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Rerefinement of $K_2[TiF_6]$

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Crystals of dipotassium hexafluorotitanate(IV), $K_2[TiF_6]$, were grown from aqueous solution. The crystal structure was refined with anisotropic displacement parameters. Ti^{4+} is octahedrally coordinated by F^- (point group $\bar{3}m$), and K^+ is 12-coordinate (point group $3m$). The dispersion of birefringence is presented.

Comment

The crystal structure of $K_2[TiF_6]$ ($P\bar{3}m1$, $Z = 1$, $K_2[GeF_6]$ structure type) was first described by Siegel (1952). However, it was not fully resolved since no displacement parameters were given. It seemed desirable to redo the refinement to achieve higher accuracy. The displacement parameters have been determined in the present study. The corresponding ellipsoids of both the K^+ and the Ti^{4+} ions were found to be elongated ellipsoids of revolution. The lattice parameters, measured by single-crystal X-ray reflections on a four-circle diffractometer, are a = 5.7354 (11) and c = 4.6635 (18) Å. These are in fair agreement with earlier results of Siegel (1952), Cox & Sharpe (1953) and Swanson *et al.* (1957).

The distances and angles within the coordination polyhedra of the two cations, calculated with *SHELXL*97 (Sheldrick, 1997) and *ORFFE*4 (Busing *et al.*, 1985), are compiled in Table 1. The $[TiF_6]$ trigonal antiprism, having symmetry $\bar{3}m$, is a slightly distorted octahedron, which is compressed along the c axis by a factor of 0.9494 (8). This leads to small deviations of some F—F—F angles from 60° (Table 1). This is contrary to Siegel's results, where an elongated antiprism with a stretch factor of 1.04 (3) was found. The Ti—F bond length is 1.8605 (6) Å. The distances between neighbouring F^- ions within the $[TiF_6]$ antiprism are 2.6754 (11) (F^- ions within the same basal plane of the antiprism) and 2.5860 (12) Å (F^- ions of two different basal planes).

The coordination polyhedron around the K^+ ion is a slightly distorted anticuboctahedron, the 12-cornered coordination polyhedron of the hexagonal closest packing with site symmetry $\bar{6}2m$. The reduced site symmetry in the case of $K_2[TiF_6]$, $3m$, causes the K^+ ion to be displaced by 0.1391 (7) Å from the midpoint of the two (triangular) basal planes of this polyhedron. The equatorial plane with six F^- anions is displaced by 0.2577 (8) Å in the opposite direction. The average K—F distance is 2.91 (8) Å.

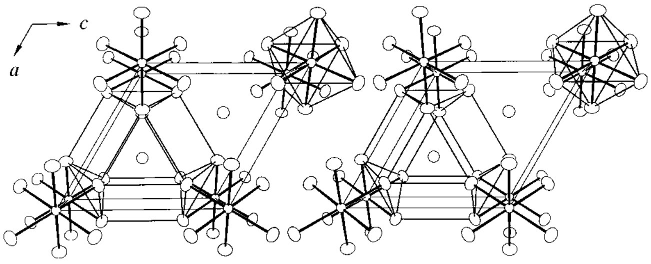

Figure 1
A view of the crystal structure of $K_2[TiF_6]$ along the c axis. In the upper right-hand corner, the edges of a $[TiF_6]$ antiprism are drawn and on the left-hand side the edges of a KF_{12} coordination polyhedron.

The optical character of $K_2[TiF_6]$ was found to be negative, in agreement with Zambonini (1930). Since the birefringence $\Delta n = n_e - n_o$ appeared to be very low for white light, there was a chance of finding a certain wavelength, λ_0, where it might vanish completely. Therefore, the dispersion of birefringence, $\Delta n(\lambda) = n_e(\lambda) - n_o(\lambda)$, was measured at room temperature. A straight line was fitted to seven data points using *GNUPLOT* (Williams *et al.*, 1998). An extrapolation of this line indicates that the birefringence should disappear at 720 nm. At this wavelength, λ_0, the optical behaviour of $K_2[TiF_6]$ should be isotropic and the sign of birefringence should change.

