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Letter to the Editors

Cuboctahedral oxygen clusters in U_3O_7

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Abstract

When UO_2 is oxidised to U_3O_7, the positions in the crystal lattice of all the uranium atoms and of about 70% of the oxygen atoms are hardly affected. The remaining oxygen atoms occupy new sites which are located 310 pm along $\langle 1\,1\,0\rangle$ vectors from the holes in the fluorite framework of UO_2. These results, which are based on the analysis of neutron diffraction powder data, are consistent with the concept that excess oxygen in U_3O_7 is accommodated in cuboctahedral anionic clusters.

1. Introduction

Uranium dioxide adopts the fluorite (CaF_2) type of crystal structure, space group $Fm\bar{3}m$. There are numerous oxidation products of UO_2, ranging from $UO_{2.00}$ to $UO_{3.00}$: the space groups and cell dimensions of most of these phases are known, but knowledge of the atomic arrangement within these unit cells is more restricted [1,2]. Within the composition range $2.00 \leqslant O/U \leqslant 2.375$, i.e. between UO_2 and U_3O_7 and including the polymorphs of U_4O_9, the crystal structures are closely related to the fluorite arrangement of UO_2. In U_4O_9 (space group $I\bar{4}3d$), the additional oxygen atoms are accommodated in cuboctahedral clusters which are centred on holes in the fluorite lattice [3]. The aim of the present investigation was to determine by powder neutron diffraction whether there are similar clusters of oxygen atoms in U_3O_7. This phase itself can be described as a layer structure which gives rise to a family of polytypes, including the tetragonal phases α-, β- and γ-U_3O_7 [4–6]. There are also monoclinic phases of similar composition, which are either produced under high pressure [7] or are formed when UO_2 is leached in water [8]. Our study concerns only the tetragonal phase β-U_3O_7, which is an important fluorite-type uranium oxide encountered in the low-temperature air oxidation of unirradiated UO_2 [9].

2. Experimental

Nuclear grade U_3O_8 powder was converted to stoichiometric UO_2 at 1000 °C under an Ar/H_2 gas mixture. The sample was then slowly oxidised in dry air at 200 °C. The average composition of the sample was monitored by themogravimetry. The thermal treatment was terminated when the composition $O/U = 2.333 \pm 0.001$ was reached. Routine XRD investigation of the sample revealed the formation of a tetragonal phase with $c/a = 1.030$, well within the range characteristic of the β-U_3O_7 phase [5,10,11]. No trace of the layered U_3O_8 phase was found. Remains of unreacted UO_2, approximately $(5 \pm 2)\%$, were present in the sample. Thus the actual composition of the β-U_3O_7 phase was estimated to be $O/U = 2.35 \pm 0.01$.

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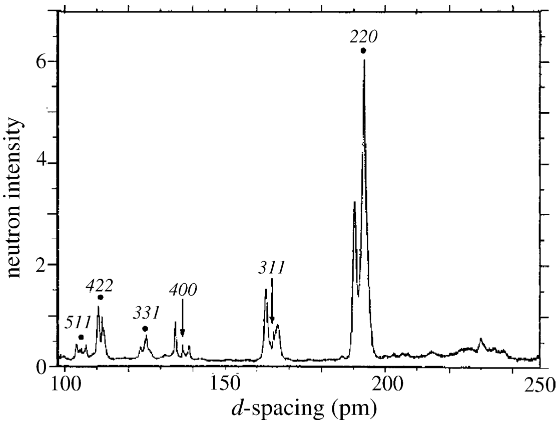

Fig. 1. Neutron powder pattern of U_3O_7. The two diffraction peaks, 311 and 400, indicated by arrows are from the minority phase of UO_2. The positions of the remaining UO_2 peaks are shown as dots with the corresponding *hkl* indices. The broader peaks are from β-U_3O_7.

The neutron powder pattern was recorded at room temperature using the high resolution powder diffractometer (HRPD) at the pulsed neutron source ISIS of the Rutherford–Appleton Laboratory. The diffraction pattern in the range of *d*-spacings $100 \text{ pm} < d < 250 \text{ pm}$ (Fig. 1) consists of a mixture of broad and much sharper diffraction lines. The broad lines index in the tetragonal system with $a = 538.3$ pm, $c = 554.7$ pm and they represent the dominant phase of β-U_3O_7. The sharper lines (of which two, 311 and 400, are indicated by the vertical arrows in Fig. 1) index in the face-centred cubic system with $a = 547.0$ pm and are due to the presence of unreacted UO_2.

The cubic fluorite structure of UO_2 gives rise to *hkl* reflections 111, 200, 220, 311,... with $h+k, k+l = 2n$. The *d*-spacings of these reflections are indicated in Fig. 1. The reflections from β-U_3O_7 are grouped around these *d*-values: it is clear that the structure of β-U_3O_7 is closely related to that of UO_2, but with a distortion from a cubic cell to a tetragonal cell, with $c/a = 1.030$, leading to a splitting of the cubic fluorite lines. The diffraction pattern also revealed the presence of weak superlattice lines in the region $d > 250$ pm, but these lines were too broad and too few to include in the structure analysis. For this reason, although we have identified the type of anionic cluster in U_3O_7, we have not determined the ordering scheme of the clusters in an enlarged supercell.

