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Structure of $UMoO_5$ Studied by Single-Crystal X-ray Diffraction and High-Resolution Transmission Electron Microscopy

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Abstract

A combination of X-ray diffraction and high-resolution transmission electron microscopy (HRTEM) has been used to study the crystal structure of molybdenum uranium pentoxide, $UMoO_5$, obtained by hydrothermal and ceramic methods. Crystal data: $M_r = 414.0$, orthorhombic, *Pbaa* (number 54), $a = 12.746(1)$, $b = 7.3494(7)$, $c = 4.1252(2)$ Å, $V = 386.4(1)$ Å^3, $Z = 4$, $D_x = 7.116$ Mg m^{-3}, $R = 0.037$ for 723 reflections. The structure of $UMoO_5$ is related to that of UVO_5. Both are built up by slabs of pentagonal UO_7 bipyramids with slabs of MO_6 octahedra in-between. They differ in symmetry due to different types of displacement of the *M* atoms from the *ab* plane. The HRTEM study revealed a few defect regions in the $UMoO_5$ crystals prepared by ceramic methods. Energy-dispersive spectroscopy (EDS) analyses indicate a slight excess of uranium in such crystals. Hypothetical models of defect regions are given.

1. Introduction

The occurrence of a phase with $UMoO_5$ composition has been known since the early sixties (Kovba, Sirotkina & Trunov, 1965). By sintering methods $UMoO_5$ and UVO_5 were made and from oscillation X-ray photographs of the latter it was possible to deduce a set of orthorhombic unit-cell parameters for UVO_5. From powder photographs the occurrence of an hexagonal sublattice was established in both compounds. They were thus judged to be isostructural. Thermal investigations in the systems UO_2–MoO_2–MoO_3 (Kovba & Trunov, 1965) and UO_2–MoO_3 (Efremova, Trunov & Kovba, 1967) confirmed the existence of $UMoO_5$ and established its interrelations with other phases in these systems.

A single-crystal structure determination of UVO_5 showed that one of the axes was doubled and the space group was given as *Pbma* (number 57), with conventional notation *Pbcm* (Chevalier & Gasperin, 1970; Kovba, 1971). From this it was inferred that the axes of $UMoO_5$ were $a = 12.761$, $b = 7.338$ and $c = 4.115$ Å (Serezhkin, Kovba & Trunov, 1973) and that the space group was *Pbma* with an axis orientation similar to UVO_5. Recently, the oxygen positions of UVO_5 were refined from powder neutron diffraction data (Dickens, Stuttard, Ball, Powell, Hull & Patat, 1992). Assuming $UMoO_5$ to be isostructural with UVO_5 (Dickens & Stuttard, 1992), a Rietveld refinement based on powder neutron diffraction data has been made. So far, however, no single-crystal X-ray diffraction study of $UMoO_5$ has been published.

In the present study hydrothermal methods were used to prepare crystals of $UMoO_5$ suitable for single-crystal X-ray investigations. Ceramic methods, on the other hand, were used for preparing microcrystalline samples which were studied by X-ray powder diffraction and high-resolution transmission electron microscopy (HRTEM).

2. Experimental

2.1. *Preparation*

$UMoO_5$ was synthesized by heating an appropriate mixture of U_3O_8 [prepared by heating $UO_2(NO_3)_2.6H_2O$ at 1020 K], MoO_3 and Mo powder in an evacuated silica tube at 970 K for 1 d and at 1170 K for 2 d. The furnace was then turned off and the sample allowed to cool. This method of synthesis produced a black microcrystalline powder, which was subsequently studied by X-ray powder diffraction and HRTEM.

In another experiment a mixture of UO_3 and MoO_3 in a 2:1 ratio was thoroughly ground and put into a teflon tube filled with water to 3/4 of its volume. The tube was hermetically closed by a teflon screw and heated at 570 K at a pressure of $\sim 5 \times 10^7$ Pa for 2 weeks. From the resulting multi-phase sample it was then possible to pick out brown to black plate-like crystals of $UMoO_5$, which were used in the single-crystal X-ray investigation.

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† Deceased.

2.2. *X-ray diffraction*

X-ray powder patterns of the ceramic specimens were registered in a Guinier–Hägg focusing camera with strictly monochromatized Cu $K\alpha_1$ radiation ($\lambda = 1.54060$ Å). Silicon was added as an internal θ standard ($a = 5.43088$ Å); $5 \leq 2\theta < 88°$. The positions of the lines and their intensities were evaluated by means of a film scanner system and the unit-cell parameters were refined by least-squares techniques.

