

Acta Cryst. (1973). B29, 2976

The crystal structure of $\text{Na}_3\text{BeTh}_{10}\text{F}_{45}$.* By GEORGE BRUNTON, *Reactor Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, U. S. A.*

(Received 22 March 1973; accepted 27 August 1973)

Tetragonal, $P4_2/ncm$, $a_0 = 11.803$ (3), $c_0 = 23.420$ (5) Å, 25°C , $Z = 4$, $D_x = 6.626$. Be-4F 1.55 (1) Å, Na(1)-8F range 2.38 (2)-2.56 (1) Å, Na(2)-6F range 2.23 (2)-2.77 (2) Å, Th(1)-9F range 2.301 (6)-2.63 (1) Å, Th(2)-9F range 2.28 (1)-2.81 (1) Å, Th(3)-9F range 2.30 (1)-2.49 (2) Å. Th(1)-Th(2) polyhedra share corners F(14) and F(16), Th(1)-Th(3) polyhedra share edge F(4)-F(11), Th(2)-Th(3) polyhedra share edge F(3)-F(12) and corner F(10). Automatic diffractometer data, θ - 2θ scan, Si-Li detector, unfiltered Mo $K\alpha$.

Introduction

Thoma, Weaver, Friedman & Harris (1960) first described the two tetragonal ternary fluoride compounds, $\text{NaBeTh}_3\text{F}_{15}$ and $\text{NaBeU}_3\text{F}_{15}$, from phase equilibria studies. The structure of the thorium compound was determined and the correct stoichiometry is $\text{Na}_3\text{BeTh}_{10}\text{F}_{45}$ and for the isomorphous uranium compound it probably is $\text{Na}_3\text{BeU}_{10}\text{F}_{45}$.

Experimental

Crystals of $\text{Na}_3\text{BeTh}_{10}\text{F}_{45}$ with 2% U substituting for Th were grown from a melt of the stoichiometric composition $\text{NaF} \cdot \text{BeF}_3 \cdot 3(0.98\text{ThF}_4 \cdot 0.02\text{UF}_4)$. The uranium was included to color the crystals for absorption spectroscopy experiments. An ellipsoidal crystal (approximately $0.217 \times 0.181 \times 0.163$ mm) was mounted on a Picker four-circle goniostat equipped with a Si-Li Kevex detector. Conditions for reflections $hk0$, $h+k=2n$ and $0kl$, $l=2n$ and diffraction symmetry $4/mmm$ are consistent with the unique space group $P4_2/ncm$.

Lattice parameters were determined by least-squares adjustment of 12 Mo $K\beta$ (0.63225 Å) reflections between 50 and $60^\circ 2\theta$; $a_0 = 11.803$ (3) and $c_0 = 23.420$ (5) Å at 25°C , $Z = 4$ and $\rho_{\text{calc}} = 6.626$ g cm^{-3} .

Independent reflections were measured by the θ - 2θ scan technique using unfiltered Mo $K\alpha$ radiation and a 400 eV detector window that excludes Mo $K\beta$. Each reflection was step-scanned at intervals of $0.02^\circ 2\theta$ with 5 s count at each

step for a total of $1.6^\circ 2\theta$. The background was counted for 25 s on each side of the peak. Total range of 2θ was 3.5 - 70° and takeoff angle was 1.5° .

A standard reflection (0,0,10) was measured every 20 reflections to monitor X-ray source variations and the net count range for 0,0,10 was 31100 to 43300. The variation in net count range is corrected for linearly every 20th reflection and the extremes of variation appear to be caused by diurnal voltage fluctuations. Lorentz and polarization and absorption corrections were made on 4061 independent reflections ($\mu = 417.5$ cm^{-1} , absorption correction range 0.0089-0.0433).

