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Introduction

This paper is the first of a planned series concerning the preparation and crystallographic characterization of compounds of berkelium.

The first structure determination of a compound of berkelium was carried out by Cunningham and Wallmann (1) in 1962 by x-ray diffraction. They reported a lattice parameter of 5.33±0.02 A based on the indexing of four lines in the face-centered cubic fluorite-type structure, obtained from 0.004 μg of berkelium "dioxide". With the present availability of microgram quantities of berkelium, a systematic study of the compounds of berkelium was undertaken. The preparative technique used was that developed by Cunningham and Wallmann (1,2) using single beads of ion exchange resin.

Experimental

A. Materials

About 16 μg of Bk^{249} were recovered and purified by extraction from an aqueous nitrate solution with hydrogen di-(2-ethylhexyl) orthophosphoric acid, followed by stripping of the organic phase with hydrogen peroxide in nitric

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*The experimental work reported is taken from a thesis to be submitted by J. R. Peterson to the Graduate Division of the University of California in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

acid solution (3). The aqueous berkelium solution was then further purified using only leached quartz containers, specially washed Dowex 50W resin, and high-purity HCl reagents. The Bk-Ce separation was carried out by loading the berkelium solution onto the top of a 1 mm diameter 2.7 cm long Dowex 50 x 4 resin bed, pretreating the resin bed with a small volume of 2 M HCl, and eluting with saturated alcoholic (20 vol. % EtOH) HCl to separate out the berkelium fraction. Under these conditions the Ce and other lanthanides remain on the column. The berkelium fraction was then loaded onto the top of another 1 mm diameter 2.7 cm long Dowex 50 x 4 resin bed in a 0.05 M HCl solution. In this clean-up column, to separate the berkelium from the common inorganic impurities like Na, Ca, Mg, Al, etc., the procedure is to elute with 1.5-2.0 M HCl until the first sign of activity, then switch to 6 M HCl and strip off the activity in as small a volume as possible.

Evaluation of sample purity was made through copper-spark emission spectrographic analyses of the reagents used and by direct mass analysis of the Bk sample for the determination of total cerium and neodymium content. Two ml samples of the HCl solutions used in the final clean-up column were analyzed spectrographically and shown to have no detectable impurities other than 5 ppb Ca. Limits of detection for the various elements by this method of analysis are given in the literature (4). Mass analysis results were 0.27 atom percent total cerium and 0.06 atom percent total neodymium.

This purified material was sorbed to saturation on specially washed Dowex 50 (<10 ppm ash) resin beads of about 0.2 μg capacity each. The "dioxide" is prepared directly from the berkelium-loaded ion exchange resin bead by calcination in air at 1200°C. The techniques employed in this air calcination and those for the subsequent hydrogen reduction have been published previously (1,2,5). Hydrogen reduction of the dioxide at 600° C leads to the body-centered cubic Mn_2O_3-type berkelium sesquioxide. Reoxidation in air or oxygen at 600°C will rapidly convert the sesquioxide back to the dioxide.

Several samples of each compound type have been prepared. Due to the rapid growth of Cf^{249} into the Bk^{249} samples (ca. 0.2% per day), all the compounds prepared contained varying amounts of Cf^{249}, but in all cases the Bk^{249} content was $\geq$ 95 atom percent.

B. Diffraction Equipment

All samples were examined by standard x-ray powder techniques. The diffraction equipment consisted of a Model 80-000 Jarrel-Ash Microfocus x-ray source and a 57.3 mm diameter Norelco Precision Powder Camera, manufactured by the Phillips Electronics Instrument Company. Exposure times varied from 8 to 12 hours running at 45 kV - 3.5 ma and using Ilford G Industrial film.

Results and Discussions

In some cases the line positions on the powder patterns were independently measured by two observers and their results averaged. Following indexing the observed Bragg angles were transferred to cards for computer determination of the most probable lattice parameter (6) according to a least-squares fit of the differences between observed and calculated $\sin^2\theta$ values.

