

COMMUNICATION

THE STRUCTURE OF δ - UO_3

M. T. WELLER,* P. G. DICKENS and D. J. PENNY

Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, U.K.

(Received 11 June 1987; accepted after revision 13 October 1987)

Abstract—The proposed structure for δ - UO_3 has been confirmed by powder neutron diffraction. Data collected from a sample of good crystallinity, by time of flight neutron diffraction techniques, are consistent with the previous description of δ - UO_3 as having the ReO_3 structure, with an unusual regular octahedral environment for U(VI).

The uranium(VI)–oxygen system is one of great complexity; at least six polymorphs of the stoichiometry UO_3 have been described.¹ This structural diversity of uranium(VI) reflects its ability to exist in a variety of low symmetry, high coordination environments with similar energies. The majority of these materials have been studied using powder or single crystal X-ray diffraction with subsequent powder neutron diffraction studies for the accurate determination of the oxygen atom positions. However, the structure proposed for δ - UO_3 by Wait² is based solely on powder X-ray diffraction data with visual estimation of the reflection intensity. The technique is very insensitive to oxygen positions and relatively large distortions of the structure could be accommodated within the accuracy of this refinement. For example tilting of the octahedra with displacement of oxygen off the U—O—U direction would be very difficult to observe using X-ray techniques. However neutron diffraction techniques are ideally suited to the observation of any such distortion. As part of an investigation of uranium oxides and their insertion compounds we have recently completed a structural study of δ - UO_3 using powder neutron diffraction.

EXPERIMENTAL

δ - UO_3 was prepared by the method described by Wait² using AnalaR grade $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as

the starting material. Uranyl nitrate was converted to γ - UO_3 by controlled thermal decomposition in a flowing oxygen atmosphere. Hydrothermal reaction of γ - UO_3 at 190°C in a sealed apparatus led to the formation of crystalline β - $\text{UO}_2(\text{OH})_2$,³ frequently described in the literature as β - $\text{UO}_3 \cdot \text{H}_2\text{O}$.

Thermogravimetric studies of β - $\text{UO}_2(\text{OH})_2$ in association with powder X-ray diffraction have shown that decomposition occurs at 375°C with the formation of δ - UO_3 : above 410°C δ - UO_3 undergoes a transformation to other polymorphs of UO_3 .⁴ In this work β - $\text{UO}_2(\text{OH})_2$ was heated at 375°C for 24 h, resulting in decomposition to brick-red δ - UO_3 . The products from decomposition at higher temperatures or longer heating times were of slightly higher crystallinity but had a considerable degree of contamination with other polymorphs of UO_3 .

Powder X-ray diffraction data showed an almost pure material, which could be indexed on a cubic cell of dimensions 4.146(12). Two very weak lines (with intensity $\sim 2\%$ that of the δ - UO_3 $\langle 100 \rangle$ reflection) were assigned to the strongest peaks from the powder X-ray pattern of α - UO_3 . It was found impossible to prepare a sample of δ - UO_3 totally free from this contaminating polymorph.

Neutron diffraction studies were carried out using the instrument GPPD at the IPNS, Argonne, Chicago; a full description of the diffractometer is given elsewhere.⁵ The sample, 10 g, was contained in a vanadium can and data were collected over a period of 20 h. Neutron pulses scattered from the sample were collected in the four time-focussed detector arrays. The higher resolution back scat-

* Author to whom correspondence should be addressed.
Present address: Department of Chemistry, The University, Southampton SO9 5NH, U.K.

