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The Crystal Structure of La_6UO_{12}

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Introduction

The phase relations in *RE*–U–O systems (*RE* = rare-earth element) have been studied extensively (*1*). An outstanding feature in these systems is the existence of rhombohedral compounds, RE_6UO_{12} (*2–4*), which form by heating the mixture of uranium oxides and rare-earth oxides in a ratio U : *RE* = 1 : 6 (where *RE* = La, Pr, Nd, Sm–Ho, Tm–Lu, and Y) above 1000°C. Bartram (*5*) has determined the crystal structures of Y_6UO_{12} and Lu_6UO_{12}.

In the present paper, the crystal structure of La_6UO_{12} was studied by the X-ray powder diffraction technique. The crystal system of La_6UO_{12} was known to be rhombohedral (*2, 6*), but no atom positional parameters had been reported.

Experimental

1. Sample Preparation

As the starting materials, U_3O_8 and La_2O_3 were used in the atomic ratio of U : La = 1 : 6. After being finely ground in an agate mortar, the mixtures were pressed into pellets and then heated at 1200°C in air for 3 days. After cooling, the sample was reground, pressed again into pellets, and heated at 1200°C for 2 days followed by slow cooling to room temperature for 3 days. The product was reddish-orange.

2. X-Ray Diffraction Analysis

The X-ray diffraction study on the sample was performed with a conventional diffractometer using Cu$K\alpha$ radiation monochromatized with curved pyrolytic graphite placed in front of the NaI(Tl) scintillation detector. The scans were made in the range $10° \le 2\theta \le 110°$, where the integrated intensities of 66 reflections were collected. To eliminate systematic errors in scattering angles, the observed ones were corrected with those of Si as a standard. Lattice parameters (Table I) were calculated by the least-squares method on a FACOM M380 computer.

The crystal data are tabulated in Table I. The observed and calculated scattering angles (2θ) are given in Table II.

Structure Analysis

The crystal system for La_6UO_{12} has already been reported to be a rhombohedral one. All reflections, indexed based on hexagonal axes, with $-h + k + l = 3n$ were

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observable; thus, the possible space groups are $R3$, $R\bar{3}$, $R32$, $R3m$, and $R\bar{3}m$. Since the space groups of Y_6UO_{12} and Lu_6UO_{12} were both $R\bar{3}$, we made the structure analysis on this compound first by assuming the same space group. All the diffraction lines observed could be indexed in this space group.

As the initial values for computation of

TABLE I

CRYSTAL DATA

Hexagonal parameters	a = 10.468(4) (Å)
	c = 9.982(3) (Å)
Rhombohedral parameters	a = 6.899(3) (Å)
	α = 98.69(1)°
Density (calculated)	d = 6.64(1) (g/cm^3)

TABLE II

OBSERVED AND CALCULATED SCATTERING ANGLES AND INTENSITIES

$h\ k\ l$	$2\theta_{obs}$	$2\theta_{calc}$	I_{obs}	I_{calc}	$h\ k\ l$	$2\theta_{obs}$	$2\theta_{calc}$	I_{obs}	I_{calc}
1 0 1	13.22	13.22	2.18	2.13	3 5 1	73.70	73.73	9.66	9.49
0 1 2	20.33	20.33	8.87	9.49	7 0 1				
0 2 1	21.53	21.55	5.09	7.32	4 1 6	74.46	74.47	6.87	6.04
0 0 3	26.80	26.80	29.88	29.81	0 7 2	75.82	75.85	6.77	6.85
2 1 1	27.52	27.53	100	100	5 3 2				
3 0 0	29.58	29.57	1.72	2.68	1 3 7	76.78	76.80	1.11	1.08
1 2 2	31.68	31.68	41.07	42.97	4 4 3	78.50	78.50	1.09	1.86
1 1 3	36.88	36.86	1.68	1.60	1 2 8	82.16	82.16	1.91	1.77
3 1 2	40.18	40.15	3.24	2.98	5 4 1	83.84	83.86	0.82	0.91
3 0 3	40.32	40.31	4.13	5.40	7 0 4	84.16	84.17	7.17	6.30
0 2 4	41.30	41.29	2.26	4.39	3 5 4				
2 2 3	44.01	44.01	1.09	1.10	3 6 0	84.79	84.83	3.39	3.35
3 2 1	44.49	44.49	0.71	1.22	7 1 3	86.10	86.01	1.83	1.85
2 1 4	44.93	44.93	28.81	28.19	2 4 7	89.32	89.32	1.65	1.57
4 1 0	45.86	45.86	29.84	30.08	5 2 6	89.55	89.55	1.71	2.14
0 1 5	46.59	46.57	2.40	2.82	0 4 8	89.63	89.63	1.21	1.43
2 3 2	47.34	47.33	3.00	4.51	5 3 5	90.29	90.32	4.32	4.43
1 3 4	51.59	51.58	1.74	2.22	1 1 9	90.47	90.47	1.94	1.76
1 2 5	53.08	53.07	11.14	11.36	7 7 2	90.90	90.88	1.32	1.37
1 4 3	53.90	53.90	22.17	25.17	3 6 3	90.96	90.98	4.65	4.86
2 4 1	54.31	54.31	15.29	14.17	5 1 7	91.76	91.80	1.12	0.95
4 0 4	54.67	54.69	1.66	1.44	2 3 8	92.11	92.11	1.40	1.54
0 0 6	55.20	55.19	1.96	1.95	4 3 7	86.78	96.83	0.87	1.04
4 2 2	56.75	56.79	10.30	10.49	4 2 8	99.57	99.60	1.46	1.57
5 1 1	57.29	57.31	2.43	2.44	3 7 2	100.84	110.86	1.12	1.27
3 2 4	57.67	57.68	0.94	1.58	1 6 7	101.80	101.81	1.07	1.64
1 1 6	58.16	58.17	1.38	2.26	8 2 0	102.28	102.30	1.57	2.25
3 1 5	59.07	59.06	1.24	2.18	7 2 5	105.35	105.38	1.15	1.52
1 5 2	59.71	59.72	1.71	1.93	1 4 9	105.52	105.55	2.15	2.13
3 0 6	63.84	63.84	1.20	1.61	3 5 7	106.92	106.93	3.13	3.11
2 3 5	64.70	64.69	1.71	2.65	7 0 7				
2 4 4	66.12	66.12	7.05	7.03	2 1 10	106.98	106.99	1.21	1.20
5 1 4	68.80	68.81	1.13	1.47	8 2 3	108.66	108.67	3.98	4.00
2 5 3	70.76	70.77	1.83	1.90	1 9 1	108.99	109.02	4.73	4.77
2 1 7	71.63	71.64	3.14	3.40	6 5 1				
4 2 5	72.68	72.69	4.56	3.50					