Theoretical line intensities were calculated by means of the POWD program developed by Smith (7). The $(Fe, Mn)_2O_3$, bixbyite, structure (8) was assumed for Bk_2O_3, whereas the CaF_2, fluorite, structure was assumed for BkO_2. In both cases all lines could be indexed on the basis of the assumed structures and agreement between observed and calculated line intensities was considered satisfactory.

Table I lists the observed lattice parameters for a few of the individual compound preparations along with their Cf^{249} content.

Note that in the case of the berkelium dioxides the cubic parameter increases with time, apparently corresponding to the formation of the larger-than-Bk^{4+} Cf^{3+} ions; however, the oxidation state assumed by Cf in a BkO_2 matrix is not known. The opposite case is evident in the sesquioxides since

TABLE I

Crystallographic Properties of the Berkelium Oxides

Sample number	Film number	Compound[a]	Cf^{249} [b] content (atom %)	Observed[c] a_0 (A)	±2σ[d]	Method of Preparation
JRP-VIII	2560 A	BkO_2	0.88	5.334	.001	air ignition at 1200°C
JRP-X	2564 A	BkO_2	1.10	5.335	.001	$Bk_2O_3 + O_2$ at 600°C for 61 min
JRP-XVII	2596 A	BkO_2	3.68	5.336	.001	air fired BkO_2 + HF at 500°C for 62 min
JRP-X	2568 A	Bk_2O_3	1.53	10.889	.003	low temp. $BkO_2 + H_2$ at 600°C for 60 min
JRP-IX	2572 A	Bk_2O_3	1.75	10.887	.001	H_2 reduction of higher oxide at 600°C for 64 min
JRP-XV	2590 A	Bk_2O_3	3.26	10.885	.001	air fired $BkO_2 + H_2$ at 600°C for 60 min

[a] The stoichiometries of both berkelium oxides were assumed. Direct determination was deemed impossible on the 0.2 μg samples.

[b] Calculated assuming Bk^{249} half-life is 314 days.

[c] Calculated least squares value. See text.

[d] This represents the 95% confidence range reflecting only the internal consistency of the data for the individual preparation.

Cf^{3+} is smaller than Bk^{3+}. The change in the cubic lattice parameter of BkO_2 with time is currently under investigation.

Table II gives the line list and indexing for a representative BkO_2 pattern, the observed and calculated 2θ values, and the observed and calculated line intensities.

A plot of the cubic lattice parameters for the actinide "dioxides" is shown in Fig. I. Dioxides of elements beyond berkelium are unknown. Although the data clearly show the "actinide contraction", the evident cusp at Cm has no immediate explanation. The similar cusp noted in sesquioxide parameters of the 4f elements has been attributed to the effect of the half-filled 4f

TABLE II

Line List and Indexing for BkO_2 (JRP-VIII, Film 2560 A)

hkl	Observed[a] 2θ	Calculated[b] 2θ	Observed[a] Line intensity	Calculated[c] Line intensity
111	28.99	29.00	10.0	10.0
200	33.60	33.61	6.5	3.8
220	48.25	48.26	8.5	4.8
311	57.24	57.29	8.5	4.7
222	60.09	60.09	4.0	1.1
$400\alpha_1$	70.54	70.57	3.5	0.8
$331\alpha_1$	78.04	78.03	5.5	2.0
$420\alpha_1$	80.49	80.46	4.5	1.5
$422\alpha_1$	90.08	90.07	5.5	1.7
$333\alpha_1$	97.33	97.25	5.5	1.8
$440\alpha_1$	109.54	109.56	3.0	0.8
$531\alpha_1$	117.38	117.39	5.5	1.8
$531\alpha_2$	117.83	117.86	3.5	0.9
$600\alpha_1$	120.08	120.11	4.5	1.0
$600\alpha_2$	120.63	120.61	2.5	0.5
$620\alpha_1$	131.93	131.96	5.5	1.3
$620\alpha_2$	132.63	132.60	3.5	0.6
$533\alpha_1$	142.58	142.53	5.0	1.4
$533\alpha_2$	143.43	143.38	3.5	0.7
$622\alpha_1$	146.63	146.66	5.0	1.4
$622\alpha_2$	147.57	147.62	3.5	0.7

[a] Two independent observer's averaged readings (2θ readings are $\pm 0.10^\circ$) and averaged intensities on a scale from 10 to 0.