A small parallelepiped was cut from one of the hydrothermally prepared $UMoO_5$ crystals and used for the X-ray single-crystal investigation. The structural refinements were carried out by means of the *CAD*-4 *SDP* package (Frenz, 1978). The structure was determined by direct methods followed by successive Fourier calculations. The experimental details are summarized in Table 1 and fractional atomic coordinates are given in Table 2.*

2.3. *Electron diffraction*

A small part of the $UMoO_5$ sample prepared by the ceramic method was ground in an agate mortar and dispersed in *n*-butanol. A few drops of the resulting suspension were placed on a perforated carbon film supported by a copper grid. The specimen was then examined in a JEOL 3010 high-resolution transmission electron microscope operated at an accelerating voltage of 300 kV. The radius of the objective aperture used corresponded to 0.69 $Å^{-1}$ in reciprocal space. Simulated HRTEM images were calculated with a locally modified PC version of the *SHRLI* set of programs (O'Keefe, Buseck & Iijima, 1978).

An electron diffraction study in combination with EDS analysis of thin crystal fragments was performed with a JEOL 2000FX-II transmission electron microscope equipped with a LINK QX-200 EDS system.

3. Results and discussion

The X-ray powder diffraction pattern of the microcrystalline product indicated an almost single-phase sample. The pattern could be indexed with a unit cell of orthorhombic symmetry, with $a = 12.744\,(1)$, $b = 7.3492\,(6)$ and $c = 4.1266\,(3)$ Å. These values are very close to those obtained in the single-crystal X-ray study of the hydrothermally prepared $UMoO_5$ crystals (see Table 2).

The structure of $UMoO_5$ is depicted in Fig. 1(*a*). Selected interatomic distances are given in Table 3. The pentagonal UO_7 bipyramids as well as the MoO_6 octahedra are distorted, but with different types of

Table 1. *Experimental details*

Crystal data	
Chemical formula	MoO_5U
Chemical formula weight	414.0
Cell setting	Orthorhombic
Space group	*Pbaa*
a (Å)	12.746 (1)
b (Å)	7.3494 (7)
c (Å)	4.1252 (2)
V ($Å^3$)	386.4 (1)
Z	4
D_x (Mg m^{-3})	7.116
Radiation type	Mo $K\alpha$
Wavelength (Å)	0.71073
No. of reflections for cell parameters	24
θ range (°)	19–22
μ (mm^{-1})	42.8
Temperature (K)	293
Crystal form	Parallelepiped
Crystal size (mm)	0.05 × 0.03 × 0.03
Crystal colour	Brown–black
Data collection	
Diffractometer	Enraf–Nonius CAD-4
Data collection method	ω–2θ scans
Absorption correction	ψ scans (empirical)
T_{min}	0.793
T_{max}	0.999
No. of measured reflections	1055
No. of independent reflections	1055
No. of observed reflections	723
Criterion for observed reflections	$I > 3\sigma(I)$
θ_{max} (°)	38
Range of h, k, l	$0 \rightarrow h \rightarrow 22$ $0 \rightarrow k \rightarrow 12$ $0 \rightarrow l \rightarrow 7$
No. of standard reflections	3
Frequency of standard reflections (min)	120
Intensity decay (%)	<2
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$	0.037
$wR(F^2)$	0.037
No. of reflections used in refinement	723
No. of parameters used	22
Weighting scheme	$w = [1.3216 - 0.0692\lvert F_o\rvert + 0.0037\lvert F_o\rvert^2]^{-1}$
$(\Delta/\sigma)_{max}$	0.005
$\Delta\rho_{max}$ (e $Å^{-3}$)	0.30
$\Delta\rho_{min}$ (e $Å^{-3}$)	−0.24
Extinction method	$\lvert F_c\rvert = \lvert F_o\rvert(1 + gI_c)$
Extinction coefficient	$g = 3.07\,(8) \times 10^{-7}$
Source of atomic scattering factors	*International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($Å^2$)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	Site	x	y	z	B_{eq}
U1	(4*d*)	0.47583 (3)	1/4	0.0	0.273 (4)†
Mo1	(4*c*)	1/4	1/2	0.1069 (3)	0.36 (1)†
O1	(8*f*)	0.0994 (5)	0.4561 (9)	0.002 (1)	0.89 (8)
O2	(4*d*)	0.2878 (7)	1/4	0.0	0.8 (1)
O3	(4*e*)	0.9735 (9)	1/4	1/2	1.1 (1)
O4	(4*c*)	1/4	1/2	−0.492 (2)	1.5 (2)

† Atom refined anisotropically.

