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Crystal structure of potassium dimagnesium disilicate hydroxide, $K_{1.3}(Mg_{0.95}Al_{0.03}Cr_{0.02})_2Si_2O_{6.4}(OH)_{0.6}$

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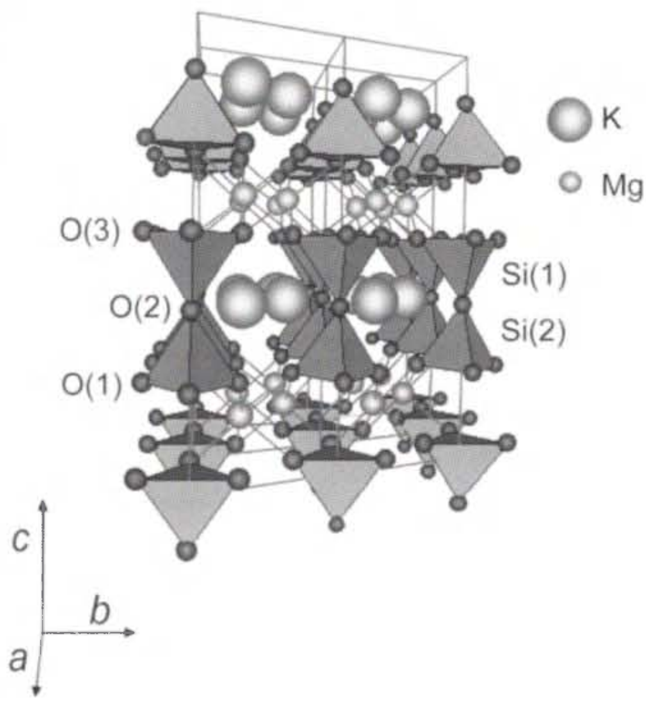

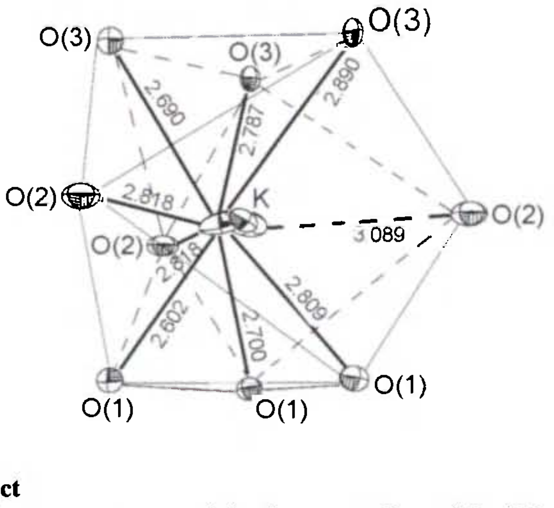

Abstract

$Al_{0.06}Cr_{0.04}H_{0.59}K_{1.31}Mg_{1.90}O_7Si_2$, hexagonal, $P6_3cm$ (No. 185), $a = 5.0279(7)$ Å, $c = 13.216(2)$ Å, $V = 289.3$ Å^3, $Z = 2$, $R_{gt}(F) = 0.023$, $wR_{ref}(F^2) = 0.057$, $T = 293$ K.

Source of material

The title compound was produced from a mixture of natural diopside $CaMgSi_2O_6$, synthetic kosmochlor $NaCrSi_2O_6$, SiO_2 and $K_2CO_3 \cdot H_2O$ (molar ratio 0.85:0.09:0.06:1), about 10 mg in total, sealed in a platinum capsule and run in a multianvile device as experiment GG307 (see [1], revised calibration $P \cong 9$ GPa and $T \approx 1573$ K). The presence of OH groups in the crystal was inferred by low oxide totals from electron microprobe analysis (CAMECA SX100) and determined by FTIR spectroscopy. The title compound was formed as a thin layer (< 100 µm thick) between clinopyroxene and quenched melt and has the formula $K_{1.3}(Mg_{0.95}Al_{0.03}Cr_{0.02})_2Si_2O_{6.4}(OH)_{0.6}$, which is close to the compound formula given by Konzett & Ulmer [2] for a phase first identified as phase-X by Luth [3].