Initial parameters for Th were determined from sections of the three-dimensional Patterson function. The structure was refined by iterative least-squares adjustment using a modification of *ORFLS* (Busing, Martin & Levy, 1962). Reflections with $\sigma(F_o^2) > F_o^2$ were omitted. All reflections were corrected for isotropic extinction (Coppens & Hamilton, 1970). Positional parameters for missing atoms were obtained from three-dimensional Fourier and difference Fourier sections. The quantity minimized by the least-squares program was $\sum w||F_o^2| - |s^2 F_c^2||^2$ with weights, w , equal to the reciprocals of the variances estimated from the empirical equation of Brown & Levy (1964); $\sigma^2(F_o^2)$ is $\{T + B + [0.03(T - B)]^2\} / \{A(Lp)^2\}$, where T = total counts, B = background counts, appropriately scaled for scan rate and time for the background count, A = absorption correction, and Lp = Lorentz and polarization corrections. Ionic scattering factors are from Cromer & Waber (1965) and anomalous dispersion terms are from Cromer (1965). Anisotropic thermal parameters were calculated for all ions except Be.

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

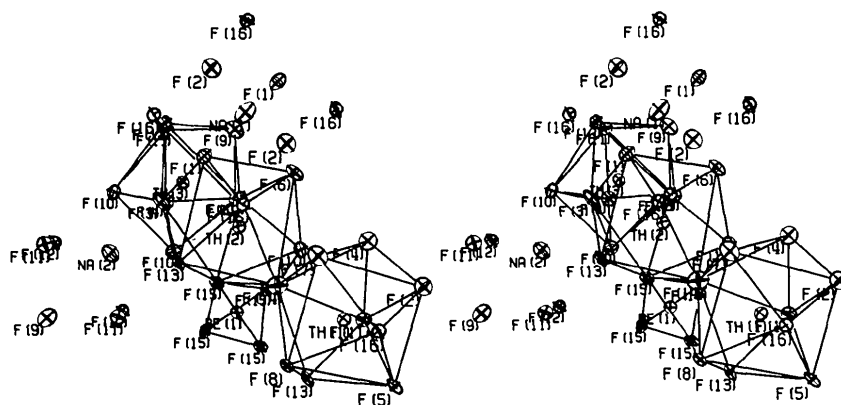


Fig. 1. Cations and polyhedra of one asymmetrical unit. View down c_0 .

Table 1. Atomic and thermal parameters, Na₃BeTh₁₀F₄₅

The standard errors are in terms of the last significant digits as estimated from the variance-covariance matrix.

