Acta Cryst. (1971). B27, 1823

The Crystal Structure of $RbTh_3F_{13}$

BY GEORGE BRUNTON*

Reactor Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, *U.S.A.*

(*Received* 23 *November* 1970)

The complex fluoride $RbTh_3F_{13}$ crystallizes with space group $P2_1ma$; $a_0 = 8{\cdot}6490$ (5), $b_0 = 8{\cdot}176$ (2) and $c_0 = 7{\cdot}4453$ (4) Å. There are two formula weights per unit cell and the calculated density is 6·488 g.cm^{-3}. There are two thorium ions in the asymmetrical unit and each of these ions has nine nearest neighbor fluorine ions at the corners of capped trigonal prisms. The Th–F distances range from 2·32 (3) to 2·48 (2) Å. The Rb ion has eleven nearest neighbor fluorine ions in the range 2·79 (3) to 3·37 (2) Å. The final discrepancy index is 0·0710 for 2134 Ag $K\alpha$ reflections $> \sigma$.

Single crystals of $RbTh_3F_{13}$ were grown as the primary phase from a melt having the composition; 40 mole% RbF and 60 mole% ThF_4. A single crystal ellipsoid $0{\cdot}312 \times 0{\cdot}234 \times 0{\cdot}312$ mm was mounted on a computer controlled Picker four-circle goniostat equipped with a scintillation counter detector.

The conditions for reflection, $hk0$, $h = 2n$, and the diffraction symmetry *mmm* are consistent with space groups *Pmma*, $P2_1ma$ and *Pm2a*. The final choice for the structure is $P2_1ma$. The more conventional space group $Pmc2_1$ may be derived by a change of axes, *bca*, from $P2_1ma$ with corresponding appropriate changes in Tables 1 and 3. Independent reflections hkl, h, k and $l \geq 0$ were measured by the θ–2θ scan technique using unfiltered Ag $K\alpha$ radiation to $2\theta = 70°$. The 2576 accessible reflections were corrected for Lorentz and polarization effects and absorption ($\mu = 466{\cdot}95$ cm^{-1}), but only the 2134 reflections $> \sigma$ were used in the least-squares adjustment for the final parameters.

* Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

The unit-cell parameters were determined by a least-squares adjustment of 33 high angle (120–145° 2θ) Cu $K\alpha_1$ reflections (Cu $K\alpha_1 = 1{\cdot}54050$ Å, $T = 24$ °C). The cell parameters are $a_0 = 8{\cdot}6490$ (5), $b_0 = 8{\cdot}176$ (2) and $c_0 = 7{\cdot}4453$ (4) Å. There are two formula weights per unit cell and the calculated density is 6·488 g.cm^{-3}.

The initial positions of the Th ions were determined from a three-dimensional plot of the Patterson function. These Th positions were tried in each of the three possible space groups and good results were obtained with only $P2_1ma$. The positions of the Rb and F ions were determined from Fourier and difference Fourier syntheses. The structure was refined by iterative least-squares adjustment using a modification of the Busing, Martin & Levy (1962) computer program. The quantity minimized by the least-squares program was $\sum w||F_o^2| - |F_c^2||$ with weights, w, equal to the reciprocals of the variances estimated from the empirical equation

$$\sigma^2(F_o^2) = \{[T + B + (0{\cdot}03(T-B)]^2\}/[A(\mathrm{Lp})^2]$$

where T = total counts, B = background counts, A = absorption correction, and Lp = Lorentz and polarization

Table 1. *Atomic parameters* ($\times 10^3$) *and temperature factors* ($\times 10^4$) *for* $RbTh_3F_{13}$