[b] Based on the cubic parameter 5.3335 A, $\lambda(\bar{\alpha}) = 1.54178$ A, $\lambda(\alpha_1) = 1.54051$ A, and $\lambda(\alpha_2) = 1.54433$ A.

[c] Calculated using the POWD intensity program and scaled such that the most intense line had I = 10.

subshell. In the actinide dioxides, however, this point should appear at Bk rather than Cm. An alternative explanation is that the oxygen-curium ratio in "CmO_2" is substantially below 2 or the oxygen-berkelium ratio in "BkO_2" is greater than 2.

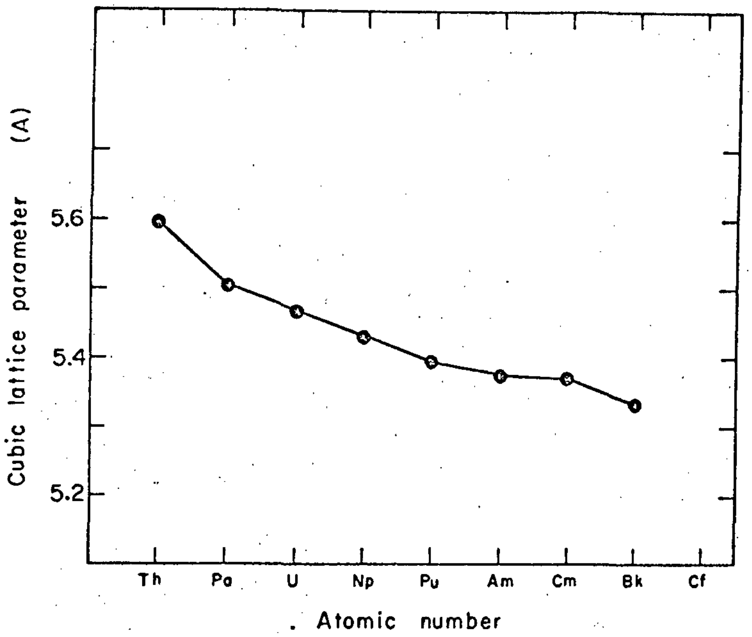

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FIG. I

Actinide dioxide lattice parameters.

Assuming that the actinide "dioxides" do in fact have that stoichiometry, a self-consistent set of actinide quadrivalent ionic radii can be calculated from their unit cell parameters. Adopting the conventions of Zachariasen (9), whereby we add 0.10 A to correct the metal oxygen distance for covalent character in the metal-oxygen bond, take the O^{2-} ionic radius to be 1.46 A, and subtract 0.08 A to correct from coordination number 8 to 6, we calculate the following quadrivalent ionic radii in angstroms:

Th^{4+}	0.984	Pu^{4+}	0.896
Pa^{4+}	0.944	Am^{4+}	0.888
U^{4+}	0.929	Cm^{4+}	0.886
Np^{4+}	0.913	Bk^{4+}	0.870

The assumptions made in calculating these numbers should be borne in mind. At best, they are relative values and in many instances were calculated from cubic parameters determined from oxides whose exact stoichiometries have not been determined. However the numbers clearly reflect an "actinide contraction".

Table III gives the line list and indexing, etc., for one of the samples of Bk_2O_3.

