.4377(2)	0.75	0.1851(2)	0.32(3)		
O1	0.5939(5)	0.75	0.0945(8)	1.5(1)		
O2	0.3083(5)	0.75	0.0437(7)	1.1(1)		
O3	0.4220(3)	0.9760(5)	0.3106(5)	0.80(9)		
Anisotropic thermal factors.						
Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
M	0.39(1)	0.87(2)	0.72(1)	0	-0.03(2)	0
S	0.23(4)	0.24(4)	0.47(4)	0	-0.05(3)	0
O1	0.9(1)	1.9(2)	1.6(2)	0	0.5(1)	0
O2	0.8(1)	1.6(2)	0.9(1)	0	-0.4(1)	0
O3	1.0(1)	0.43(8)	0.9(1)	0.2(1)	-0.16(9)	-0.29(9)

The form of the anisotropic thermal parameter is:

$$\exp[-1/4(\beta_{11}h^2a^{*2} + \beta_{22}k^2b^{*2} + \beta_{33}l^2c^{*2} + 2\beta_{12}hka^*b^* + 2\beta_{13}hla^*c^* + 2\beta_{23}klb^*c^*)].$$

the trend previously reported for celestine and baryte: isotropic thermal factors of oxygen atoms lying on the mirror plane (O1 and O2) are significantly higher than that of O3 in general position (Hill, 1977).

The structure of Ba-rich celestine consists of isolated ( $\text{SO}_4$ ) tetrahedra linked by Sr (or Ba) twelve-coordinated atoms. This implies that every O atom is fourfold coordinated and linked to three Sr (or Ba) atoms and to one S atom.

The tetrahedral mean bond length (1.477  $\text{\AA}$ ) is close to the mean bond distances reported both for celestine (1.473  $\text{\AA}$ , Hawthorne and Ferguson, 1975; 1.474  $\text{\AA}$ , Miyake *et al.*, 1978) and baryte (1.476  $\text{\AA}$ , Hill, 1977; 1.478  $\text{\AA}$ , Miyake *et al.*, 1978) and to the mean sulphur-oxygen distance of 1.473  $\text{\AA}$  after Baur (1970) for sulphate structures. Furthermore, Ba-rich celestine shows a small increase in tetrahedral distortions (TAV = 2.58, BLD<sub>T</sub> = 1.34%) with respect to those observed both for celestine and for baryte. According to Hawthorne and Ferguson (1975), this indicates that tetrahedral distortions are a function of the geometry of the structure rather than the chemistry of the twelve-coordinated site.

The metal-oxygen mean bond length decreases according to the ionic radius of the twelve

coordinated cation M, from baryte ( $\langle\text{M}-\text{O}\rangle = 2.952 \text{\AA}$ , Hill, 1977;  $\langle\text{M}-\text{O}\rangle = 2.952 \text{\AA}$ , Miyake *et al.*, 1978) to celestine ( $\langle\text{M}-\text{O}\rangle = 2.827 \text{\AA}$ , Hawthorne and Ferguson, 1975;  $\langle\text{M}-\text{O}\rangle = 2.831 \text{\AA}$ , Miyake *et al.*, 1978). In Ba-rich celestine the  $\langle\text{M}-\text{O}\rangle$  bond length agrees with a site occupancy of Sr 87% and Ba 13% (ionic radii by Shannon, 1976). The site occupancy was also confirmed by the evaluation of the ionic radii and cell volume, as suggested by Hawthorne and Ferguson (1975) ( $V^{1/3} = 6.783 \text{\AA}$ ,  $r_M = 1.462 \text{\AA}$ ).

The bond strengths for Ba-rich celestine, calculated using the curves and parameters given by Brown and Shannon (1973) and Brown and Wu (1976), compared with those of the end-member celestine (Hawthorne and Ferguson, 1975), confirm that all twelve M-O interactions are significant: the two longest M-O interactions also have to be taken into account, as indicated by the bond strength sums around O1 and M (Table 4).

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TABLE 3. Selected bond-lengths and angles from structure refinement of Ba-rich celestine from Montecchio Maggiore (Vicenza, Italy)

SO <sub>4</sub> <sup>2-</sup> group		Metal ion–oxygen polyhedra M = Sr, Ba	
S - O(1) (Å)	1.454(5)	M - O(1) (Å)	2.558(5)
S - O(2) (Å)	1.461(5)	M - O(1) (× 2) (Å)	3.269(3)
S - O(3) (× 2) (Å)	1.497(3)	M - O(2) (Å)	2.658(5)
<S - O> (Å)	1.477	M - O(2) (× 2) (Å)	2.990(2)
O(1) - O(2) (Å)	2.427(6)	M - O(3) (× 2) (Å)	2.655(3)
O(1) - O(3) (× 2) (Å)	2.405(5)	M - O(3) (× 2) (Å)	2.699(3)
O(2) - O(3) (× 2) (Å)	2.403(5)	M - O(3) (× 2) (Å)	2.832(3)
O(3)' - O(3)'' (Å)	2.428(6)	<M - O> (Å)	2.842
<O - O> (Å)	2.412		
		Selected distortion parameters.	
O(1) - S - O(2) (°)	112.7(3)	BLD <sub>T</sub> <sup>†</sup> (%)	1.34
O(1) - S - O(3) (× 2) (°)	109.2(2)	ELD <sub>T</sub> <sup>††</sup> (%)	0.44
O(2) - S - O(3) (× 2) (°)	108.7(2)	TAV <sup>‡</sup> (°)	2.58
O(3)' - S - O(3)'' (°)	108.4(3)	BLD <sub>1121</sub> <sup>†</sup> (%)	6.74
<O - S - O> (°)	109.5		

$$\dagger \text{ BLD (bond length distortions)} = \frac{100}{n} \sum_{i=1}^n \frac{|(X-O)_i - (X-O)_m|}{(X-O)_m} \%$$

$$\dagger\dagger \text{ ELD (edge length distortions)} = \frac{100}{n} \sum_{i=1}^n \frac{|(O-O)_i - (O-O)_m|}{(O-O)_m} \%$$

(Renner and Lehmann, 1986; Kunz *et al.*, 1991).

$$\dagger\dagger \text{ TAV (tetrahedral angle variance)} = \sum_{i=1}^6 (\theta_i - 109.47)^2 / 5 \text{ (Robinson } et al., 1971).$$

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TABLE 4. Bond strengths<sup>(1)</sup> for Ba-rich celestine compared with those reported for celestine by Hawthorne and Ferguson (1975)

	This study			Hawthorne and Ferguson (1975)		
	S	M	Σ*	S	M	Σ*
O1	1.599	0.309 0.056(× 2)	2.020 (1.908)*	1.512	0.325 0.054(× 2)	1.945 (1.837)*
O2	1.566	0.236 0.104(× 2)	2.010	1.589	0.244 0.098(× 2)	2.029
O3	1.411(× 2)	0.238(× 2) 0.212(× 2) 0.152(× 2)	2.013	1.469(× 2)	0.206(× 2) 0.226(× 2) 0.148(× 2)	2.049
Σ*	5.987	2.069 (1.957)*		6.039	2.033 (1.925)*	

<sup>(1)</sup> Calculated from the curves and parameters of Brown and Shannon (1973) and Brown and Wu (1976), considering the linear relation between metal–oxygen bond lengths and SrSO<sub>4</sub> molar fraction.

\* Values in parentheses are for a M coordination of [10].

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