3. Rietveld refinement

The diffraction pattern in Fig. 1 was refined by the Rietveld procedure [12] employing the GSAS program of Larson and von Dreele [13]. The dimensions of the tetragonal cell of U_3O_7 (given above) corresponded to a cell volume at room temperature of 0.1607 nm^3. This volume is a little less than the volume 0.1637 nm^3 of the cubic cell of stoichiometric UO_2 at the same temperature. In view of the close similarity of the dimensions of the tetragonal and cubic cells we shall present the structural results in terms of a cubic cell.

The Rietveld analysis showed that on oxidation from UO_2 to U_3O_7 the uranium atoms retain their positions in the fluorite structure of UO_2. The principal changes concern the oxygen atoms. These atoms occupy two kinds of sites, labelled O and O′. The O atoms are in normal fluorite positions, but 30% of these positions are unoccupied, giving a fractional occupancy of the sites of 0.70 ± 0.02. The O′ atoms occupy non-fluorite positions, which are located 310 pm along the $\langle 1\,1\,0 \rangle$ directions from the holes in the cation lattice. Small displacements of U and O atoms from the fluorite positions were accounted for in the refinement by increasing the Debye–Waller factors of both types of atom.

These results are summarised in Table 1. In this table the composition of the fluorite-type subcell of U_3O_7 is expressed as $U_4O_{8-m}O'_n$, where *m* is the number of empty O sites and *n* is the number of interstitial O′ sites. (In UO_2 *m* and *n* are zero and the composition of the unit cell is U_4O_8.)

4. Conclusions from Rietveld analysis

We shall now show that the results in Table 1 are entirely consistent with the concept that the excess anions in U_3O_7 are accommodated in cuboctahedral

Table 1
Rietveld refinement of the subcell of composition $U_4O_{8-m}O'_n$

Type of atom	Atomic coordinates			*m* and *n*	
	x	*y*	*z*	Observed	Theory
U	0	0	0	4.0	4.0
O	1/4	1/4	1/4	$m = 2.42 \pm 0.16$	$m = 2.67$
O′	$1/2 + v$ with $v = 0.41(1)$	$1/2 + v$	1/2	$n = 4.0 \pm 0.3$	$n = 4.0$

Space group $Fm\bar{3}m$.

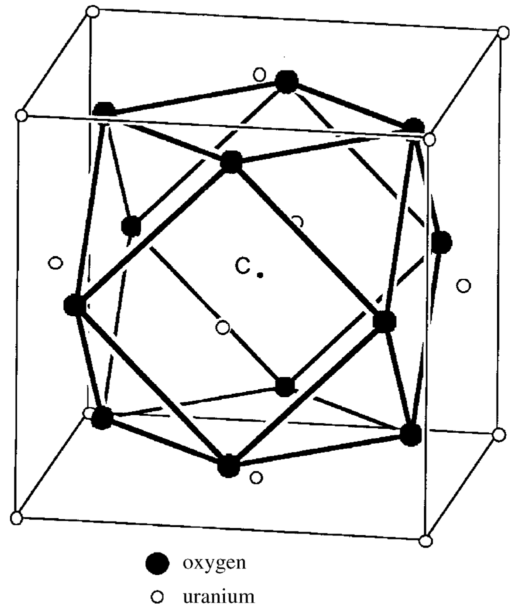

Fig. 2. A schematic diagram of the cuboctahedral cluster. Eight oxygen anions inside the cationic cube are replaced by twelve anions located along the ⟨1 1 0⟩-type directions from the centre C of the cube.

clusters. Such agglomerates of anions were found in several ordered anion-excess compounds based on the CaF_2 structure [14,15]. The configuration of the atoms in the cuboctahedral cluster is shown in Fig. 2. The cluster can be described with reference to the holes in the UO_2 structure, i.e. to the centres of oxygen cubes of 8 atoms. Additional oxygen atoms are incorporated in this structure by replacing an oxygen cube by an oxygen cuboctahedron. A single cuboctahedron has 12 O′ atoms at its vertices and these atoms are located along the 12 ⟨1 1 0⟩-type directions from the hole.

Since a cuboctahedron replaces 8 atoms by 12, then $m/n = 8/12$ and, to satisfy the overall composition of U_3O_7, the condition $8 - m + n = 28/3$ must hold. Hence $m = 8/3$ and $n = 4$, giving the theoretical occupancy numbers listed in Table 1, which are in reasonable agreement with those observed. The size of the clusters, which is determined by the magnitude of the v parameter (defined in Table 1), is somewhat larger than the cluster size in U_4O_9. Note that the value of $v = 0.132$ reported in Ref. [3] is equivalent to $0.5-0.132 = 0.368$ since [0.5,0.5,0] is a translation vector of the matrix lattice. In U_4O_9 the clusters are sufficiently far apart for the lattice symmetry to remain cubic; in U_3O_7 the cluster concentration exceeds that in U_4O_9 and, in order to accommodate additional clusters, the lattice is distorted from cubic to tetragonal symmetry.

According to Nowicki et al. [4] U_3O_7 occurs as a family of polytypes with different stackings of identical layers. It is known that U_3O_7 exists over a narrow range of the O/U ratio close to O/U = 2.33, and this may account for the small discrepancy between the observed and theoretical occupancies in Table 1. We should also mention that the possible presence of a thirteenth oxygen, encapsulated in the centre of the cuboctahedron, was not considered in the refinement.

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