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The crystal structure of $\beta\text{-KCeF}_4^*$. By GEORGE BRUNTON, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, U.S.A.

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The crystal structure of $\beta\text{-KCeF}_4$ has been determined by X-ray diffraction. The space group is $Pnma$, $a_0 = 6.2895 \pm 0.0003$, $b_0 = 3.8040 \pm 0.0003$, $c_0 = 15.596 \pm 0.002$ Å. The structure consists of a three-dimensional framework of 9-coordinated Ce–F and K–F polyhedra.

Alkali metal complexes with the rare earth fluorides are being studied because of their relationship to the corresponding actinide elements which are of interest to molten salt breeder reactor technology. Cerium is analogous in its properties to plutonium and a preliminary study of the

phase relationships in the system KF-CeF_3 (Barton, Brunton, Hsu & Insley, 1967) showed that there are two stable phases of KCeF_4 : $\alpha\text{-KCeF}_4$, fluorite-cubic and $\beta\text{-KCeF}_4$, orthorhombic.

$\beta\text{-KCeF}_4$ is the first polymorph of orthorhombic symmetry which has been described. Zachariasen (1948a,b) described compounds $\beta_1\text{-KLaF}_4$ and $\beta_1\text{-KCeF}_4$ and reported them to be isostructural with $\beta_1\text{-K}_2\text{UF}_6$ which has $P62m$ symmetry. Sears (1967) has determined the crystal structure

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Table 1. *Atomic parameters for $\beta\text{-KCeF}_4$*

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ce	0.25105 (0.4)	0.25	0.43765 (0.2)	0.00338 (0.8)	0.0077 (2)	0.00072 (0.1)	0.0	-0.00002 (0.1)	0.0
K	0.2766 (3)	0.75	0.20178 (0.9)	0.0046 (2)	0.0250 (8)	0.00104 (0.4)	0.0	0.00008 (0.7)	0.0
F(1)	0.1376 (6)	0.25	0.0364 (3)	0.0060 (7)	0.020 (30)	0.0015 (2)	0.0	0.0004 (3)	0.0
F(2)	-0.0053 (6)	0.75	0.4406 (2)	0.0062 (8)	0.018 (30)	0.0009 (2)	0.0	0.0002 (2)	0.0
F(3)	0.3970 (7)	0.75	0.3638 (3)	0.0095 (8)	0.010 (20)	0.0013 (2)	0.0	0.0008 (3)	0.0
F(4)	0.0849 (7)	0.25	0.3044 (3)	0.0131 (9)	0.015 (20)	0.0012 (2)	0.0	-0.0003 (3)	0.0

* Coefficients in the temperature factor; $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The number in parentheses is $\sigma \times 10^4$.

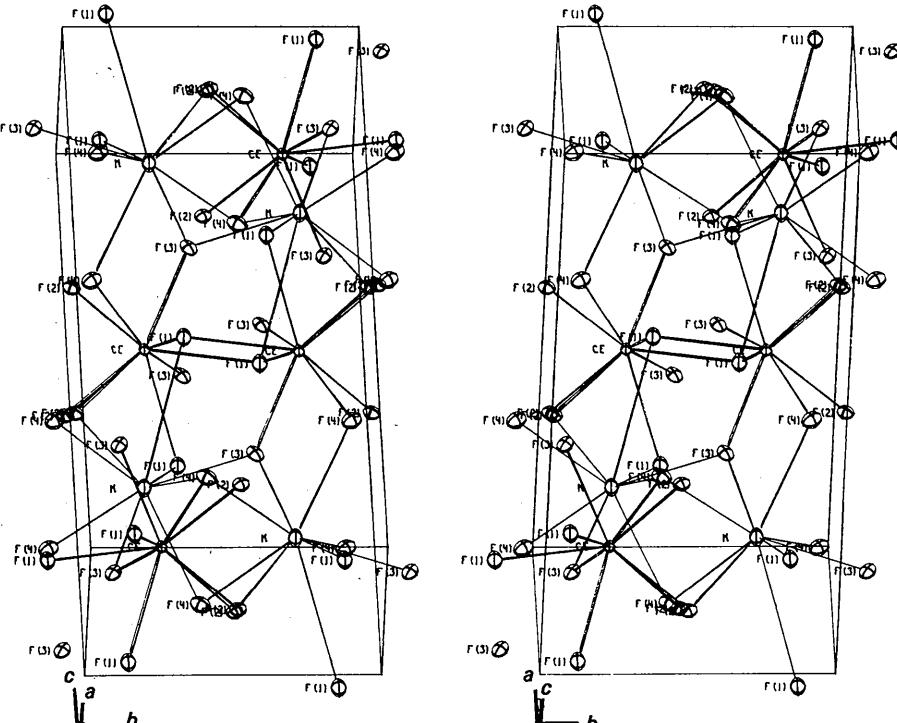


Fig. 1. The contents of one unit cell (outlined) of $\beta\text{-KCeF}_4$ tilted 45° around a_0 .

of β_1 -KLaF₄ and has shown that it is not isostructural with β_1 -K₂UF₆ as had been proposed. Sears shows that the space group for β_1 -KLaF₄ is $P\bar{6}$, that one of the cation positions is statistically occupied by 0.5K⁺ and 0.5La³⁺, and that there is statistical occupation of two of the F⁻ positions.

