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Crystal structure of langite from Mine du Pradet (France)

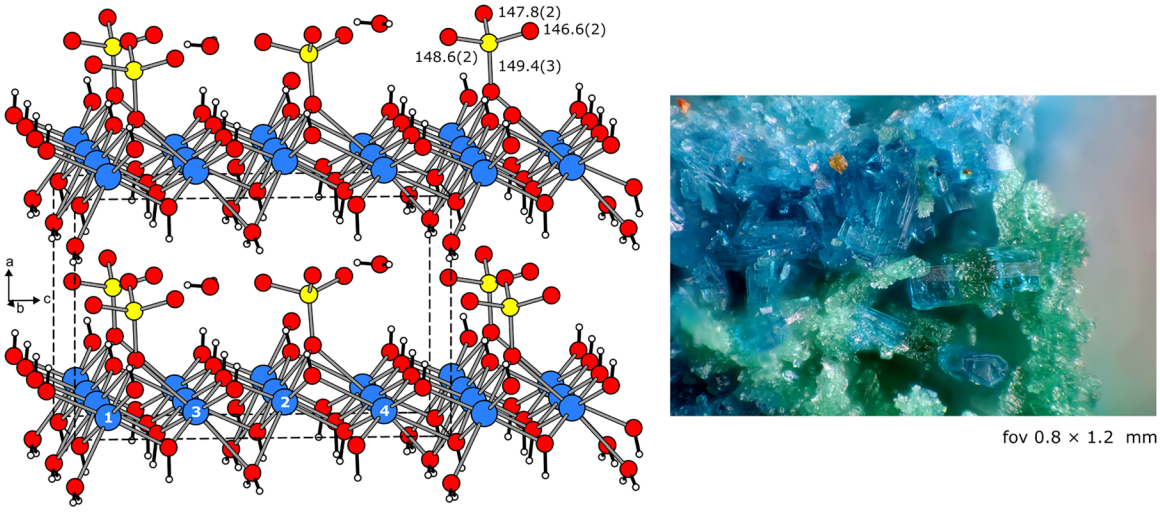

Figure: The crystal structure of $Cu_4(OH)_6SO_4{\cdot}2H_2O$ is shown in the left-hand part of the figure, emphasizing the condensed CuO_6 octahedra, the sulfate groups as well as the hydroxide units and coordinating water molecules. Atom designations and relevant interatomic distances are indicated. The mineral specimen from Cap Garonne used for the study is presented at the right.

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Abstract

$Cu_4(OH)_6SO_4{\cdot}2H_2O$, monoclinic, *Pc* (no. 7), a = 7.1026(2) Å, b = 6.0143(1) Å, c = 11.1645(3) Å, β = 90.1103(8)°, V = 476.91(2) Å^3, Z = 2, $R_{gt}(F^2)$ = 0.0206, $wR_{ref}(F^2)$ = 0.0563, T = 100 K.

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The structure is shown in the figure. 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:	Blue plate
Size:	30 × 40 × 55 µm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	9.10 mm^{-1}
Diffractometer, scan mode:	Bruker D8 Venture
θ_{max}, completeness:	32.1°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	8815, 3244, 0.016
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 3147
$N(param)_{refined}$:	185
Programs:	X-Area [1], JANA2020 [2], SUPERFLIP [3, 4]

1 Source of material

Langite has been originally observed on pillars 79 of the Fond de Mine and 25 of the Galerie du Mirror de Faille in the north part (Mine du Nord) of Mine du Pradet, Cap Garonne (France). Transparent blue platelets (see Figure) for the present investigation were selected from a specimen which was collected from the mine ceiling in the Salle des Racines (root vault). The langite crystals were accompanied/intergrown by greenish brochantite crystals ($Cu_4(OH)_6SO_4$).

2 Experimental details

The $Cu_4(OH)_6SO_4{\cdot}2H_2O$ crystals were carefully broken out of the sample using a medical cannula as lever. The quality of the crystals was first examined by Laue photographs (Buerger camera, white Mo radiation, image plate detection system). Single crystal X-ray diffraction data was collected at