TABLE III

Line List and Indexing for Bk_2O_3 (JRP-IX, Film 2572 A)

hkl	Observed[a] 2θ	Calculated[b] 2θ	Observed[a] Line intensity	Calculated[c] Line intensity
222	28.40	28.40	10	100
321	30.80	30.73	0-1	2.5
400	32.90	32.91	8	39.8
411	34.92	34.97	2-3	5.3
332	38.72	38.80	1	2.3
431	42.32	42.33	6	7.3
125	45.52	45.64	0-1	1.7
440	47.22	47.23	9	38.6
433	48.82	48.77	1	2.2
600	50.22	50.28	1	0.4
611	51.82	51.76	3	4.6
541	54.52	54.63	2	3.6
622	56.02	56.03	8	35.5
631	57.34	57.41	4	5.7
444	58.84	58.76	4	8.1
543	60.04	60.09	2	2.4
640	61.34	61.41	1	1.1
633	62.74	62.71	1-2	2.9
642	64.04	64.00	4	1.4
156	67.74	67.78	2	3.2
800	69.04	69.01	3	4.9
811	70.24	70.24	2	4.1
820	71.54	71.45	1	2.0
653	72.64	72.66	2	2.4
822	73.84	73.86	2	1.3
831	75.04	75.06	3	4.1

(continued)

TABLE III

(continued)

hkl	Observed[a] 2 θ	Calculated[b] 2 θ	Observed[a] Line intensity	Calculated[c] Line intensity
662	76.24	76.24	6	10.7
840	78.54	78.60	6	8.6
833	79.66	79.77	0-1	1.3
842	81.06	80.93	0-1	1.1
655	82.16	82.09	2	2.9
851	84.36	84.41	3	3.1
763	86.76	86.71	2-3	2.4
844	87.86	87.86	5	7.4
853α_1	88.86	88.92	3	3.0
860α_1	89.96	90.07	0-1	1.6
1011α_1	91.16	91.22	0-1	1.1
862α_1	92.36	92.36	3	3.6
1022α_1	94.66	94.66	5-6	7.5
765α_1	95.76	95.82	3-4	3.5
855α_1	98.16	98.13	3	3.2
864α_1	99.26	99.29	2-3	2.9
1033α_1	100.56	100.45	2	2.4
1042α_1	101.76	101.62	0-1	2.8
873α_1	102.98	102.80	1-2	2.5
1051α_1	105.16	105.16	3	3.1
880α_1	106.38	106.35	2-3	2.2
1053α_1	109.88	109.98	3	2.8
875α_1	112.48	112.44	0-1	2.5
1062α_1	113.68	113.68	4-5	7.3
884α_1	116.18	116.21	3	3.8
981α_1	117.38	117.50	2-3	4.1
1220α_1	118.78	118.80	0-1	2.5
1071α_1	120.08	120.12	0-1	2.9
1222α_1	121.28	121.46	0-1	3.7
983α_1	122.78	122.81	1-2	3.0
1161α_1	125.50	125.58	2	3.5
1240α_1	127.00	127.01	2	5.0
1242α_1	129.80	129.94	2	7.1
976α_1	131.40	131.45	0-1	3.3

(continued)

TABLE III

(continued)

hkl	Observed[a] 2θ	Calculated[b] 2θ	Observed[a] Line intensity	Calculated[c] Line intensity
$1082\alpha_1$	132.90	133.00	2	5.4
$985\alpha_1$	134.60	134.59	2	3.7
$1066\alpha_1$	136.30	136.23	1	2.0
$1066\alpha_2$	137.00	136.94	0-1	0.9
$1075\alpha_1$	137.90	137.91	1	2.8
$1244\alpha_1$	139.60	139.65	1	3.8
$1253\alpha_1$	141.50	141.46	0-1	2.1
$1260\alpha_1$	143.40	143.34	3	10.5
$1091\alpha_1$	145.20	145.31	1-2	5.1
$1262\alpha_1$	147.30	147.38	2	9.5
$1181\alpha_1$	149.62	149.57	1-2	6.8
$1093\alpha_1$	154.62	154.46	2-3	3.9
$987\alpha_1$	160.42	160.45	3	12.4
$987\alpha_2$	162.32	162.17	1-2	6.2
$1264\alpha_1$	164.22	164.23	2-3	18.7

[a] A single reading of the powder pattern (2θ readings are $\pm 0.10^{\circ}$). Observed intensities are on a scale of 10 to 0.

[b] Based on the cubic parameter 10.8865 A, $\lambda(\bar{\alpha}) = 1.54178$ A, $\lambda(\alpha_1) = 1.54051$ A, $\lambda(\alpha_2) = 1.54433$ A.