Standard errors in parentheses, corresponding to the last significant digit, are given by the variance-covariance matrix. Temperature factor $= \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The F temperature factors are constrained to be isotropic; $\beta_{22} = \beta_{11}$ (b^{*2}/a^{*2}), $\beta_{33} = \beta_{11}$ (c^{*2}/a^{*2}), $\beta_{12} = \beta_{13} = \beta_{23} = 0$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Th(1)	0*	0	108·2 (2)	11·7 (6)	18·6 (8)	19 (1)	0	5 (2)	0
Th(2)	834·3 (2)	252·83 (9)	602·01 (8)	14·2 (4)	16·4 (4)	26·5 (6)	+13 (5)	11 (1)	−0·4 (9)
Rb	695·9 (5)	½*	104·1 (8)	52 (5)	121 (7)	60 (6)	0	10 (6)	0

	x	y	z	β_{11}
F(1)	848 (4)	½†	453 (3)	30 (8)
F(2)	596 (2)	302 (2)	452 (3)	37 (7)
F(3)	144 (2)	744 (2)	173 (3)	27 (5)
F(4)	457 (2)	803 (2)	111 (3)	46 (7)
F(5)	865 (2)	176 (2)	304 (3)	35 (6)
F(6)	366 (3)	½†	230 (3)	23 (8)
F(7)	737 (3)	0	037 (3)	38 (9)
F(8)	179 (3)	0	364 (3)	26 (8)
F(9)	460 (3)	0	409 (4)	31 (8)

* Arbitrary value to establish origin on 2_1 axis.

† These values are not multiplied by 10^3.

Table 2. *Interatomic distances for* $RbTh_3F_{13}$

Th(1)—F(7)	2·32 (3) Å	2(Th(1)–F(4))	2·32 (2) Å	Th(1)—F(7)	2·33 (3) Å
2(Th(1)–F(5))	2.36 (3)	2(Th(1)–F(4))	2.45 (2)	Th(1)—F(7)	2.48 (3)
Th(2)—F(5)	2·32 (2)	Th(2)—F(9)	2·34 (1)	Th(2)—F(2)	2·34 (2)
Th(2)—F(3)	2·35 (2)	Th(2)—F(1)	2·38 (1)	Th(2)—F(2)	2·38 (2)
Th(2)—F(6)	2·39 (2)	Th(2)—F(4)	2·43 (2)	Th(2)—F(8)	2·48 (2)
Rb——F(1)	2·79 (3)	Rb——F(6)	2·89 (2)	2(Rb—F(3))	2·91 (2)
Rb——F(6)	3·00 (2)	2(Rb—F(2))	3·17 (2)	2(Rb—F(4))	3·22 (2)
2(Rb—F(5))	3·37 (2)	2(Rb—F(4))	3·72 (2)	F(1)—F(6)	2·50 (3)
2(F(1)—F(2))	2·72 (3)	2(F(1)—F(2))	2·82 (3)	2(F(1)—F(5))	2·83 (2)
F(2)—F(9)	2·75 (2)	F(2)—F(5)	2·77 (3)	F(2)—F(3)	2·85 (2)
F(2)—F(5)	2·90 (3)	F(2)—F(8)	2·91 (2)	F(2)—F(4)	2·94 (3)
F(2)—F(6)	3·05 (3)	F(3)—F(8)	2·54 (2)	F(3)—F(5)	2·68 (2)
F(3)—F(4)	2·70 (3)	F(3)—F(7)	2·73 (2)	F(3)—F(4)	2·80 (2)
F(3)—F(6)	2·81 (2)	F(4)—F(7)	2·72 (3)	F(4)—F(9)	2·74 (3)
F(4)—F(6)	2·75 (2)	F(4)—F(7)	2·96 (3)	F(5)—F(7)	2·69 (3)
F(5)—F(9)	2·70 (3)	F(5)—F(5)	2·88 (3)	F(8)—F(9)	2·45 (3)
F(8)—F(9)	2·54 (3)				

corrections (Brown & Levy, 1964). The scattering factors for the ions were taken from Cromer & Waber (1965) and the anomalous dispersion terms for Rb and Th for Ag $K\alpha$ radiation were taken from Cromer (1965). The values of

$$R_1 = \sum||F_o^2| - |F_c^2||/\sum|F_o^2| = 0{\cdot}0910 \text{ for } 2134 \text{ reflections} > \sigma$$

and

$$R_2 = \sum||F_o| - |F_c||/\sum|F_o| = 0{\cdot}0710 \text{ for } 2134 \text{ reflections} > \sigma.$$