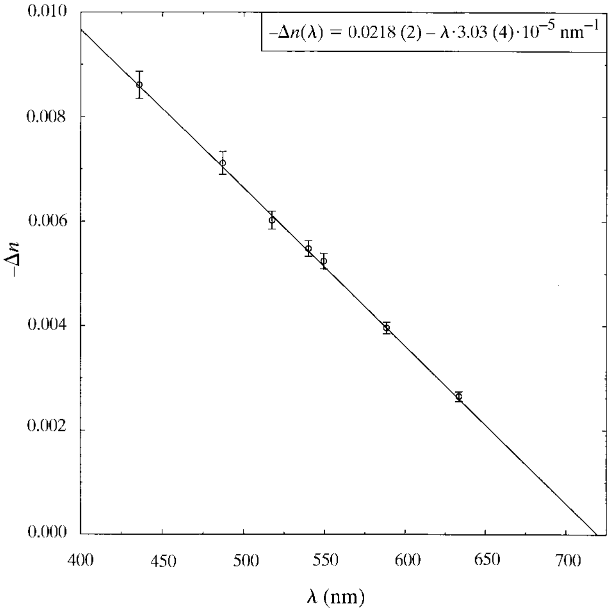

Figure 2
The birefringence of $K_2[TiF_6]$ as a function of wavelength.

Experimental

Crystals were grown by slowly diffusing acetone into a saturated aqueous solution of the title compound at 278 (1) K. This yielded well developed clear colourless isometric crystals approximately 110 µm in diameter. The predominating form was the rhombohedron {101}, but some very small pinacoids {001} were observed.

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Crystal data

$K_2[TiF_6]$
$M_r = 240.10$
Trigonal, $P\bar{3}m1$
$a = 5.7354$ (11) Å
$c = 4.6635$ (18) Å
$V = 132.85$ (6) Å^3
$Z = 1$
$D_x = 3.001$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 26 reflections
$\theta = 8.38$–$12.06°$
$\mu = 3.213$ mm^{-1}
$T = 298$ (2) K
Rhombohedron, colourless
$0.12 \times 0.12 \times 0.12$ mm

Data collection

Siemens AED-II four-circle diffractometer
$\theta/2\theta$ scans
4637 measured reflections
553 independent reflections
$R_{\rm int} = 0.054$
$\theta_{\rm max} = 49.76°$

$h = -12 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = -8 \rightarrow 10$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.050$
$S = 1.152$
553 reflections
13 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0183P)^2 + 0.0142P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.57$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.70$ e Å^{-3}
Extinction correction: *SHELXL* (Sheldrick, 1997)
Extinction coefficient: 0.54 (3)

Table 1
Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2).

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^ia^j\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
K	1/3	2/3	0.69254 (7)	0.02169 (8)
Ti	0	0	0	0.01220 (7)
F	0.15549 (6)	0.31099 (11)	0.22237 (13)	0.02376 (12)

Table 2
Selected geometric parameters (Å, °).

K—F	2.8158 (9)	Ti—F	1.8605 (6)
K—F$^{\rm i}$	2.8972 (6)	F—F$^{\rm iii}$	2.5860 (12)
K—F$^{\rm ii}$	3.0375 (11)	F—F$^{\rm iv}$	2.6754 (11)
F$^{\rm v}$—Ti—F	88.05 (3)	F$^{\rm iii}$—F—F$^{\rm v}$	62.30 (4)
F$^{\rm iv}$—Ti—F	91.95 (3)	F$^{\rm iii}$—F—F$^{\rm iv}$	58.85 (2)

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

The dispersion of birefringence, $\Delta n(\lambda) = n_e(\lambda) - n_o(\lambda)$, was determined at room temperature under a polarizing microscope with an Ehringhaus compensator. A crystal of approximately 140 µm in diameter and 76 (2) µm thickness was placed on a rhombohedral face so that the viewing direction and the optical axis formed an angle of 43.20 (2)°. For seven wavelengths, $\Delta n'(\lambda) = n_e'(\lambda) - n_o(\lambda)$ was measured and the values of $\Delta n(\lambda)$ were calculated under the assumption of an ordinary refractive index n_o of 1.475. This value was given by Zambonini (1930) for n_o(598 nm).

Data collection: *CD* (Stoe & Cie, 1987); cell refinement: *DL* (Stoe & Cie, 1987); data reduction: *REDU*4 (Stoe & Cie, 1987); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1278). Services for accessing these data are described at the back of the journal.

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