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$K_2Zr_3OF_{12}$: microwave-assisted hydrothermal synthesis and powder diffraction study

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Dipotassium trizirconium oxide dodecafluoride, $K_2Zr_3OF_{12}$, obtained by microwave-assisted hydrothermal synthesis, crystallizes in the trigonal space group $R\bar{3}m$ (No. 166) and is isostructural with $Tl_2Zr_3OF_{12}$. The structure was determined from X-ray powder diffraction data and is described in terms of fluorine- or oxygen-centered cation polyhedra and consists of $[F_{12}O_2KZr_6]_\infty$ and $[F_{12}K_3Zr_6]_\infty$ layers connected by Zr^{4+} cations.

Key indicators

Powder X-ray study
T = 293 K
Mean σ(K–F) = 0.006 Å
R factor = 0.120
wR factor = 0.139
Data-to-parameter ratio = 18.1

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

Comment

Because of their potential activity in non-linear optics or catalysis, attention has been paid recently to fluoride salts, fluoride borates (Becker, 1998; Dorozhkin *et al.*, 1981), fluoride carbonates (Mercier *et al.*, 1997), fluoride sulfates (Wickleder, 1999), and fluoride phosphates (Zhizhin *et al.*, 2001). The object of our work was to investigate the crystallization of zirconium fluoride silicates from hydrothermal solutions under microwave heating. No fluoride silicate was found in the KOH–SiO_2–ZrF_4–H_2O system and only one oxide fluoride was obtained. This phase, $K_2Zr_3OF_{12}$, is isostructural with both $Tl_2Zr_3OF_{12}$ (Mansouri & Avignant, 1984) and $Rb_2Zr_3OF_{12}$ (Koller & Muller, 2002). The structure of $K_2Zr_3OF_{12}$ was determined by powder diffraction. The X-ray diffraction pattern is given Fig. 1. Calculated bond valences (Brese & O'Keeffe, 1991) show that the interatomic distances are satisfactory and in agreement with bibliographic

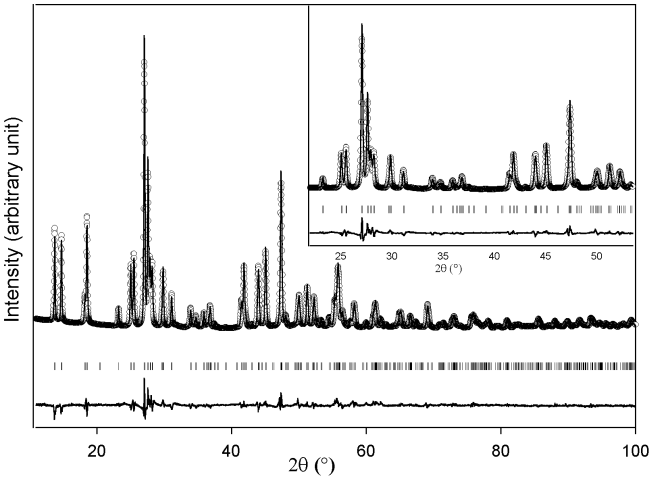

Figure 1
Final profile refinement of $K_2Zr_3OF_{12}$: observed (circle), calculated (line), and difference (bottom) profiles of X-ray diffraction data. Vertical bars are related to the calculated Bragg reflection positions. The first peak (near 2θ = 9.2°) is not included in the final refinement due to its high asymmetry.

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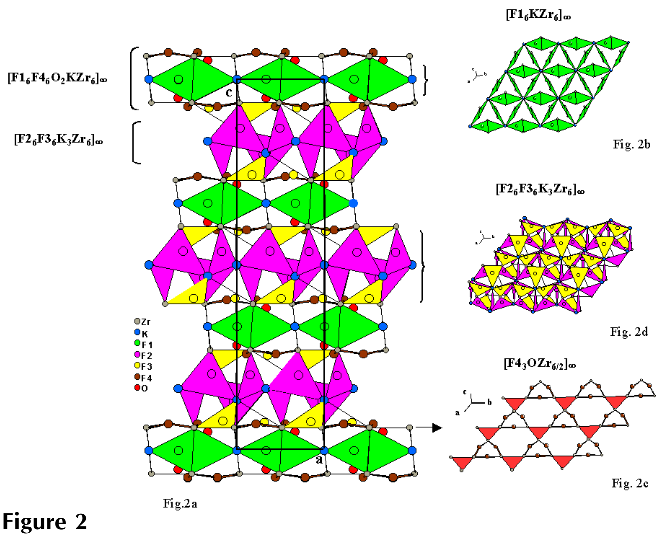

Figure 2
(a) The structure of $K_2Zr_3OF_{12}$ and succession of the layers (*b*) [F1$_6$KZr$_6$]$_\infty$, (*c*) [F2$_6$F3$_6$K$_3$Zr$_6$]$_\infty$ and (*d*) [F4$_3$OZr$_{6/2}$]$_\infty$.