Table 1. Calculated and observed intensities for δ - UO_3

<i>h</i>	<i>k</i>	<i>l</i>	<i>I</i> _{obs}	<i>I</i> _{calc}
1	0	0	150.8	157.3
1	1	0	10.0	12.2
1	1	1	41.0	71.22
2	0	0	468.2	479.6
2	1	0	631.2	588.2
2	1	1	34.2	27.6
2	2	0	849.2	878.9
3	0	0	664.0	687.2
2	2	1		
2	2	2	385.0	359

tered data (150°) and that from the 90° and 60° banks were considered for the refinement. Although the higher angle data is generally better resolved and is used in profile refinements, for this material the line widths were such that an increase in resolution at the higher scattering angle was only weakly apparent. As a result it was decided to use the higher intensity 60° data for the refinement. This also had the advantage of allowing the $\langle 100 \rangle$ reflection to be included in the refinement; peaks with large *d*-spacings are beyond the maximum time of flight for the higher angle detector banks. The data were corrected for the distribution of wavelength intensities, and instrumental and geometrical factors controlled the scattered intensities by comparison with a spectrum obtained from a standard vanadium sample. The resultant diffraction profile showed nine well resolved peaks and some additional incompletely resolved low *d*-spacing peaks which could be indexed on the cubic unit cell of δ - UO_3 . A refined lattice parameter of 4.165(8), in good agreement with the powder X-ray data, was determined. Three additional very weak features in the diffraction profile were assigned to reflections from α - UO_3 , but these were sufficiently resolved from the δ - UO_3 peaks and could be ignored. No peak that would indicate a larger unit cell for δ - UO_3 was observed.

The background under the peaks was determined by linear extrapolation of that on either side and the intensity of the nine well resolved peaks determined by summing the counts under each. Calculated intensities based on the perfect ReO_3 structure were generated for the peaks observed in the experimental pattern and scaled to give the best fit to the experimental data. Reasonable temperature factors of 0.3 and 1.0 were assigned to uranium and oxygen, respectively taken from previous neutron diffraction work on uranium oxides.⁶ The results are shown in Table 1 and the atomic coordinates summarized in Table 2. A reliability index of 5.3%

Table 2. Atomic coordinates for δ - UO_3
(Space group $Pm\bar{3}m$ No. 221 *International Tables*)

Atom	Scattering length ^a	Wyckoff symbol	<i>x</i>	<i>y</i>	<i>z</i>	B
U	0.850	1a	0	0	0	0.3 ^b
O	0.5807	3d	$\frac{1}{2}$	0	0	1.0 ^b

^a 10^{-12} cm.^b Not refined.

was calculated using the expression

$$R = 100 \times \sum_i (I_{\text{obs}} - I_{\text{calc}}) / \sum_i I_{\text{obs}} \%$$

Weak features apparent in the profile at the positions expected for the 310 and 311 reflections were of an intensity consistent with that calculated for these peaks.

DISCUSSION

The experimental neutron diffraction data are consistent with a description of δ - UO_3 with the ReO_3 structure. The agreement of the calculated and experimental intensity data coupled with the ability to index all the observed reflections on the simple unit cell suggests that there is no deviation from the perfect cubic structure. The sensitivity of neutron diffraction to scattering from oxygen, supports the model suggested by Wait with an unusual regular six-fold coordination for uranium. The derived uranium–oxygen single bond length of 2.08 Å is in good agreement with that found in other uranium(VI) oxides with low uranium coordination numbers such as α - UO_3 .⁶

Acknowledgements—The authors wish to thank the Argonne National Laboratory for the provision of neutron beam facilities and R. L. Hitterman for help in analysing the data. We also wish to thank the S.E.R.C. for a travel grant for P.G.D. and M.T.W. and a research studentship for M.T.W., and the U.S.A.F. Office of Scientific Research for financial support (Grant AFOSR-83-0052).

REFERENCES

- Gmelin, *Handbook of Inorganic Chemistry*, Chap. 2: Uranium. Springer (1978).
- E. Wait, *J. Inorg. Nucl. Chem.* 1955, **1**, 309.
- V. J. Wheeler, R. M. Dell and E. Wait, *J. Inorg. Nucl. Chem.* 1964, **26**, 1829.
- H. R. Hoekstra and S. Siegel, *J. Inorg. Nucl. Chem.* **18**, 154.
- J. D. Jorgensen and F. J. Rotella, *J. Appl. Cryst.* 1982, **15**, 27.
- C. Greaves and B. E. F. Fender, *Acta Cryst.* 1972, **B28**, 3609.