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Crystal structure of Al-rich fluorophlogopite, $K_{1.0}(Mg_{2.8}Al_{0.2})(Si_{2.8}Al_{1.2})O_{10}F_2$

Table 1: Data collection and handling.

Crystal:	Colourless flake
Size:	0.10 × 0.10 × 0.05 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.28 mm ⁻¹
Diffractometer, scan mode:	XtaLAB, φ and ω
θ_{max} , completeness:	33.7°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	2246, 940, 0.017
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 874
$N(param)_{refined}$:	53
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], Olex2 [4]

Source of material

Pure raw materials of 11.6 wt% SiO₂, 32.6 wt% Al₂O₃, 30.7 wt% MgO, and 25.1 wt% K₂SiF₆ were ground in an agate mortar and loaded into a corundum crucible. The muffle furnace was heated to 1450 °C in 4 h to completely melt the reactants. Then, the muffle furnace was cooled to 1000 °C at a rate of 10 °C/h to make the fluorophlogopite crystallize during this period. At last, the furnace was freely cooled to room temperature. The specimen thus obtained was an intimate aggregate of flakes of colorless and transparent crystals.

Experimental details

Crystals were selected from the aggregate and cut to a suitable size for the single crystal measurement. The chemical compositions of the measured single crystal were determined by electron microprobe analysis (EPMA, JEOL-JXA8230). Atomic occupancy of Si/Al ratio in the tetrahedral sites and Mg/Al ratio in the octahedral sheets were constrained according to the EPMA results. Moreover, atoms sharing the same sites were constrained to have identical thermal displacements.

Comment

Synthetic fluorophlogopite attracts considerable interest because of its wide applications to material science [5–7].

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Abstract

$K_{1.0}(Mg_{2.8}Al_{0.2})(Si_{2.8}Al_{1.2})O_{10}F_2$, monoclinic, $C2/m$ (no. 12), $a = 5.3040(11)$ Å, $b = 9.2288(18)$ Å, $c = 10.1286(20)$ Å, $\beta = 100.173(3)^\circ$, $V = 488.00(17)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0387$, $wR_{ref}(F^2) = 0.1086$, $T = 298$ K.

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The molecular 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.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
K1	1.000000	0.000000	0.000000	0.0287 (3)
F1	0.3672 (3)	0.500000	0.59653 (16)	0.0122 (3)
O1	0.5119 (4)	0.000000	0.1673 (2)	0.0163 (4)
O2	0.8282 (3)	0.22812 (18)	0.16727 (14)	0.0164 (3)
O3	0.6313 (3)	0.16655 (14)	0.39191 (14)	0.0098 (3)
Si1 ^a	0.57553 (9)	0.16665 (5)	0.22461 (5)	0.00728 (15)
Al1 ^b	0.57553 (9)	0.16665 (5)	0.22461 (5)	0.00728 (15)
Mg2 ^c	0.500000	0.33029 (9)	0.500000	0.0084 (2)
Al3 ^d	0.500000	0.33029 (9)	0.500000	0.0084 (2)
Mg1 ^c	0.000000	0.500000	0.500000	0.0089 (3)
Al2 ^d	0.000000	0.500000	0.500000	0.0089 (3)

^aOccupancy: 0.7, ^bOccupancy: 0.3, ^cOccupancy: 0.934, ^dOccupancy: 0.066.

Fluorophlogopite belongs to tetrahedron-octahedron-tetrahedron (TOT) type in which one octahedral sheet is sandwiched between two tetrahedral sheets (Figure 1a). Cation substitutions of Al^{3+} for Si^{4+} in the tetrahedral sheet lead to a positive charge deficiency in the TOT layer. The negative charge of the TOT unit is balanced and bonded together by the K^+ in the interlayer (Figure 1a) [8]. To date, fluorophlogopite with different Al content, $\text{K}_{1.0}\text{Mg}_{2.5}\text{Si}_4\text{O}_{10}\text{F}_2$, $\text{K}_{1.0}\text{Mg}_{2.75}(\text{Si}_{3.5}\text{Al}_{0.5})\text{O}_{10}\text{F}_2$, and $\text{K}_{1.0}\text{Mg}_3(\text{Si}_3\text{Al})\text{O}_{10}\text{F}_2$ have been synthesized [9–11]. Previous research shows that $\text{K}_{1.0}\text{Mg}_{2.5}\text{Si}_4\text{O}_{10}\text{F}_2$ is considerably brittle, while $\text{K}_{1.0}\text{Mg}_3(\text{Si}_3\text{Al})\text{O}_{10}\text{F}_2$ is much more flexible. This suggests that the Al content has an important influence on the amount of negative charge which could affect the physical and chemical properties of the compound. However, Al-rich fluorophlogopite is poorly known.