Coefficients in the temperature factor: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Wyckoff position	10 ⁴ x	10 ⁴ y	10 ⁴ z	10 ⁴ β ₁₁	10 ⁴ β ₂₂	10 ⁴ β ₃₃	10 ⁴ β ₁₂	10 ⁴ β ₁₃	10 ⁴ β ₂₃	R.m.s. components (10 ² Å) along principal axes		
										1	2	3
Na(1)	2500	2500	4465 (9)	49 (8)	β ₁₁	7 (3)	20 (14)	0	0	14 (3)	14 (3)	22 (3)
Na(2)	843 (9)	x	6984 (9)	43 (6)	β ₁₁	18 (3)	-7 (7)	5 (4)	β ₁₃	15 (2)	19 (2)	23 (2)
Be	7500	2500	7500	1-3 (6)*								
Th(1)	2579-7 (6)	x	479-9 (2)	20-6 (4)	20-1 (3)	4-5 (1)	-1-3 (3)	0-4 (1)	0-4 (2)	11-0 (1)	11-8 (1)	12-4 (1)
Th(2)	2445-1 (6)	-195-8 (5)	3529-9 (2)	21-4 (4)	20-4 (4)	4-6 (1)	0-4 (3)	0-5 (1)	0-1 (1)	11-3 (1)	12-0 (1)	12-4 (1)
Th(3)	1059-3 (5)	x	1996-5 (4)	219 (3)	β ₁₁	4-1 (1)	-2-3 (4)	-0-2 (2)	β ₁₃	10-7 (1)	11-8 (1)	13-1 (1)
F(1)	1579 (13)	x	3655 (8)	33 (7)	β ₁₁	9 (3)	11 (9)	-7 (4)	β ₁₃	12 (3)	12 (3)	21 (3)
F(2)	1655 (13)	x	282 (7)	37 (7)	β ₁₁	4 (2)	5 (9)	2 (3)	β ₁₃	10 (3)	15 (3)	17 (3)
F(3)	489 (11)	x	2944 (10)	44 (8)	β ₁₁	10 (4)	-22 (11)	8 (4)	β ₁₃	6 (5)	20 (3)	22 (3)
F(4)	581 (12)	x	989 (7)	39 (7)	β ₁₁	3 (2)	-3 (9)	-2 (3)	β ₁₃	9 (3)	16 (3)	17 (3)
F(5)	1000 (10)	x	5392 (7)	28 (6)	β ₁₁	6 (2)	-12 (8)	-3 (3)	β ₁₃	9 (4)	14 (3)	17 (2)
F(6)	1161 (14)	x	8656 (7)	35 (8)	β ₁₁	8 (3)	18 (10)	-4 (4)	β ₁₃	11 (3)	14 (3)	20 (3)
F(7)	879 (12)	-x	0	42 (8)	β ₁₁	5 (2)	10 (10)	1 (4)	β ₁₃	12 (3)	15 (3)	19 (3)
F(8)	1613 (10)	-x	5000	18 (5)	β ₁₁	8 (3)	-6 (7)	-2 (4)	β ₁₃	9 (3)	13 (3)	15 (2)
F(9)	2500	-x	2019 (13)	47 (11)	β ₁₁	5 (3)	-14 (17)	0		12 (4)	15 (4)	21 (4)
F(10)	4203 (11)	2500	1922 (5)	34 (8)	β ₁₁	7 (2)	1 (6)	2 (3)	-5 (3)	12 (2)	16 (2)	17 (2)
F(11)	600 (10)	5869 (12)	1401 (4)	30 (7)	35 (8)	4 (1)	1 (7)	2 (3)	4 (3)	9 (2)	15 (2)	15 (2)
F(12)	577 (11)	2583 (13)	2618 (5)	32 (8)	29 (8)	10 (2)	7 (7)	3 (3)	3 (4)	13 (2)	14 (2)	18 (2)
F(13)	1049 (11)	2575 (14)	1056 (5)	30 (7)	28 (8)	8 (2)	13 (6)	1 (3)	2 (3)	8 (3)	15 (2)	17 (2)
F(14)	1640 (14)	5920 (10)	992 (5)	40 (10)	17 (6)	7 (2)	-3 (8)	1 (5)	6 (5)	13 (2)	17 (2)	21 (2)
F(15)	1926 (10)	8335 (15)	2906 (4)	30 (7)	59 (12)	4 (2)	-6 (6)	3 (3)	-4 (3)	9 (2)	12 (2)	16 (2)
F(16)	2452 (15)	8357 (9)	4501 (6)	29 (7)	21 (6)	8 (2)	-6 (8)	-4 (3)	2 (4)	12 (2)	13 (2)	17 (2)

* Isotropic B.

Table 2. *Interatomic distances, Na₃BeTh₁₀F₄₅*

2[Na(1)—F(2)]	2.38 (2) Å	2[Na(1)—F(1)]	2.44 (2) Å	4[Na(1)—F(16)]	2.56 (1) Å
Na(2)—F(3)	2.23 (2)	2[Na(2)—F(11)]	2.32 (2)	2[Na(2)—F(12)]	2.41 (2)
Na(2)—F(9)	2.77 (2)	4[Be—F(15)]	1.55 (1)	Th(1)—F(7)	2.301 (6)
Th(1)—F(5)	2.322 (5)	Th(1)—F(14)	2.33 (2)	Th(1)—F(11)	2.34 (1)
Th(1)—F(8)	2.35 (3)	Th(1)—F(16)	2.37 (1)	Th(1)—F(2)	2.37 (2)
Th(1)—F(13)	2.43 (2)	Th(1)—F(4)	2.63 (1)	Th(2)—F(13)	2.28 (1)
Th(2)—F(14)	2.29 (2)	Th(2)—F(6)	2.315 (2)	Th(2)—F(12)	2.33 (1)
Th(2)—F(15)	2.33 (1)	Th(2)—F(1)	2.349 (7)	Th(2)—F(16)	2.36 (1)
Th(2)—F(10)	2.36 (1)	Th(2)—F(3)	2.81 (1)	2[Th(3)—F(10)]	2.30 (1)
2[Th(3)—F(11)]	2.34 (1)	2[Th(3)—F(12)]	2.38 (1)	Th(3)—F(9)	2.41 (1)
Th(3)—F(3)	2.41 (2)	Th(3)—F(4)	2.49 (2)	F(1)—F(3)	2.47 (3)
2[F(1)—F(16)]	2.68 (2)	2[F(1)—F(6)]	2.71 (2)	F(2)—F(4)	2.44 (3)
2[F(2)—F(16)]	2.63 (2)	2[F(3)—F(12)]	2.58 (2)	F(4)—F(11)	2.55 (2)
2[F(4)—F(10)]	2.79 (2)	2[F(5)—F(13)]	2.75 (2)	2[F(5)—F(16)]	2.81 (2)
2[F(6)—F(10)]	2.70 (2)	2[F(6)—F(16)]	2.75 (2)	2[F(7)—F(14)]	2.66 (2)
2[F(7)—F(16)]	2.70 (2)	2[F(8)—F(13)]	2.69 (1)	2[F(8)—F(16)]	2.76 (1)
4[F(9)—F(11)]	2.67 (2)	4[F(9)—F(12)]	2.67 (2)	F(10)—F(14)	2.57 (2)
F(10)—F(12)	2.68 (2)	F(10)—F(10)	2.78 (3)	F(11)—F(13)	2.55 (2)
F(13)—F(16)	2.76 (2)	F(15)—F(15)	2.44 (2)	2[F(15)—F(15)]	2.57 (2)