data (Table 1). The isotropic atomic displacement parameters are also acceptable. The structure of $K_2Zr_3OF_{12}$ consists of $ZrOF_7$ and KF_6 polyhedra. O atoms lie at the common vertex of three edge-sharing $ZrOF_7$ polyhedra. These polyhedra, linked by corners or edges, build hexameric Zr_3OF_{18} units which share edges in order to form [$Zr_6O_4F_{30}$] polyanions. The polyanions, linked by corners, build infinite [$ZrOF_{12}$] double layers running perpendicular to the *c* axis. The structure can be also described in terms of fluorine- or oxygen-centered cation polyhedra (Fig. 2*a*). In $K_2Zr_3OF_{12}$, the F4 atoms adopt a twofold coordination. All other F atoms, together with O atoms, are in a triangular environment and form [FK_2Zr], [$FKZr_2$] and [OZr_3] entities. The triangular groups [F1KZr$_2$] (green), sharing Zr–Zr edges, form [F1KZr]$_2$ dimers. These dimers, connected by K atoms, build infinite chains along the [100], [010] and [110] directions. The resulting [F1$_6$KZr$_6$]$_\infty$ layers (Fig. 2*b*) include F4 and O atoms, which form [F4$_3$Zr$_3$] triangular cycles and [OZr_3] triangular entities (red) (Fig. 2*c*); they build [F1$_6$F4$_6$O$_2$Zr$_6$K1]$_\infty$ layers perpendicular to the *c* axis. [F2K2K3Zr] and [F3K3Zr$_2$] entities, purple and yellow, respectively, are linked by corners and define cages of six triangles (4 × F2 and 2 × F3). These cages, connected one to each other, build [F2$_6$F3$_6$K$_3$Zr$_6$]$_\infty$ layers parallel to the *ab* plane (Fig. 2*d*). The [F1$_6$F4$_6$O$_2$Zr$_6$K]$_\infty$ and [F2$_6$F3$_6$K$_3$Zr$_6$]$_\infty$ sheets which alternate along the *c* direction, are linked through Zr atoms.

Experimental

A powder sample of $K_2Zr_3OF_{12}$ was prepared from 0.6688 g of ZrF_4 and 10 ml of a 0.4 *M* KOH solution. The reaction mixture was then heated for 1 h at $T = 463$ K ($P = 12 \times 10^5$ Pa) in a CEM microwave oven (MDS 2100) using a Teflon-lined autoclave. The compound was then washed with acetone and dried in air. The product was characterized by X-ray powder diffraction on a Siemens Brucker D8 diffractometer. Thermal analysis was performed with a DTA–TGA TA Instrument 260 (heating rate 10 K min^{-1}; argon atmosphere). Above 908 K, $K_2Zr_3OF_{12}$ decomposes and undergoes hydrolysis to give ZrO_2 and K_3ZrF_7. Owing to the absence of IR lines around 3300 and 1600 cm^{-1}, the F$^-$–OH$^-$ substitution, expected from the preparation mode, is excluded.

Crystal data

$K_2Zr_3OF_{12}$
$M_r = 595.85$
Trigonal, $R\overline{3}m$
$a = 7.6887$ (3) Å
$c = 28.870$ (1) Å
$V = 1478.0$ (2) Å^3
$Z = 6$
$D_x = 4.016$ Mg m^{-3}

Cu *Kα* radiation
Cell parameters from 235 reflections
$\theta = 5.5$–50.0 °
$\mu = 2.75$ mm^{-1}
$T = 293$ K
White

Data collection

D8 Bruker diffractometer
Specimen mounting: packed powder pellet

$2\theta_{\min} = 5$, $2\theta_{\max} = 100°$
Increment in $2\theta = 0.02°$

Refinement

$R_p = 0.12$
$R_{wp} = 0.139$
$R_{exp} = 0.057$
$R_B = 0.066$
$S = 2.43$
$2\theta_{\min} = 11$, $2\theta_{\max} = 100°$
Increment in $2\theta = 0.02°$

Wavelength of incident radiation: 1.54178 Å
Excluded region(s): 5.00 → 11.00°
Profile function: pseudo-Voigt
470 reflections
26 parameters

Table 1
Selected geometric parameters (Å).

K1—F1^{i}	2.595 (5)	Zr—F4^{v}	2.139 (3)
K2—F2^{ii}	2.679 (4)	Zr—F4^{vi}	2.139 (3)
K3—F3^{iii}	2.711 (5)	Zr—F1^{vii}	2.198 (2)
K3—F2^{iv}	2.726 (6)	Zr—F1^{vi}	2.198 (2)
K3—F2	2.726 (6)	Zr—F3^{viii}	2.237 (3)
Zr—F2^{v}	1.997 (6)	Zr—F3^{ix}	2.237 (3)
Zr—O^{v}	2.044 (2)		

Symmetry codes: (i) $-x+y, -x, z$; (ii) $x-y-\frac{2}{3}, x-\frac{1}{3}, \frac{2}{3}-z$; (iii) $y, -x+y, 1-z$; (iv) $-y, x-y, z$; (v) $\frac{2}{3}-x, -\frac{2}{3}-y, \frac{1}{3}-z$; (vi) $1-x+y, -x, z$; (vii) $x-y, x-1, -z$; (viii) $1+y, -x+y, 1-z$; (ix) $x-y, x-1, 1-z$.

Reflection positions were determined by means of the *EVA* program (available in the Socabim PC software package *DIFFRAC–AT* supplied by Siemens (1996–98), derivative method) after $K_{\alpha 2}$ radiation stripping. Auto-indexing of 13 intense reflections by using the *McMaille* program (Le Bail, 2002) leads to an hexagonal cell similar to that of $Tl_2Zr_3OF_{12}$. The atomic positions of $Tl_2Zr_3OF_{12}$ were used as a starting model.

Data collection, cell refinement and data reduction: *STADI*4; program(s) used to refine structure: *FULLPROF* (Rodriguez-Carvajal, 1998); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *FULLPROF.*

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