[c] Calculated using the POWD intensity program and scaled such that the most intense line had I = 100.

A plot of the cubic lattice parameters of the lanthanide and actinide Mn_2O_3-type sesquioxides is given in Fig. II. The cubic Cf_2O_3 sample whose lattice parameter is plotted here is from a single sample known to contain rare earth contamination (estimated at 1.6 atom percent)(10). A second preparation of the cubic sesquioxide has been obtained recently (11), but the resulting lattice parameter is not yet available.

Both series of sesquioxides show the characteristic 4f and 5f contractions, as well as the cusp at the point of the half-filled electron subshell.

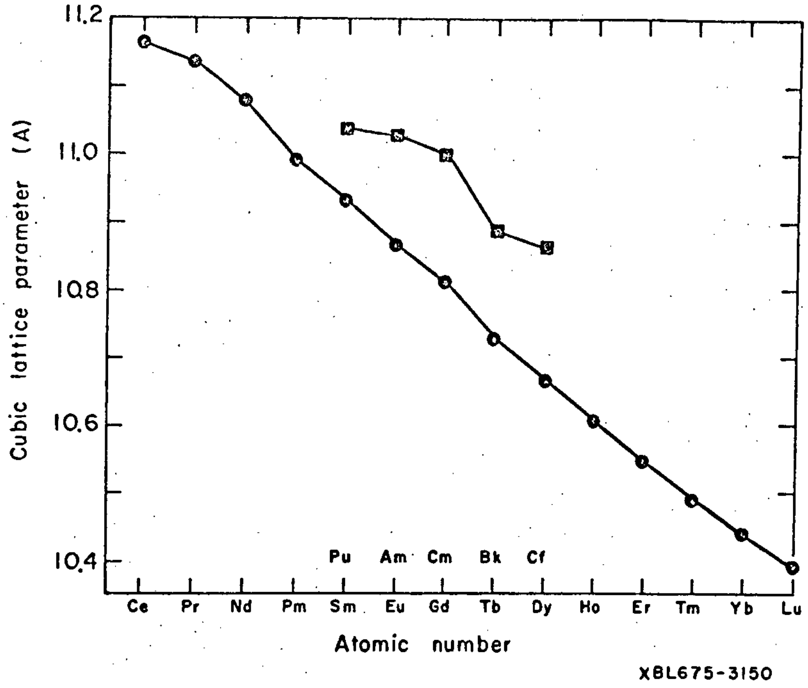

FIG. II

Cubic Lattice Parameters for the Lanthanide and Actinide Mn_2O_3-Type Sesquioxides

This series of isomorphic compounds lends itself for calculation of the corresponding trivalent ionic radii. Again, following the method of Zachariasen (9), whereby we assume a 0.08 A correction for covalent character in the metal-oxygen bond, and take the O^{2-} radius to be 1.46 A, we calculated the six-fold coordinated trivalent ionic radii to be as tabulated in Table IV.

The numbers given in Table IV should be regarded with caution and considered only as relative values. Such relative values are often very useful, however, for predicting actinide crystal chemistry on the basis of radius ratios and known lanthanide crystal chemistry. They are also useful in the correlation of various thermodynamic properties.

TABLE IV

Ionic Radii of the Trivalent Lanthanide (12) and Actinide Ions
(Based on Cubic Sesquioxide Data--See Text)

Ion	Radius, A	Ion	Radius, A	Ion	Radius, A
Ce^{+++}	1.018	Tb^{+++}	0.920	Pu^{+++}	0.987
Pr^{+++}	1.008	Dy^{+++}	0.907	Am^{+++}	0.985
Nd^{+++}	0.995	Ho^{+++}	0.894	Cm^{+++}	0.979
Pm^{+++}	0.976	Er^{+++}	0.881	Bk^{+++}	0.954
Sm^{+++}	0.964	Tm^{+++}	0.869	Cf^{+++}	0.949
Eu^{+++}	0.950	Yb^{+++}	0.858		
Gd^{+++}	0.938	Lu^{+++}	0.848		

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