Zachariasen's β_1 -KCeF₄ does not occur as an equilibrium compound and has not been re-examined.

Experimental

Single crystals of β -KCeF₄ were grown as the primary phase from a melt having the composition 35 mole % KF, 65 mole % CeF₃. At the stoichiometric composition, β -KCeF₄ becomes fluorite-cubic α -KCeF₄ above 755°C. Fragments of the crystals were ground to approximately spherical shape in an air-driven race and an ellipsoid of dimensions 0.182 by 0.252 by 0.234 mm was selected for single-crystal diffraction. The intensities of the reflections were measured with a computer-operated Picker four-circle goniostat and a scintillation-counter detector using unfiltered Mo $K\alpha$ radiation ($K\alpha_1 = 0.70926$ and $K\alpha_2 = 0.713543$ Å). Twelve hundred and seventy nine independent reflections out to $80^\circ 2\theta$ were measured by the 2θ scan technique. The linear absorption for Mo $K\alpha$ radiation by β -KCeF₄ is 13.396 mm⁻¹ and an absorption correction was calculated for each reflection.

Refinement and results

The observed conditions for diffraction, hkl : no conditions, $0kl$: $k+l=2n$, and $hk0$: $h=2n$, are consistent with the space group *Pnma*. The lattice parameters were refined as part of the set up procedure on the X-ray diffractometer (Busing, Ellison, Levy, King & Roseberry, 1968). Twenty nine additional high angle reflections were measured at plus and minus 2θ and the final least-squares results for the lattice parameters are: $a_0 = 6.2895 \pm 0.0003$, $b_0 = 3.8040 \pm 0.0003$ and $c_0 = 15.596 \pm 0.002$ Å. The calculated density is 4.5424 g.cm $^{-3}$ and $Z = 4$. The reflections were corrected for Lorentz-polarization factors and for absorption and a three-dimensional Patterson was calculated from these data. All of the atoms in the asymmetric unit are at special position 4(c) with $y = 0.25$. The x and z positional parameters and the anisotropic temperature factors were refined using a modification of the Busing, Martin & Levy (1962) least-squares computer program. The quantity $\Sigma w(F_o - F_c)^2$ was minimized with weights, w , equal to the reciprocals of the variances which were estimated from the empirical equation: $\sigma^2(F_o^2) = s(T + B + 0.0036(T - B)^2)/(Lp)^2$, where s = scale factor, T = total, B = background count, and Lp =

Lorentz-polarization correction. Scattering factors for K^+ , Ce^{3+} and F^- were taken from Cromer & Waber (1965) and the values of $4f' = -0.3$ and $4f''' = 3.0$ electrons were taken for the anomalous dispersion of Mo $K\alpha$ radiation by

Table 3. Observed and calculated structure factors for β - $KCeF_4$

Table 2. Interatomic distances for β -KCeF₄

Ce–F(4)	2·326 (4) Å	K–F(3)	2·587 (5) Å
2[Ce–F(3)]	2·406 (3)	K–F(2)	2·611 (4)
Ce–F(2)	2·448 (4)	K–F(3)	2·639 (5)
Ce–F(1)	2·465 (4)	2[K–F(4)]	2·717 (3)
2[Ce–F(2)]	2·494 (3)	2[K–F(4)]	2·763 (4)
2[Ce–F(1)]	2·546 (4)	2[K–F(1)]	3·321 (4)
F(1)–F(3)	2·701 (6)	F(1)–F(2)	2·753 (6)
2[F(1)–F(1)]	2·812 (6)	2[F(1)–F(3)]	2·885 (5)
2[F(1)–F(2)]	2·965 (5)	2[F(2)–F(2)]	2·655 (5)
F(2)–F(3)	2·800 (6)	2[F(2)–F(4)]	2·907 (4)
2[F(3)–F(4)]	2·887 (5)		

Table 3 (*cont.*)

cerium [Dauben & Templeton (1955)]. The positional parameters and anisotropic temperature factors are listed in Table 1. The discrepancy index $R = \Sigma ||F_o - |F_0|| / \Sigma |F_0| = 0.0433$. The standard deviation of an observation of unit weight = $[\Sigma w(F_o - F_c)^2 / (n_o - n_v)]^{1/2} = 1.5688$ where n_o is the number of reflections and n_v the number of variables.

Table 2 contains a list of the interatomic distances and Table 3 contains the observed and calculated structure factors. Fig. 1 is a stereoscopic pair of drawings showing

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The crystal and molecular structure of strontium tartrate trihydrate. A correction. By G. K. AMBADY, *Centre of Advanced Study in Biophysics and Crystallography, University of Madras, Madras 25, India*

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A corrected value for one atomic coordinate is given.

In Table 3 of a recent article (Ambady, 1968) the incorrect value 0.6787 is given for the y coordinate of atom C(3). The correct value is 0.6687.

Reference

AMBADY, G. K. (1968). *Acta Cryst.* B24, 1548.