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* Lists of atomic coordinates, anisotropic displacement parameters, structure factors and powder diffraction data have been deposited with the IUCr (Reference: AB0350). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

distortion. The U atom is located at $z = 0$, while the Mo atom is displaced by 0.441 (1) Å from that plane. Similar observations have been reported for orthorhombic UMo_2O_8 (Cremers, Eller, Penneman & Herrick, 1983). In the latter structure the Mo atom is displaced by 0.390 (1) Å from the plane of the U atoms at $z = 0$. Each U atom coordinates two O atoms along the *c* axis, thereby forming infinite linear and equidistant —O—U—O—U—O— strings [U—O = 2.063 (1) Å]. In the equatorial plane of the pentagonal UO_7 bipyramid, U is coordinated by five O atoms with U—O distances ranging from 2.185 (6) to 2.397 (9) Å. A similar type of distortion of the pentagonal UO_7 bipyramid was observed in the UVO_5 structure (Dickens, Stuttard, Ball, Powell, Hull & Patat, 1992) and orthorhombic UMo_2O_8 (Cremers, Eller, Penneman & Herrick, 1983).

Table 3. *Selected interatomic distances (Å)*

U1—O1	2.185 (6) × 2	Mo1—O1	1.994 (6) × 2
U1—O1	2.363 (7) × 2	Mo1—O2	1.950 (2) × 2
U1—O2	2.397 (9)	Mo1—O4	1.655 (8)
U1—O3	2.063 (1) × 2	Mo1—O4	2.471 (8)

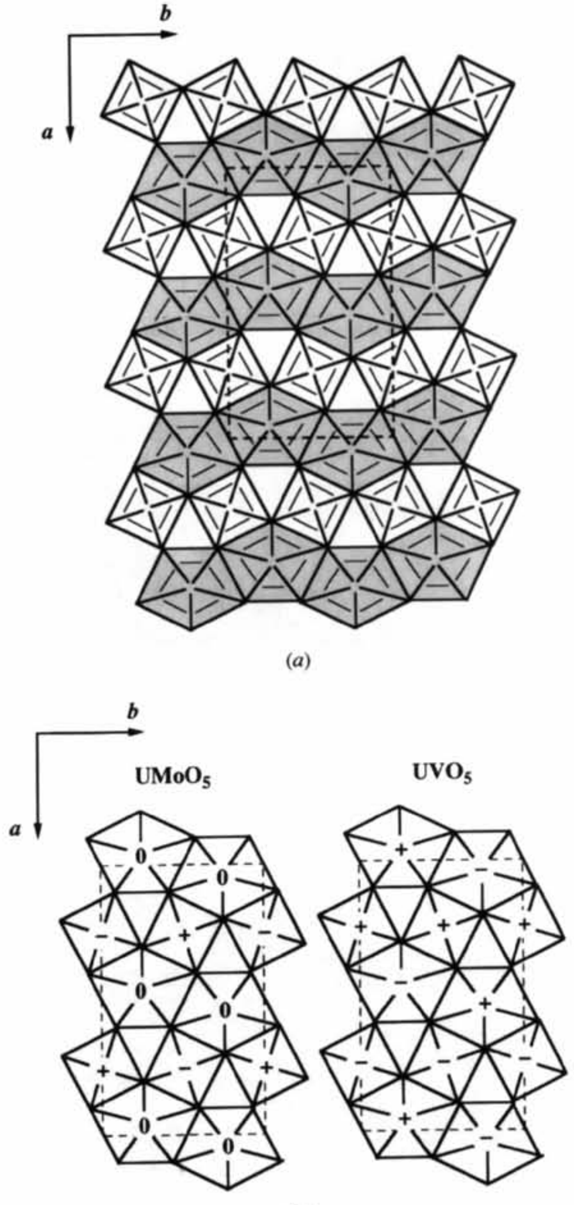

Fig. 1. (*a*) The crystal structure of $UMoO_5$ (idealized). (*b*) Comparison between the (idealized) structures of $UMoO_5$ and UVO_5. + and − represent metal-atom displacements from the equatorial plane of a bipyramid or an octahedron. In $UMoO_5$ there is no displacement of the U atoms, as indicated by zero in the figure.