TABLE III

POSITIONAL PARAMETERS IN HEXAGONAL COORDINATES

	x	y	z
3 U	0	0	0
18 La	0.1254 ± 0.0004	0.4150 ± 0.0004	0.0205 ± 0.0004
18 O(1)	0.200 ± 0.006	0.026 ± 0.006	0.126 ± 0.006
18 O(2)	0.145 ± 0.006	0.453 ± 0.006	0.270 ± 0.006

the position parameters of lanthanum atom and of two oxygen atoms, those for Y_6UO_{12} were used. Atomic scattering factors for U^{6+} and La^{3+} were those listed in the "International Tables for X-ray Crystallography" (*7*, *8*), and the factors for O^{2-} were those from Tokonami (*9*). Anomalous dispersion corrections, f' and f'' values of -5.359 and 13.409 for U^{6+} and -1.716 and 9.036 for La^{3+} (*10*), were applied to the scattering factors.

To determine the positional parameters the reliability index $R = \Sigma w|I_{obs} - I_{calc}|/\Sigma w I_{obs}$ was minimized. The weight, w, was regarded as $w = 1/\sqrt{I_{obs}}$ for all the integrated intensities. The integrated observed intensities, I_{obs}, and the calculated intensities, I_{calc}, at the minimum are shown in Table II. The positional parameters in the hexagonal cell are listed in Table III. Final refinement gave $R = 0.092$.

Discussion of the Structure

Our hexagonal cell parameters on La_6UO_{12} are well in accord with those by Aitken *et al.* (*2*) and by Diehl and Keller (*6*). They are larger than the values for the other rhombohedral compounds M_6UO_{12} (M = Pr, Nd, Sm–Ho, Tm–Lu, and Y). The reason for this is considered to be the larger ionic radius of La^{3+} compared with the other trivalent rare-earth ions.

A view of the structure of La_6UO_{12} is shown in Fig. 1. In this figure, one hexagonal unit is depicted. Atoms are drawn with the sizes in proportion to their atomic radii. Interatomic distances and bond angles are given in Table IV. A uranium atom is surrounded by six O(1) atoms which form a distorted octahedron (Fig. 2). All the U–O(1) distances are 2.34 Å; in this structure the uranyl group does not exist. The U–O(1) bond length is longer than those of Y_6UO_{12} and Lu_6UO_{12}. This can be, as with the lattice constants, ascribed to the larger ionic radius of La^{3+} than those of Y^{3+} and Lu^{3+}. The lanthanum atom is considered to

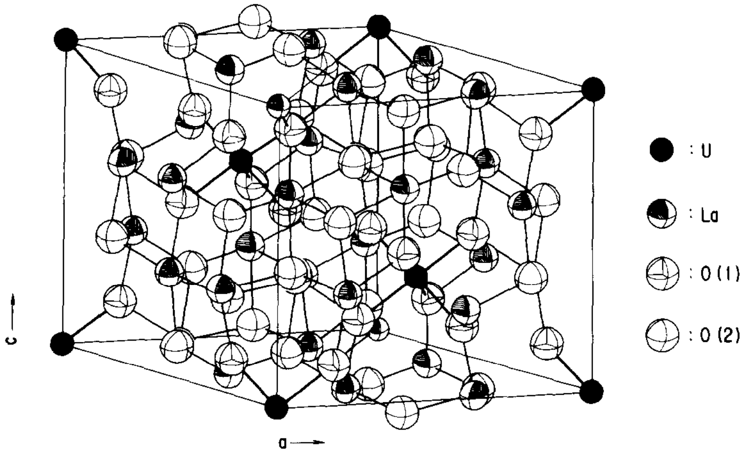

FIG. 1. A stereodrawing of the structure of La_6UO_{12}. One hexagonal unit is depicted.