Tetrahedral angles around Be 2[104.0 (8)°] 4[112.3 (4)°]

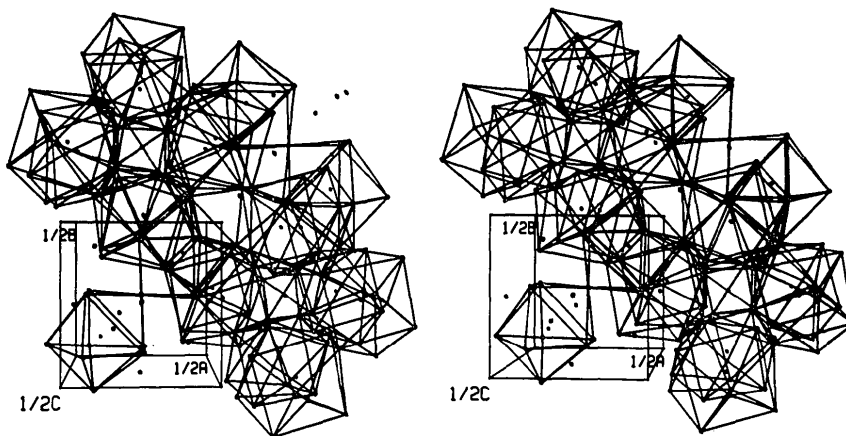


Fig. 2. One half unit cell of Na₃BeTh₁₀F₄₅, showing Th polyhedra and Na ions.

Results

Tables 1 and 2 list respectively the atomic and thermal parameters, interatomic distances and angles.* The discrepancy index $R(F^2) = \frac{\sum(F_o^2 - \sum F_c^2)/F_o^2}{0.0797}$ for 2885 reflections $> \sigma(F_o^2)$ and 0.1157 for all reflections. The discrepancy index $R(F) = \frac{\sum||F_o| - |F_c||}{\sum|F_o|} = 0.0642$ for $F_o > \sigma(F_o)$ and 0.1104 for all F_o . The standard deviation of an observation of unit weight is 1.481. Each of the three independent Th ions is surrounded by nine F⁻, forming a polyhedron that is a trigonal prism capped on each prism face. A framework structure is formed by edge and corner sharing Th-F polyhedra and Be-F tetrahedra as illustrated in Figs. 1 and

2. Polyhedron Th(1) shares two corners, F(14) and F(16) with Th(a) and an edge, F(4)—F(11) with Th(3). Th(2) shares corners with the Be tetrahedron and an edge, F(3)—F(12) and a corner F(10) with Th(3). Two Na ions complete the framework.

Dr L. M. Toth supplied the crystals.

References

- BROWN, G. M. & LEVY, H. A. (1964). *J. Phys.* **25**, 497–502.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. USAEC Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
 COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* **A26**, 71–83.
 CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
 THOMA, R. E., WEAVER, C. F., FRIEDMAN, H. A. & HARRIS, L. A. (1960). *J. Amer. Ceram. Soc.* **48**, 608–609.

* A table of observed and calculated structure factors, and extinction corrections, EC, less than 1.0 has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30205 (34 pp., 1 microfiche). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.