



Synthesis and crystal structure of a novel uranium oxytelluride $U_4O_4Te_3$

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Received 18 May 1994

Abstract

A new uranium compound has been prepared in a single-crystal form. Its crystal structure was determined from single-crystal X-ray data and refined to a residual value $R=0.037$ for 443 independent reflections. The compound crystallizes in a tetragonal unit cell of its own type with the $I4/mmm$ space group, $Z=2$ and the lattice parameters $a=4.010(2)$ Å and $c=27.54(2)$ Å. A close relationship between the structure of $U_4O_4Te_3$ and those of $UOTe$ and U_2O_2Te is briefly discussed.

Keywords: Structure refinement; Uranium oxytelluride; Single crystal growth

1. Introduction

In the ternary system U–O–Te, the existence of only two phases, i.e. $UOTe$ [1] and U_2O_2Te [2], has been reported up to date. The former compound crystallizes in a primitive tetragonal structure of the $PbFCl$ type (space group $P4/nmm$), while U_2O_2Te is isostructural with La_2O_2Te and possesses a body-centred unit cell (space group $I4/mmm$) being closely related to that of $UOTe$.

Here we report for the first time on the synthesis and single-crystal X-ray structure determination of a new uranium oxytelluride with the chemical formula $U_4O_4Te_3$.

2. Experimental details

2.1. Sample preparation

Single crystals of the new compound were prepared by melting a U_3Te_4 powder that was placed in an alumina crucible and then sealed in a molybdenum crucible. The sample was heated to 1560 °C and annealed at this temperature for 100 h, using a graphite high temperature resistance furnace. Afterwards, it was slowly cooled down, first to 1300 °C with a rate of

20 °C h⁻¹, and then down to 900 °C with a rate of 120 °C h⁻¹. The crystals obtained had the form of very thin plates with maximum dimensions of 10 mm × 10 mm × 0.1 mm. They had a black-metallic lustre and were rather sensitive to air and humidity. Energy-dispersive X-rays analysis (EDAX) of a single crystal has shown the presence in the sample of uranium, tellurium and oxygen with an approximate ratio 3:3:4. Because no oxygen was introduced intentionally into the sample, we think that the amount of oxygen necessary to form the oxytelluride came out from the alumina crucible used for the crystal growth process.

2.2. Crystallographic studies

A small single crystal with the form of a platelet was chosen for diffraction studies which were performed on an Enraf-Nonius CAD4 diffractometer with Mo K α radiation. Rather large diffraction spots were obtained, owing to the lamellar and rather soft habit of the crystal, usually characterizing low dimensional solids. The lattice vectors could be identified by application of the automated indexing routine of the diffractometer to the positions of 25 centred reflections.

The conditions limiting possible reflections hkl , $h+k+l=2n$, indicated a body-centred tetragonal unit cell and the structure could be successfully determined

Table 1
Crystallographic data

Formula	U ₄ O ₄ Te ₃
Crystal dimensions (mm ³)	0.11 × 0.17 × 0.02
Crystal system	Tetragonal
Space group	I4/mmm
Lattice parameters (Å)	a = 4.010(2) c = 27.54(2)
Volume (Å ³)	V = 442.8(4)
Formula units per cell	Z = 2
Formula weight	348.54
Calculated density (g cm ⁻³)	10.54
Radiation λ (Å)	0.710 69
μ(Mo Kα) (cm ⁻¹)	792
Scan mode	ω-2θ
2θ range (deg)	2–90
Reflections measured	1084
Independent reflections	611
Observed reflections (I _o > 3σ(I _o))	434
R = Σ[F _o - F _c] / Σ F _o	0.038
R _w = [Σw(F _o - F _c) ² / Σw F _o ²] ^{1/2}	0.044
Goodness of fit	1.00

Table 2
Positional parameters and isotropic thermal factors of the atoms in U₄O₄Te₃

Atom	Position	x	y	z	B _{eq} (Å ²)
U(1)	4e	0	0	0.160 99(3)	0.61(1)
U(2)	4e	0	0	0.429 69(3)	0.69(1)
Te(1)	2a	0	0	0	0.99(2)
Te(2)	4c	0	0	0.287 46(5)	0.69(1)
O	8g	0	0.5	0.111 7(4)	1.2(2)

Table 3
Anisotropic displacement parameters in U₄O₄Te₃^a

Atom	β(1,1)	β(2,2)	β(3,3)
U(1)	0.60(1)	β(1,1)	0.64(2)
U(2)	0.65(1)	β(1,1)	0.77(2)
Te(1)	1.15(4)	β(1,1)	0.69(4)
Te(2)	0.73(2)	β(1,1)	0.62(3)
O	1.5(4)	0.9(3)	1.3(3)

^a(1) The form of the anisotropic displacement parameter is $\exp\{(-1/4)[h^2a^{*2}\beta(1,1) + k^2b^{*2}\beta(2,2) + l^2c^{*2}\beta(3,3) + 2hka^*b^*\beta(1,2) + 2hla^*c^*\beta(1,3) + 2klb^*c^*\beta(2,3)]\}$ where a^* , b^* and c^* are reciprocal lattice constants.

(2) $\beta(1,2) = \beta(1,3) = \beta(2,3) = 0$.

in the centrosymmetric space group I4/mmm. A gaussian integration absorption correction was applied to all the intensity data measured.