Discussion

The structure is built up of octahedral sheets and layers containing disilicate groups, Si_2O_7, parallel to (001). Within the framework of Si_2O_7 groups are channel structures parallel to [100], [010] and [110] that contain K atoms in the center of large trigonal cavities. The octahedral sheet is based on a hexagonal closest-packed array of two layers of non-equivalent oxygens, O(1) and O(3); two-thirds of all edge-sharing octahedra sites are filled with Mg. Cr and Al replace Mg to a minor (*ca.* 4.5%) but significant extent. Each SiO_4 tetrahedron shares edges with the K antiprism and corners with the octahedral layer (above and below vacancies in the layer). Like the Mg octahedron, the K antiprism is centered on the 3-fold axis and shares basal triangular faces with the octahedron and quadratic lateral faces with other symmetrically related ones. FTIR spectrum in the O–H stretching region shows a sharp peak at 3602 cm^{-1} due to structurally bonded OH$^-$ groups; hydrogen serving as charge balance substitution for the partially occupied K position. Cation coordination numbers, ranges of individual interatomic distances and means of distances in Å are as follows Si(1): 4/1.635 – 1.635/1.635; Si(2): 4/1.626 – 1.701/1.644; Mg: 6/2.105 – 2.092/2.098. A remarkable feature in the region near the 4*b* K site is the presence of residual electron density (0.82 eÅ^{-3}), indicating site splitting. A split model was therefore refined, yielding K—O distances in the range 2.602 Å – 3.089 Å (figure below); however, bond valences suggest an effective coordination number of N = 5. Among the two non-equivalent Si atoms, the thermal ellipsoid of Si2 is flattened perpendicular to the *c*-direction ($U_{33} < U_{11}$, U_{22}; Table 3), which is ascribed to static (positional) disorder possibly driven by vacancies in the K site. The mean tetrahedral bond lengths agree with the sum of Si^{4+} and O^{2-} ionic radii (1.64 Å). Also the mean octahedral bond length M—O (2.098 Å) is consistent with the sum of

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ionic radii (2.12 Å). On the opposite, the mean K—O interatomic distance (2.76 Å) is significantly shorter than the sum of the ionic radii (2.95 Å), a contraction due to the partial occupancy of the K site (0.65).

Table 1. Data collection and handling.

Crystal:	light-green, prismatic, size 0.02 × 0.02 × 0.03 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	18.54 cm^{-1}
Diffractometer, scan mode:	Bruker 1K Smart CCD, 1650 exposures, $\Delta\omega = \Delta\phi = 0.3°$
$2\theta_{max}$:	54.8°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1521, 255
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 239
$N(param)_{refined}$:	38
Programs:	SHELXS-86 [4], SHELXL-93 [5], JANA98 [6]

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

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si(1)	2*a*		0	0	0.0123(3)	0.009(1)	U_{11}	0.009(2)	0.0044(7)	0	0
Si(2)	2*a*		0	0	0.2598(2)	0.012(1)	U_{11}	0.001(1)	0.0058(7)	0	0
Mg(1)	4*b*	1.062(6)	−1/3	1/3	0.1370(4)	0.0099(5)	U_{11}	0.0164(6)	0.0049(2)	0	0
K(3)	12*d*	0.219(2)	0.356(7)	0.646(9)	0.3857(5)	0.016(6)	0.026(9)	0.0101(7)	−0.000(2)	−0.005(5)	0.002(7)
O(1)	6*c*		0.310(1)	0	0.2294(8)	0.013(2)	0.011(3)	0.010(2)	0.006(1)	0.001(3)	0
O(2)	2*a*	1.05(1)	0	0	−0.113(2)	0.021(1)	U_{11}	0.009(2)	0.0104(6)	0	0
O(3)	6*c*		−0.313(1)	0	0.0507(8)	0.007(2)	0.011(3)	0.012(2)	0.006(1)	0.000(3)	0

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