TABLE IV

INTERATOMIC DISTANCES AND ANGLES

Atoms	Distances (Å)	Angles (deg.)
U-O(1) (all)	2.34 ± 0.02	
O(1)-U-O(1')	3.20 ± 0.02	86.2 ± 0.6
O(1)-U-O(1'')	3.42 ± 0.02	93.8 ± 0.7
O(1)-U-O(1'''')	4.68 ± 0.03	180.0
La-O(1)	2.45 ± 0.02	
La-O(1')	2.32 ± 0.02	
La-O(2)	2.51 ± 0.02	
La-O(2')	2.23 ± 0.02	
La-O(2'')	2.44 ± 0.02	
La-O(2''')	2.47 ± 0.02	
O(1)-La-O(1')	4.28 ± 0.03	127.3 ± 1.3
O(1)-La-O(2)	2.93 ± 0.02	72.3 ± 0.6
O(1)-La-O(2')	3.73 ± 0.02	105.8 ± 0.8
O(1)-La-O(2'')	4.38 ± 0.03	127.5 ± 1.3
O(1)-La-O(2''')	3.19 ± 0.02	80.8 ± 0.6
O(1')-La-O(2)	4.77 ± 0.03	160.4 ± 1.5
O(1')-La-O(2')	3.38 ± 0.02	95.8 ± 0.7
O(1')-La-O(2'')	3.40 ± 0.02	91.2 ± 0.7
O(1')-La-O(2''')	2.93 ± 0.02	75.2 ± 0.6
O(2)-La-O(2')	2.96 ± 0.02	76.8 ± 0.6
O(2)-La-O(2'')	2.96 ± 0.02	73.3 ± 0.6
O(2)-La-L(2''')	4.12 ± 0.03	111.5 ± 1.0
O(2')-La-O(2'')	3.67 ± 0.02	103.5 ± 0.8
O(2')-La-O(2''')	4.69 ± 0.03	171.0 ± 1.5
O(2'')-La-O(2''')	3.04 ± 0.02	76.4 ± 0.6

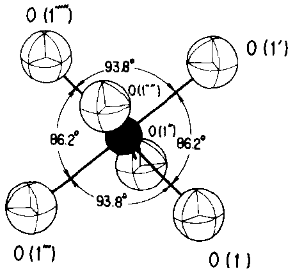

FIG. 2. A view of the uranium coordination polyhedron. Atom designations are the same as in Table IV.

be concerned mainly with the La_6UO_{12} cell size, because the number of lanthanum atoms is six times larger than that of uranium atoms. The oxygen atoms are located at nearly the same positions in the unit cell for the above three compounds. Then, the longer U–O(1) distance of La_6UO_{12} is brought about as the result of larger lattice constants.

A lanthanum atom is also surrounded by six oxygen atoms, two O(1) atoms, and four O(2) atoms. The highly distorted octahedron of oxygen atoms surrounding the lanthanum atom is shown in Fig. 3. The La–O bond lengths are 2.23–2.51 Å. In La_2O_3 each lanthanum atom has four oxygen neighbors at a distance of ca. 2.30 Å and the other three at ca. 2.70 Å; i.e., the coordination number of the lanthanum atom is seven (*11, 12*). Therefore, the La–O bond lengths obtained are quite reasonable, because the coordination number is decreased to six in La_6UO_{12}.

The two uranium polyhedra in the nearest-neighbor relation are linked through one lanthanum polyhedron. One of the two O(1) atoms of this lanthanum polyhedron is shared with the uranium polyhedron and the other with the other uranium polyhedron. The two uranium polyhedra aligned along the hexagonal *c*-axis are linked by two lanthanum polyhedra. These two lanthanum polyhedra share an edge formed by two O(2) atoms, while the uranium polyhedron and lanthanum polyhedron are linked together at one corner; that is, they share one O(1) atom.

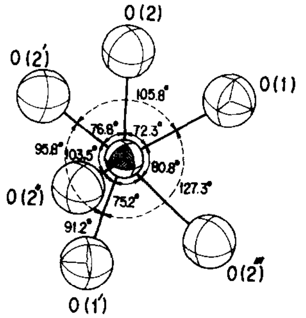

FIG. 3. A view of the lanthanum coordination polyhedron. Atom designations are the same as in Table IV.

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