The standard deviation of an observation of unit weight $[\sum w(F_o - F_c)^2/(n_o - n_v)]^{1/2}$ is 1·387 where n_o is the number of reflections, 2134, and n_v the number of variables, 53. The atomic parameters and temperature factors are listed in Table 1, the interatomic distances in Table 2

Table 3. *Observed and calculated structure factors and phase angles for* $RbTh_3F_{13}$

ALPHA = Phase angle $\alpha \times 10$

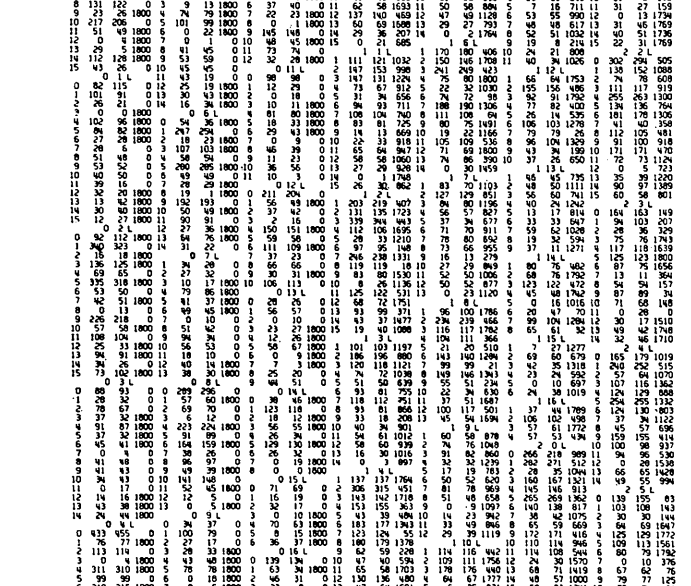

Table 3 (*cont.*)

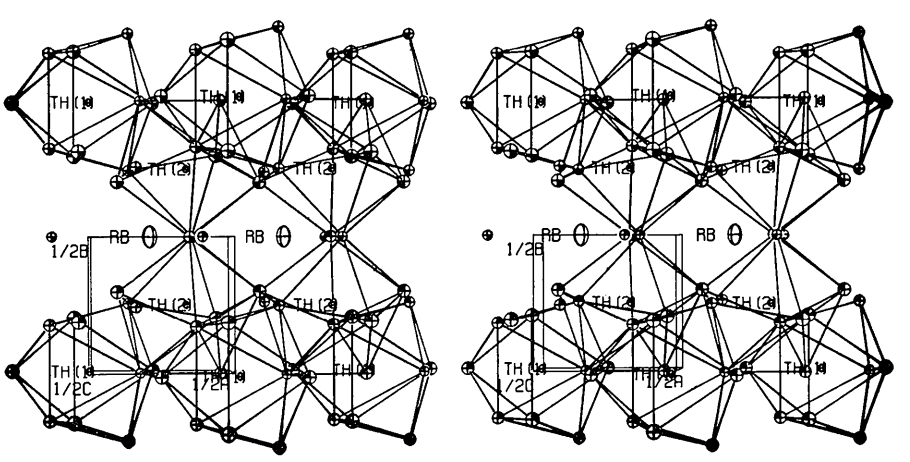

Fig. 1. The crystal structure of $RbTh_3F_{13}$.

and the observed and calculated structure factors in Table 3. An extinction correction was applied to F_c by the method suggested by Zachariasen (1967, 1968).

