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Reinvestigation of polyhalite, $K_2Ca_2Mg(SO_4)_4\cdot 2H_2O$

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(S–O) = 0.003 Å
H-atom completeness 0%
R factor = 0.048
wR factor = 0.143
Data-to-parameter ratio = 12.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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The crystal structure of the mineral polyhalite, or dipotassium dicalcium magnesium tetrakis[sulfate(VI)] dihydrate, was reinvestigated by means of single-crystal X-ray diffraction data. The structural model previously reported was confirmed, although a higher precision of the refinement has been achieved. The structure consists of $K^{[11]}$ and $Ca^{[8]}$ polyhedra and $[MgO_4(H_2O)_2]$ octahedra sharing edges and faces; SO_4 tetrahedra share edges with the polyhedra.

Comment

Polyhalite is a very common mineral. It is widely formed as a constituent of marine evaporites, associated with halite (NaCl) and anhydrite ($CaSO_4$). Polyhalite single crystals are very rare. However, individuals having an orthorhombic appearance can occur. The crystal structure of polyhalite was originally solved by Schlatti *et al.* (1970) in the space group $F\bar{1}$ (R = 9.0%) by means of photographic data and a three-dimensional Patterson function. The low quality of those structural data, however, did not allow an anisotropic model of the structure to be obtained. The structural model reported by Schlatti *et al.* (1970) was confirmed during the present investigation, although a higher precision of the refined structure has been achieved.

Fig. 1 displays the asymmetric unit of the structure. It consists of $K^{[11]}$ and $Ca^{[8]}$ polyhedra and $[MgO_4(H_2O)_2]$ octahedra sharing edges and faces. SO_4 tetrahedra share edges with the $[MO_x]$ polyhedra (M = K, Ca, Mg; Fig. 2). Each H_2O molecule (O9) is bonded to one Mg^{2+} and one K^+.

Experimental

A natural specimen from the mineralogical collection of the Natural History Museum of Florence (catalogue number 9034/G) was used.

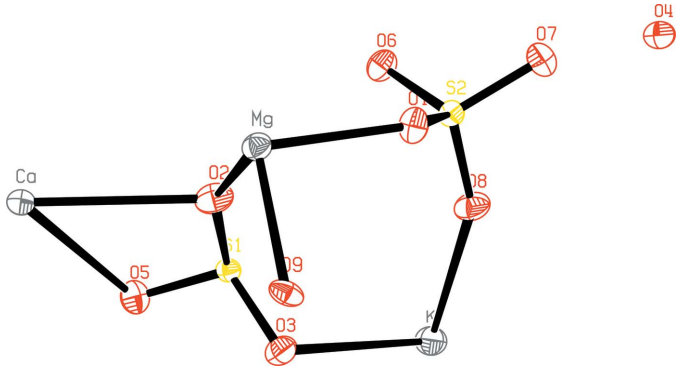

Figure 1
The asymmetric unit of polyhalite, showing the atom-labelling scheme. Displacement parameters are drawn at the 50% probability level.

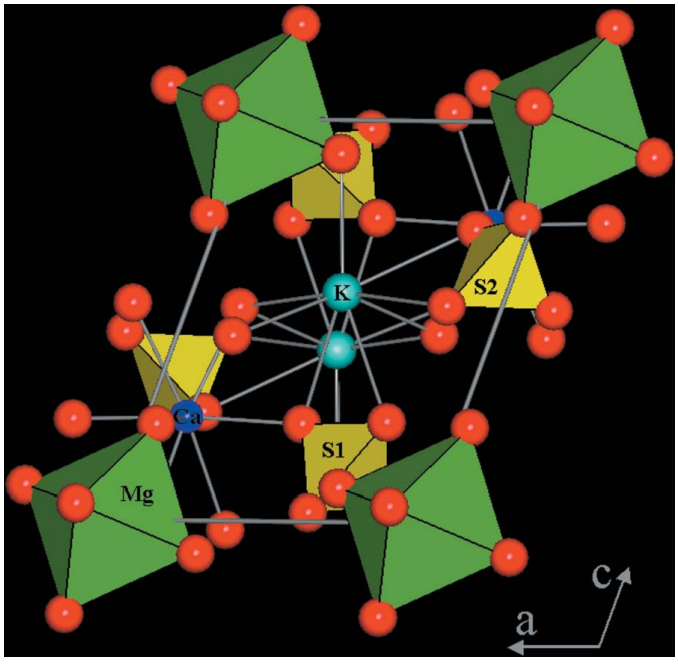

Figure 2
The crystal structure of polyhalite projected along the *b* axis. The unit cell is outlined.