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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}
Cu1	0.1417 (3)	0.50212 (3)	0.0607 (2)	0.00498 (7)
Cu2	0.1480 (3)	0.00724 (3)	0.0586 (2)	0.00482 (9)
Cu3	0.1372 (3)	0.25601 (3)	0.3077 (2)	0.00486 (7)
Cu4	0.1325 (3)	0.75481 (3)	0.3086 (2)	0.00468 (9)
S1	0.5634 (2)	0.31480 (7)	0.14010 (12)	0.00626 (9)
O1	0.2528 (3)	0.49939 (18)	0.39736 (18)	0.0058 (3)
O2	0.2519 (3)	0.00503 (18)	0.39525 (18)	0.0055 (3)
O3	0.0227 (3)	0.01044 (19)	0.21762 (19)	0.0059 (3)
O4	0	0.25383 (19)	0	0.0053 (3)
O5	0.2810 (3)	0.24515 (17)	0.61778 (17)	0.0056 (3)
O6	0.0148 (3)	0.50640 (19)	0.22111 (18)	0.0057 (3)
O7	0.8799 (3)	0.2423 (2)	0.45876 (18)	0.0093 (3)
O8	0.6241 (3)	0.0711 (2)	0.86428 (17)	0.0127 (4)
O9	0.3572 (3)	0.26850 (18)	0.14817 (17)	0.0065 (3)
O10	0.6020 (3)	0.4330 (2)	0.02589 (16)	0.0110 (3)
O11	0.6635 (3)	0.0994 (2)	0.13828 (16)	0.0108 (3)
O12	0.6248 (3)	0.4511 (2)	0.24177 (17)	0.0119 (3)
H1	0.349 (5)	0.504 (4)	0.403 (3)	0.007*
H2	0.348 (5)	0.999 (4)	0.398 (3)	0.0066*
H3	0.898 (4)	0.031 (4)	0.207 (2)	0.0071*
H4	0.892 (4)	0.251 (3)	0.015 (2)	0.0063*
H5	0.371 (4)	0.248 (3)	0.604 (3)	0.0067*
H6	0.881 (4)	0.489 (3)	0.224 (2)	0.0069*
H7a	0.813 (4)	0.334 (4)	0.473 (2)	0.0112*
H7b	0.823 (4)	0.159 (4)	0.449 (2)	0.0112*
H8a	0.632 (4)	0.067 (4)	0.804 (2)	0.0153*
H8b[a]	0.636 (5)	0.199 (6)	0.881 (3)	0.0153*

[a]Occupancy: 0.75 (5).

100 K on a Bruker D8 Venture single-crystal diffractometer, equipped with a MoKα microfocus source and a CCD detection system (Photon 100 CMOS). A numerical absorption 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 Jana2020 software package [2]. For the final refinement we used the standardized setting listed in the Pearson database [5].

3 Comment

Langite, $Cu_4(OH)_6SO_4{\cdot}2H_2O$, is one of the rare minerals in Mine du Pradet at Cap Garonne in France [6]. This basic copper sulfate was first discovered in the mine by Sarp [7]; however, no structural characterization was performed. Langite originating from pillars 25 and 79 was later confirmed in 2009 and 2011 by the Jean Wyart association (https://www.amis-mineraux.fr/partenaires.html) with the help of EDX analyses.

In the present study we initially collected data at room temperature (the refinement of the non-hydrogen positions is deposited under CCDC-2301061) but could not reliably refine the hydrogen positions. The crystal chemical discussion thus relies on the 100 K diffraction data. The positions of the non-hydrogen atoms fully agree with the refinements of the langite structure from crystals originating from different deposits [8–17].

The langite structure (see Figure) contains four crystallographically independent copper atoms, which all have the typical 4 + 2 oxygen coordination as a consequence of Jahn–Teller distortion. The Cu–O distances range from 190.5 to 201.7 pm for the CuO_4 square planes and from 229.5 to 266.7 pm for the apical oxygen atoms. These elongated CuO_6 octahedra condense to layers via six common edges in a distorted rock salt-type arrangement (similar to the layers of condensed octahedra in the CdI_2 structure). Consequently, temperature dependent magnetic susceptibility studies indicated a quasi-two-dimensional spin-1/2 substructure that is subjected to magnetic frustration. Langite shows antiferromagnetic ordering below the Néel temperature of ca. 5.7 K [17].

The slightly distorted sulfate tetrahedra (146.6–149.4 pm S–O; 108.0–111.0° O–S–O) condense with the copper-oxygen layer via a common oxygen atom, however, solely on one side of the layer. All sulfate tetrahedra point in the *-a* direction, thus the non-centrosymmetric space group symmetry. The water entities in the langite structure have different crystal chemical function. Part of them coordinates to copper and is member of the condensed layer. The remaining ones are typical crystal water molecules and thus part of the hydrogen bonding network that holds the layers together.

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