The absolute configuration of the crystal was determined by Hamilton's (1965) test on the discrepancy factor to be such that the $\Delta f''$s are positive [$R_2(-\Delta f'')$ $=0{\cdot}0734$]. The ratio $\dfrac{0{\cdot}0734}{0{\cdot}0710}$ is 1·034 which is significant

Table 3 (*cont.*)

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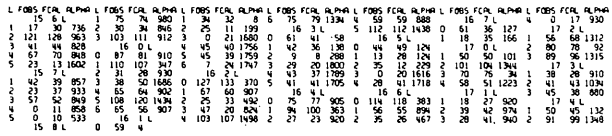

at the 0·005 significance level for a one-dimensional hypothesis and 2081 degrees of freedom.

Results

The final structure of $RbTh_3F_{13}$ is illustrated in Fig. 1. The two Th ions in the asymmetrical unit have nine nearest neighbor F ions at the corners of a trigonal prism with each of the prism faces capped by an F ion. The Th–F distances in both polyhedra range from 2·32 to 2·48 Å (Table 2) with minor differences in the standard errors. The Th(1) polyhedra form columns parallel to $\mathbf{b}_0$ by sharing edges and the shared edge, F(1)–F(6), alternates successively parallel to $\mathbf{a}_0$ at $y=0·5$ and parallel to $\mathbf{c}_0$ at $y=0·0$. The columns of Th(1) polyhedra are connected by corner sharing, F(2). The columns are intersected by layers of Rb ions and Th(2) polyhedra at $y=0·5$ and $y=0·0$ respectively. The layers are parallel to (010). Each Th(2) polyhedron shares an edge, F(3)–F(8), with each of two Th(1) polyhedra and a corner, F(4) and F(5), with each of four other Th(1) polyhedra. The F(1)–F(6) and F(3)–F(8) interatomic distances representing the shared edges are 2·50 (3) and 2·54 (2) Å respectively (Table 2). The Th(2) polyhedra do not touch one another. The Rb ions have eleven nearest neighbor F ions at distances of 2·79 (3) to 3·37 (2) Å.

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Acta Cryst. (1971). B**27**, 1826

Refinement of the Structure of Sodium β-Alumina

BY C. R. PETERS AND M. BETTMAN

Scientific Laboratory, Ford Motor Company, Dearborn, Michigan, U.S.A.

AND J. W. MOORE AND M. D. GLICK

Department of Chemistry, Wayne State University, Detroit, Michigan, U.S.A.

(*Received* 15 *September* 1970)

An X-ray diffractometer re-investigation has been carried out on a clear crystal of fusion-cast sodium β-alumina, hexagonal, space group $6_3/mmc$, $a=5·594$, $c=22·53$ Å, $D_x=D_m=3·24\pm0·02$ g.cm^{-3}; probable unit-cell content = $Na_{2·58}\ Al_{21·81}\ O_{34}$. Using Mo $K\alpha$ radiation, 1175 measured intensities were combined into 545 symmetry-independent values of significant magnitude above background. A least-squares refinement based on these 545 data yielded $R_1=0·034$. The crystal was apparently typical in that both neutron activation analysis and X-ray intensity analysis found 29 % excess soda, relative to the classical formula Na_2O . 11 Al_2O_3. In the averaged unit cell, sodium atoms are smeared out in a complex pattern in the basal mirror plane. About 0·75 sodium atoms are near each of two Beevers–Ross positions, but spread into a broad triangular pattern. The remaining sodium scattering matter is in elongated ellipsoids centered near the positions that are halfway between the oxygen atoms of the basal mirror planes. This is a sixfold set of positions, containing a total of about one sodium ion. Indications are that the counter-ion defects consist of aluminum vacancies distributed over the (single) 12-fold set of aluminum atoms. Speculations are offered concerning the structure of local defects that would average out to the mean unit cell found.

Introduction

The main features of the β-alumina structure were deduced by Bragg, Gottfried & West (1931). These authors were troubled by the small percentage of sodium found by chemical analysis, which was inconsistent with the space-group symmetry and suggested a degree of randomness in the structure. Subse-