

UCRL- 1886

DECLASSIFIED

UNIVERSITY OF CALIFORNIA - BERKELEY

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

RADIATION LABORATORY

UCRL-1886
Unclassified-Chemistry Distribution

UNIVERSITY OF CALIFORNIA

Radiation Laboratory

Contract No. W-7405-eng-48

THE CRYSTAL STRUCTURES OF NpC AND Pu₂O₃

D. H. Templeton and Carol H. Dauben

July 14, 1952

Berkeley, California

THE CRYSTAL STRUCTURES OF NpC AND Pu₂O₃

D. H. Templeton and Carol H. Dauben
Radiation Laboratory and Department of Chemistry
University of California, Berkeley, California

July 14, 1952

ABSTRACT

NpC and Pu₂O₃ have been identified by x-ray diffraction. NpC is face-centered cubic, NaCl structure with

$$\underline{a} = 5.004 \pm 0.005 \text{ \AA}$$

Pu₂O₃ is isomorphous with the hexagonal "A form" for the rare earth sesquioxides with

$$\underline{a} = 3.840 \pm 0.004 \text{ \AA}$$

$$\underline{c} = 5.957 \pm 0.006 \text{ \AA}$$

and has essentially the same atomic parameters as La₂O₃. The lattice dimensions are smaller than predicted for pure Pu₂O₃, implying that the average oxidation number of plutonium is between (III) and (IV).

THE CRYSTAL STRUCTURES OF NpC AND Pu₂O₃

D. H. Templeton and Carol H. Dauben
 Radiation Laboratory and Department of Chemistry
 University of California, Berkeley, California

The compounds NpC and Pu₂O₃ have been prepared for the first time in this laboratory and have been examined by x-ray powder diffraction methods.

NpC was prepared by Dr. W. A. Jenkins by heating neptunium oxide in a carbon crucible. The diffraction pattern gave two phases, NpC and another phase as yet unidentified. NpC is face-centered cubic, NaCl structure, isostructural with UC⁽¹⁾ and PuC⁽²⁾, with

$$a = 5.004 \pm 0.005 \text{ \AA.}$$

(1) R. E. Rundle, N. C. Baenziger, A. S. Wilson and R. A. McDonald, J. Am. Chem. Soc., 70, 99 (1948).

L. M. Litz, A. B. Garrett and F. C. Croxton, ibid, 1718 (1948).

(2) W. H. Zachariasen, Acta Cryst. 2, 388 (1948).

The second phase in this pattern does not have a pattern similar to that of UC₂.

Pu₂O₃ was prepared by S. C. Carniglia in an attempt to vaporize plutonium metal in a beryllium oxide crucible. The pattern included the lines of BeO, a second group which is attributed to Pu₂O₃, and some weak lines which are not yet identified. The Pu₂O₃ lines were indexed on a hexagonal lattice with

$$a = 3.840 \pm 0.004 \text{ \AA}$$

$$c = 5.957 \pm 0.006 \text{ \AA}$$

The intensities of these lines cannot be distinguished visually from those of La_2O_3 , which has the so-called "A-form" rare earth sesquioxide structure. The identification of Pu_2O_3 is based on this similarity of intensities and of unit cell dimensions.

With one molecule in the unit cell, the x-ray density of Pu_2O_3 is 11.48 g.cm^{-3} .

According to Pauling,⁽³⁾ the atoms of La_2O_3 are in the following

(3) L. Pauling, Z. Krystallogr. 69, 415 (1928).

special positions of $D_{3d}^3 - C_{3m}$:

$$2 \text{ La in } 2(d) \quad 1/3, 2/3, u; 2/3, 1/3, \bar{u}; u = 0.235$$

$$1 \text{ O I in } 1(a) \quad 0,0,0;$$

$$2 \text{ O II in } 2(d) \quad 1/3, 2/3, v; 2/3, 1/3, \bar{v}; v = 0.63$$

The intensities for Pu_2O_3 require that the atomic parameters, at least for the metal atoms, should be nearly the same. With these parameters, plutonium has four oxygen neighbors at 2.36 Å and three at 2.62 Å. These distances correspond to a crystal radius for the plutonium of 0.96 Å on Zachariasen's scale,⁽⁴⁾ if we compare with Ac_2O_3 to eliminate effects

(4) W. H. Zachariasen, Abstract of paper presented at American Crystallographic Association meeting, April, 1950.

due to the structure type. Zachariasen gives 1.00 Å as the crystal radius of plutonium(III). The discrepancy indicates that there is a

deficiency of plutonium in the compound and that it is partly in the (IV) state. The 4 percent difference in radius corresponds to 40 percent plutonium(IV), though this figure is, of course, very approximate.

Previously Zachariasen⁽⁵⁾ had predicted that Pu₂O₃ would have

(5) W. H. Zachariasen, Metallurgical Laboratory Report CK-1367
(June 25, 1944).

lattice constants,

$$\underline{a} = 3.87 \text{ \AA} \text{ (converted from kX)}$$

$$\underline{c} = 6.03 \text{ \AA}$$

with an x-ray density 11.2 g.cm⁻³. The differences between the observed dimensions and these predictions are equivalent to the discrepancy in radii discussed above.

Zachariasen⁽⁶⁾ reported a sample which was identified as containing

(6) W. H. Zachariasen, Metallurgical Laboratory Report CK-1530
(March 30, 1944).

35 percent Pu₂O₃ where Pu₂O₃ was of the body-centered cubic "C form" with

$$\underline{a} = 11.03 \text{ \AA} \text{ (converted from kX),}$$

but believed this to be the "abnormal" form and that the normal form would be the hexagonal form. This lattice dimension also is smaller than expected for pure Pu₂O₃.

We wish to thank Dr. Jenkins and Mr. Carniglia for the preparation of the samples. The x-ray diffraction patterns were taken by Mrs. Helena W. Ruben. This research was performed under the auspices of the U.S. Atomic Energy Commission.