Crystal data

$K_2Ca_2Mg(SO_4)_4{\cdot}2H_2O$
M_r = 602.92
Triclinic, $P\overline{1}$
a = 6.975 (3) Å
b = 6.984 (3) Å
c = 8.899 (3) Å
α = 104.01 (3)°
β = 101.19 (3)°
γ = 114.10 (6)°
V = 362.3 (4) Å^3
Z = 1
D_x = 2.763 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1206 reflections
θ = 10.2–26.4°
μ = 2.09 mm^{-1}
T = 298 (2) K
Prism, colourless
0.35 × 0.33 × 0.32 mm

Data collection

Oxford Diffraction Xcalibur-3 diffractometer
ω scans
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
T_{min} = 0.493, T_{max} = 0.510
2629 measured reflections
1525 independent reflections
1305 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 31.3°
$h = -9 \rightarrow 6$
$k = -7 \rightarrow 10$
$l = -10 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.143
S = 0.97
1525 reflections
124 parameters
H-atom parameters not defined
$w = 1/[\sigma^2(F_o^2) + (0.0856P)^2 + 1.9844P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.68 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—O3	1.461 (3)	Ca—O1^{ii}	2.479 (3)
S1—O4^{i}	1.471 (3)	Ca—O8^{iii}	2.516 (4)
S1—O5	1.482 (3)	Ca—O5	2.554 (4)
S1—O2	1.484 (4)	Ca—O7^{iii}	2.609 (4)
S2—O6	1.461 (3)	Ca—O2	2.686 (4)
S2—O8	1.472 (4)	K—O8	2.768 (4)
S2—O7	1.473 (3)	K—O8^{vi}	2.787 (4)
S2—O1	1.504 (3)	K—O7^{vii}	2.804 (4)
Mg—O9^{ii}	2.017 (3)	K—O9^{vi}	2.815 (4)
Mg—O9	2.017 (3)	K—O7^{i}	2.886 (4)
Mg—O2	2.045 (3)	K—O4^{i}	2.916 (4)
Mg—O2^{ii}	2.045 (3)	K—O3	2.928 (3)
Mg—O1^{ii}	2.164 (3)	K—O6^{i}	2.998 (4)
Mg—O1	2.164 (3)	K—O4^{vii}	3.129 (4)
Ca—O4^{iii}	2.399 (3)	K—O1^{vi}	3.164 (4)
Ca—O6^{iv}	2.407 (3)	K—O3^{vi}	3.196 (4)
Ca—O3^{v}	2.413 (4)		
O3—S1—O4^{i}	109.71 (18)	O6—S2—O8	111.4 (2)
O3—S1—O5	111.3 (2)	O6—S2—O7	111.0 (2)
O4^{i}—S1—O5	109.75 (19)	O8—S2—O7	107.1 (2)
O3—S1—O2	111.0 (2)	O6—S2—O1	109.36 (18)
O4^{i}—S1—O2	110.41 (19)	O8—S2—O1	109.03 (19)
O5—S1—O2	104.6 (2)	O7—S2—O1	108.91 (19)

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x, -y, -z$; (iii) $x, y, z-1$; (iv) $-x, -y+1, -z$; (v) $-x+1, -y+1, -z$; (vi) $-x+1, -y+1, -z+1$; (vii) $x+1, y+1, z$.

For the present investigation, the standard setting in space group $P\overline{1}$ was chosen. H atoms were not located. The highest peak is located 1.33 Å from O5.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Xtal–DRAW* (Downs & Hall-Wallace, 2003) and *ORTEP3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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