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Redetermination of the crystal structure of calcium sulphate dihydrate, $CaSO_4 \cdot 2H_2O$

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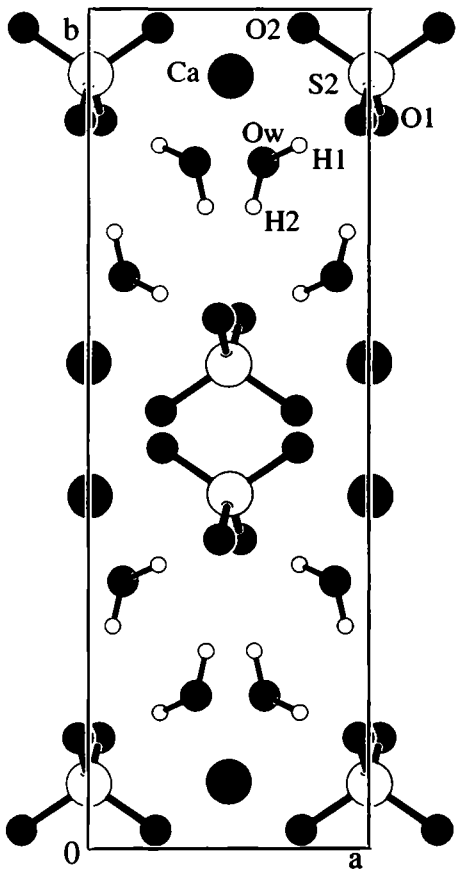

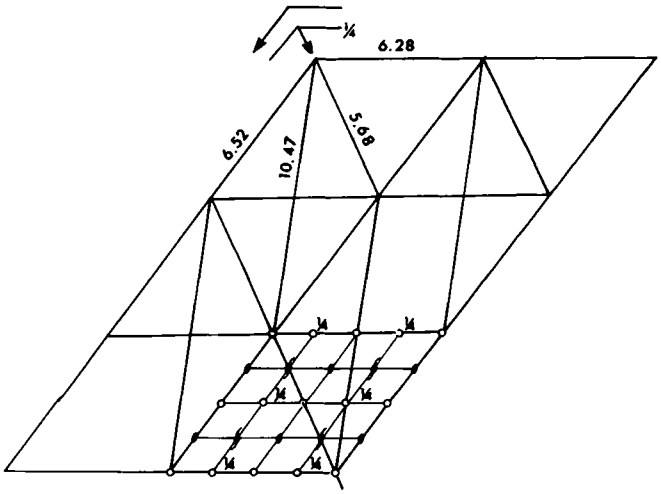

Abstract

CaH_4O_6S, monoclinic, $C12/c1$ (No. 15), $a = 6.284(1)$ Å, $b = 15.200(1)$ Å, $c = 6.523(1)$ Å, $\beta = 127.41(1)°$, $V = 494.9$ Å^3, $Z = 4$, $R_{gt}(F) = 0.028$, $wR_{ref}(F^2) = 0.079$, $T = 293$ K.

Source of material

The crystallising solution was made up from commercial 0.5 M aqueous solutions of A. R. grade.

Discussion

In order to standardize all entries of powder diffraction patterns for gypsum and synthetic calcium sulphate dihydrate, the JCPDS [1,2] uses the reduced cell: $a, b, c = 5.68$ Å, 6.29 Å, 8.22 Å; $\alpha, \beta, \gamma = 67.5°$, 81.0°, 65.8°, and indexing based on the monoclinic cell: $a', b', c' = 6.29$ Å, 15.18 Å, 5.68 Å; $\beta = 114.2°$, and space group $C2/c$. This now seems to be generally accepted as the standard setting, but although it has the correct systematic absences, the symmetry is wrong, and according to International Tables [3] this is cell choice 2 ($A2/n$) in the setting $C2/n$. This incorrect assignment was noticed in the course of the present work, only after data collection according to this cell choice and then transformed to the correct $C2/c$ cell with $a, b, c = 6.28$ Å, 15.20 Å, 6.52 Å; $\beta = 127.4°$, where $a\mathbf{i} + b\mathbf{j} + c\mathbf{k} = -a'\mathbf{i} - b'\mathbf{j} + (a' + b')\mathbf{k}$; with **i**, **j**, **k** being the unit vectors. This choice of unit cell [3] has the correct setting of the space group, but being less eccentric, is now recommended as the standard setting. In the lower figure, a projection along the b axis of the actual unit cell (drawn to scale) is shown together with all previous choices. The unique b axis is common for all cell choices. The space group symmetry for the standard cell is also shown as a guide to the different specifications of the space group.

A comparison of the crystal structures of the mineral gypsum with the synthetic material confirmed that there are no differences between the structures. The agreement with the neutron results is particularly striking, with the only significant difference related to the position of H(2), which is clearly wrong in the present work. It is still an improvement over the previous best X-ray study of Cole & Lancucki [4] in which hydrogen position could not be refined against the data. Important issues for discussion are the shape of the sulphate ion and the hydrogen bonding. The known deviation of the sulphate geometry from a symmetrical tetrahedron is convincingly confirmed, while the observed hydrogen-bonding is essentially the same as observed before.

In the final analysis the structure of pure gypsum is now known in sufficient detail from X-ray diffraction to allow an analysis of distortions, introduced by dopants, such as lanthanide ions.

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Table 1. Data collection and handling.

Crystal:	clear prism, size 0.08 × 0.16 × 1.2 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	16.32 cm^{-1}
Diffractometer, scan mode:	Enraf Nonius CAD4, $\omega/2\theta$
$2\theta_{max}$:	69.9°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4287, 109
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 971
$N(param)_{refined}$:	46
Program:	SHELXL-93 [5]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	8*f*	0.749(3)	0.162(1)	0.251(4)	0.031(8)
H(2)	8*f*	0.584(5)	0.235(2)	0.073(5)	0.057(7)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca	4*e*	1/2	0.07956(1)	3/4	0.0105(1)	0.0124(1)	0.0104(1)	0	0.0057(1)	0
S(2)	4*e*	0	0.07724(2)	3/4	0.0084(2)	0.0108(2)	0.0090(1)	0	0.0046(1)	0
O(1)	8*f*	0.0372(1)	0.13198(5)	0.5872(1)	0.0163(3)	0.0187(3)	0.0145(3)	0.0006(2)	0.0093(2)	0.0052(2)
O(2)	8*f*	0.2424(1)	0.02211(4)	0.9092(1)	0.0115(3)	0.0179(3)	0.0172(3)	0.0052(2)	0.0075(2)	0.0068(2)
OW	8*f*	0.6202(2)	0.18197(5)	0.0784(2)	0.0304(4)	0.0182(3)	0.0157(3)	0.0013(3)	0.0099(3)	-0.0028(2)

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