EPMA shows that the chemical compositions of the synthetic Al-rich fluorophlogopite are: SiO_2 40.03 wt%, Al_2O_3 17.06 wt%, FeO 0.02 wt%, MgO 26.87 wt%, Na_2O 0.01 wt%, K_2O 11.09 wt%, and F 9.05 wt%. The crystal formula based on EMPA is $\text{K}_{1.0}(\text{Mg}_{2.8}\text{Al}_{0.2})(\text{Si}_{2.8}\text{Al}_{1.2})\text{O}_{10}\text{F}_2$, which is consistent with the result of structural refinement. This Al-rich fluorophlogopite belongs to the 1 M polytype (space group $C2/m$) with cell dimensions of $a = 5.3040(11) \text{ \AA}$, $b = 9.2288(18) \text{ \AA}$, $c = 10.1286(20) \text{ \AA}$, and $\beta = 100.173(3)^\circ$. In the tetrahedral sheet, an individual TO_4 tetrahedron is linked with neighboring TO_4 by sharing the three basal oxygen atoms (i.e., O1 and O2) to form an infinite two-dimensional hexagonal mesh pattern (Figure 1b). Si and Al occupy the tetrahedral sites in a ratio $\text{Si}:\text{Al} = 2.8:1.2$. The average bond distance ($\langle\text{T}-\text{O}\rangle = 1.658 \text{ \AA}$) of the Al-rich fluorophlogopite is obviously longer than in $\text{K}_{1.0}\text{Mg}_{2.5}\text{Si}_4\text{O}_{10}\text{F}_2$ ($\langle\text{T}-\text{O}\rangle = 1.625 \text{ \AA}$), $\text{K}_{1.0}\text{Mg}_{2.75}(\text{Si}_{3.5}\text{Al}_{0.5})\text{O}_{10}\text{F}_2$ ($\langle\text{T}-\text{O}\rangle = 1.638 \text{ \AA}$), and $\text{K}_{1.0}\text{Mg}_3$

$(\text{Si}_3\text{Al})\text{O}_{10}\text{F}_2$ ($\langle\text{T}-\text{O}\rangle = 1.642 \text{ \AA}$) [9–11]. Substitutions of Al^{3+} for Si^{4+} in the tetrahedral sheet decrease the bond lengths because the ionic radius of Al^{3+} (0.53 $\text{\AA}$) is larger than that of Si^{4+} (0.40 $\text{\AA}$). The tetrahedral rotation angle α is 8.66° . In the octahedral sheet, each octahedral coordination unit is comprised of four apical oxygen atoms (i.e., O3) and two F anions (Figure 1a). An individual octahedron is linked laterally by sharing edges to form octahedral sheets (Figure 1c). The octahedral sites are mainly occupied by Mg (2.8 atoms per formula unit) and minor amounts of Al (0.2 atoms per formula unit). The average bond distance of $\langle\text{M1}-\text{O}\rangle$ and $\langle\text{M2}-\text{O}\rangle$ are 2.058 and 2.054 $\text{\AA}$, respectively. Similar bond distances between M1 and M2 sites confirm that Al is disordered in the octahedral sites [12]. The interlayer K^+ is coordinated with 12 oxygen atoms (six from the upper and six from the lower tetrahedral sheets) (Figure 1a). The mean bond length of $\langle\text{K}-\text{O}\rangle$ is 3.138 $\text{\AA}$.

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