In the MoO_6 octahedron the Mo atom is shifted towards one of the apices, perpendicular to the *ab* plane. As a result one short [1.655 (8) Å], one long [2.471 (8) Å] and four rather similar [1.950 (2)–1.994 (6) Å] Mo—O distances are formed. In neighbouring MoO_6 octahedra the Mo atoms are shifted in opposite directions from the *ab* plane, thus forming a puckered arrangement. A similar arrangement of the Mo atoms has been found in the orthorhombic UMo_2O_8 structure (Cremers, Eller, Penneman & Herrick, 1983), but not for the V atoms in the UVO_5 structure (Chevalier & Gasperin, 1970; Dickens, Stuttard, Ball, Powell, Hull & Patat, 1992). Consequently, there is a difference in symmetry of UVO_5 and $UMoO_5$, which was not possible to reveal until single-crystal data of the latter eventually became available (see Fig. 1*b*).

Formally, the crystal structure of $UMoO_5$ in Fig. 1(*a*) can be described as an ordered intergrowth structure of thin pleated slabs of edge-sharing pentagonal UO_7

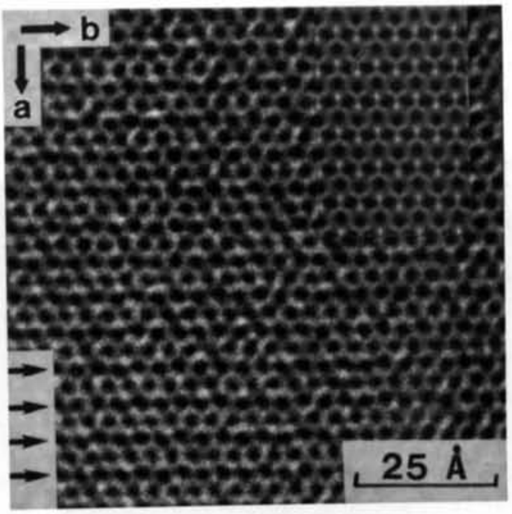

Fig. 2. HRTEM image ([001] projection) of a thin crystal fragment of microcrystalline $UMoO_5$ with a simulated image inserted; crystal thickness ~20 Å, defocus value −320 Å.

bipyramids (PB), one pentagonal bipyramid wide, and ReO_3-type slabs of corner-sharing MoO_6 octahedra, one octahedron wide ($n = 1$). The two types of slab are infinite in the b and c directions. The $UMoO_5$ structure has been denoted (1)-PB (Sundberg & Tabachenko, 1990). It has been considered as the first member of a homologous series of related phases, (n)-PB, with the general formula $UO.M_nO_{3n+1}$, where n represents the number of octahedra in the ReO_3-type slabs and $M = $ Mo, W.

Fig. 2 shows the HRTEM image ([001] projection) of a thin crystal fragment from the microcrystalline $UMoO_5$ sample. The dark dots in the image correspond to projected columns of metal atoms in the structure. The rows of black spots in a slightly zigzag-shaped pattern (see arrows) are characteristic of the thin pleated slabs of edge-sharing pentagonal UO_7 bipyramids in the structure (Fig. 1*a*), while the black spots in-between represent the projected Mo atoms in the octahedra. Synthetic HRTEM images of $UMoO_5$ were calculated using the atomic parameters given in Table 2. There is good agreement between the simulated image inserted in Fig. 2 and the experimental one, which confirms the $UMoO_5$ structure.

The electron diffraction study showed that some crystals contained defects in the ab plane. The reflections in the electron diffraction patterns were sharp (no streaking), but different regions of the same fragment could not be perfectly aligned at the same time. The corresponding HRTEM images showed a few defect regions. EDS analyses of such crystals also indicated a slight excess of U of up to 5 atom %. The EDS data from well ordered crystals, however, showed a U:Mo ratio of 1:1, which is in agreement with the formula $UMoO_5$. The HRTEM image in Fig. 3 shows that two $UMoO_5$ regions are displaced by about one quarter of the length of the a axis and linked at the edge by a narrow, disordered, almost amorphous region. The area to the right is not perfectly aligned. The crystal fragment is slightly bent.

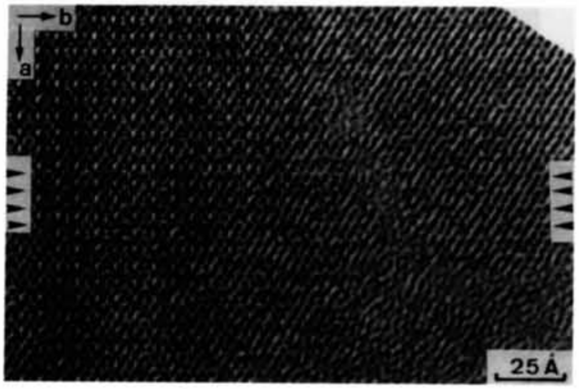

Fig. 3. HRTEM image showing two $UMoO_5$ regions displaced along the a axis and linked by an amorphous region.

