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Crystal structure of baryte from Mine du Pradet (France)

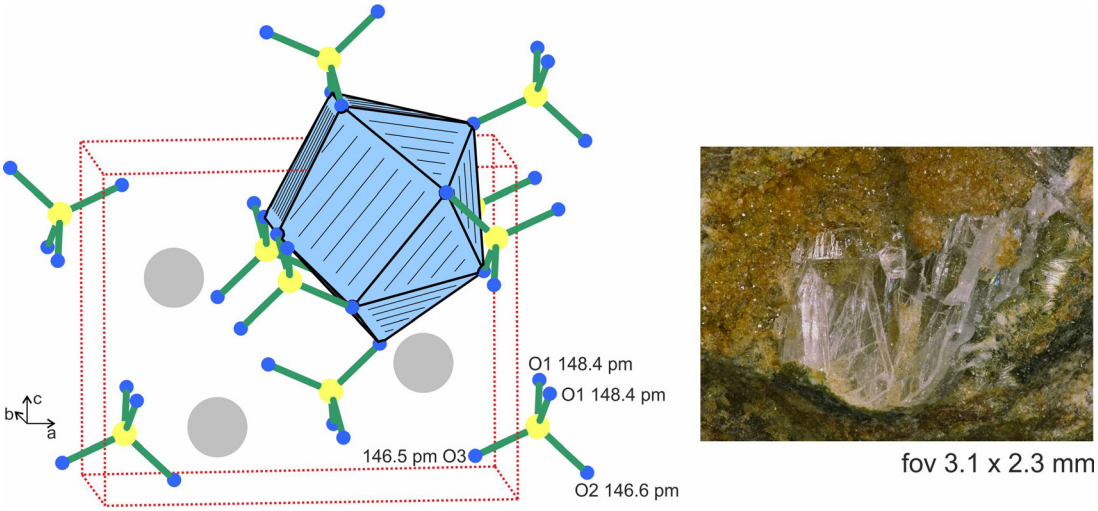

Figure 1: The crystal structure of $BaSO_4$ is shown in the left-hand part of the figure, emphasizing the sulfate groups and the barium coordination. The mineral sample is presented at the right.

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Abstract

$BaSO_4$, orthorhombic, *Pnma* (no. 62), a = 8.8806(8) Å, b = 5.4539(5) Å, c = 7.1570(7) Å, V = 346.64(6) Å^3, Z = 4, $R_{gt}(F^2)$ = 0.0141, $wR_{ref}(F^2)$ = 0.0329, T = 293 K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colorless platelets
Size:	0.05 × 0.04 × 0.03 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	11.9 mm^{-1}
Diffractometer, scan mode:	IPDS-II, Stoe
θ_{max}, completeness:	33.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	4105, 729, 0.032
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 559
$N(param)_{refined}$:	35
Programs:	X-Area [1], JANA2006 [2], SUPERFLIP [3, 4]

1 Source of material

Transparent, platelet-shaped baryte crystals (see Figure 1) were selected from a specimen of Mine du Pradet, Cap Garonne (France), which was collected in the *Salle du Grand Bassin* in the north part of the mine (Mine du Nord). The baryte crystals were accompanied by olivenite and pharmacosiderite.

2 Experimental details

The $BaSO_4$ crystals were selected from the carefully, mechanically fragmented sample. The crystal quality was tested by Laue photographs, using a Buerger camera, which was equipped with an image plate detection system. Single crystal X-ray diffraction data was collected at room temperature on a Stoe IPDS–II diffractometer (graphite monochromatized Mo–K_α radiation; oscillation mode). A numerical absorption

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Ba	0.18452 (2)	0.25	0.65843 (3)	0.01054 (5)
S	0.06250 (9)	0.25	0.19095 (10)	0.00902 (17)
O1	0.08056 (18)	0.0301 (3)	0.3111 (2)	0.0130 (4)
O2	0.1824 (3)	0.25	0.0501 (3)	0.0154 (6)
O3	0.4120 (3)	0.25	0.3927 (4)	0.0223 (7)

correction was applied. The starting atomic parameters were deduced with the charge-flipping algorithm [3] implemented in Superflip [4] and the structure was refined on F^2 with the Jana2006 software package [2]. For the final refinement we used the standardized setting listed in the Pearson database [5]. An EDX analyses of the studied crystal gave no hint for contamination with other cations, especially Sr^{2+}, Pb^{2+} or Cd^{2+}.

3 Comment

Baryte is one of the frequently occurring minerals in Mine du Pradet at Cap Garonne in France [6]. It was already mentioned in the early work of Ferdinand [7] and Lacroix [8]. The present single crystal data are of high quality and fully confirm previous refinements (powder and single crystal X-ray data) on natural [9–15] and synthetic barium sulfate [16–19]. The $BaSO_4$ structure (see Figure 1) contains three crystallographically independent oxygen atoms, which lead to S–O distances in the range of 146.5–148.4 pm. The slight orthorhombic distortion is also expressed in the O–S–O angles (107.8–112.4°), which slightly deviate from the ideal tetrahedron angle. The barium atoms are coordinated by 12 oxygen atoms from seven sulfate tetrahedra. Five of these tetrahedra coordinate side-on as chelate ligands and two end-on. The Ba–O distances cover a broader range from 277.5 to 331.4 pm with an average of 295 pm, a consequence of the orthorhombic distortion. It is worthwhile to note, that the $BaSO_4$ structure can geometrically be derived from the NaCl type. The barium and sulfur atoms (i.e. the centers of the sulfate tetrahedra) correspond to the sodium and chlorine sites. The room temperature modification (*Pnma* phase) shows a strong orthorhombic distortion. Above 1425 ± 5 K [20], $BaSO_4$ transforms to its cubic polymorph with space group $F\bar{4}3m$ [21], where the barium and chlorine atoms have NaCl-like topology. The Ba–O distances within the regular $Ba@O_{12}$ polyhedra of 310 pm are larger than the average distance of 295 pm in the *Pnma* phase.

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