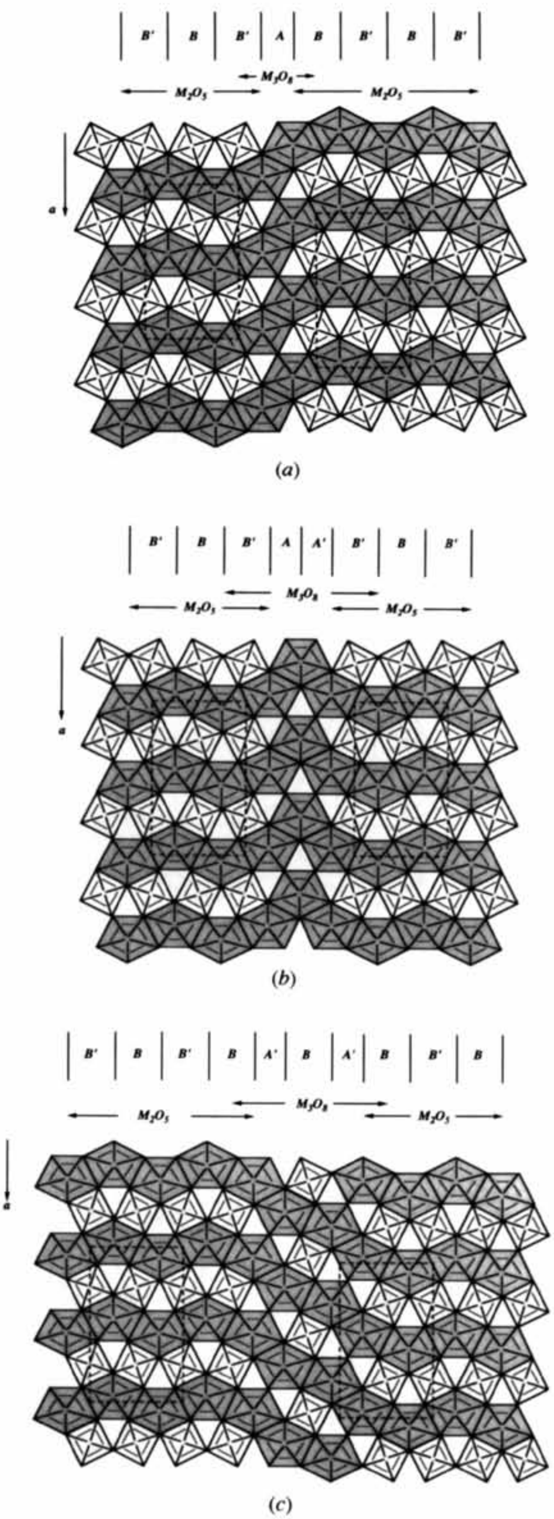

Fig. 4. Two $UMoO_5$ regions are shown as built up of B modules. In (*a*) an A module has been inserted at the boundary between them. In (*b*) and (*c*) two A modules have been inserted. The structure of the boundary is closely related to U_3O_8.

Figures 4(*a*)–(*c*) illustrate some idealized hypothetical models of conceivable defect boundaries between regular regions of $UMoO_5$ structure type. The $UMoO_5$ structure type can be regarded as formed through chemical twinning on the unit-cell level. It is built up of modules of *B*- and *B*′-type of M_2O_5 composition (Marinder, 1990). In the boundary a further module of an *A*-type has been introduced. This module has an MO_3 composition. Assuming that the metal content of the *A* module is mostly made up of U, there will be an excess of uranium at the boundary. In Fig. 4(*a*) there is one *A* module inserted between the $UMoO_5$ regions, while two *A* modules make up the boundary in Figs. 4(*b*) and (*c*). Of the three models in Fig. 4, that in Fig. 4(*a*) would be easiest to observe in an HRTEM image due to the marked displacement along the *a* axis of the rows of U atoms at the boundary. The displacement is about a quarter of the length of the *a* axis and is thus in agreement with that observed in the HRTEM image in Fig. 3. However, the two regions in Fig. 3 are connected through an amorphous part at the edge of the crystal fragment. Thus, a detailed interpretation of the defect boundary cannot be given. The models shown are all in concordance with the observed excess of uranium in some of the examined crystal fragments. It is noteworthy that the structure of the boundaries in the three models is closely related to U_3O_8.

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