All calculations were carried out on a microVAX 3100 computer with the use of SDP crystallographic software [3]. The positions of the uranium atoms were determined from a three-dimensional Patterson map. A difference Fourier map subsequently indicated the positions of the tellurium and oxygen atoms. The com-

Table 4
Interatomic distances (ångströms) in U₄O₄Te₃

U(1)–O	2.422(6)	Te(1)–8U(2)	3.433(1)
–4Te(2)	3.171(1)	–8O	3.671(9)
–1Te(2)	3.483(1)		
–4U(2)	3.778(1)	Te(2)–4U(1)	3.171(1)
		–4O	3.426(9)
U(2)–O	2.306(6)	–1U(1)	3.483(1)
–4Te(1)	3.433(1)	–4Te(2)	3.507(2)
–4U(1)	3.778(1)		
		O–2U(2)	2.306(6)
		–2U(1)	2.422(6)

position of the new oxytelluride was found to be U₄O₄Te₃. The final refinement for the above composition gave values of the discrepancy factors $R = 0.038$ and $R_w = 0.044$.

A summary of the crystallographic data for U₄O₄Te₃ is given in Table 1. The final positional and thermal parameters for this compound are listed in Tables 2 and 3, while selected interatomic distances are shown in Table 4.

3. Description of the structure

The crystal structure of U₄O₄Te₃ is displayed in Fig. 1. For comparison, the unit cells of the other oxytellurides known, i.e. UOTe and U₂O₂Te, are also shown. It is clear from this figure that the structure of U₄O₄Te₃ can be represented as an intergrowth of the unit cell of U₂O₂Te between two unit cells of the UOTe type. The latter segments are inverted relative to each other along the *c* axis to keep the body-centred symmetry. The resulting structure type exhibits a typical layered character, and its *c/a* ratio is as large as 6.87.

The coordination polyhedra of atoms in U₄O₄Te₃ are therefore essentially the same as those in the other oxytellurides. The oxygen ion is located in a slightly distorted tetrahedron built up of the uranium atoms as in UOTe and U₂O₂Te (see Fig. 1 and Table 4). The Te(1) anion is surrounded by eight U(2) atoms which form a perfect square prism as in U₂O₂Te. In turn, the coordination polyhedron of Te(2) consists of one uranium and one tellurium plane of which the tellurium plane is capped with an additional U(1) atom. The very same environment of a chalcogen atom is characteristic of all the UOY (Y ≡ S, Se and Te) compounds. In a similar way, the surroundings of the uranium atoms in U₄O₄Te₃ have their close counterparts either in UOTe (for U(1)) or in U₂O₂Te (for U(2)). The uranium atoms are always located in the sites of C_{4v} point symmetry, i.e. in the centre of a square parallelepiped formed by the tellurium and oxygen ions, and the only difference is that in the case of U(1) this

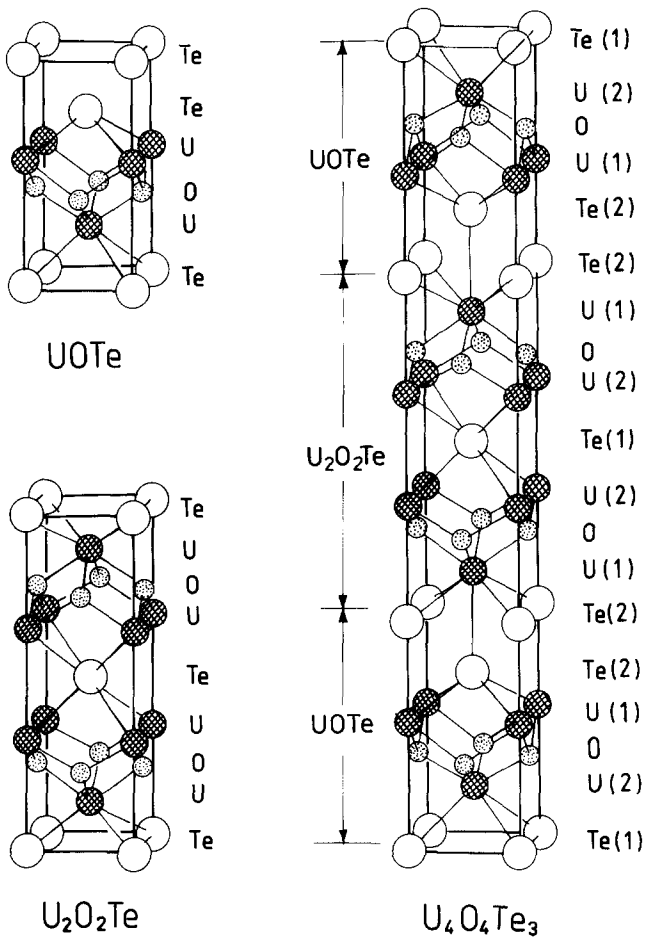


Fig. 1. The crystal structure of $\text{U}_4\text{O}_4\text{Te}_3$. For comparison the unit cells of UO_2Te and $\text{U}_2\text{O}_2\text{Te}$ are also shown.

polyhedron is completed by a further tellurium atom which is placed above the tellurium atom plane (as in UO_2Te).

It is believed that the oxidation state of the uranium atoms in $\text{U}_2\text{O}_2\text{Te}$ and UO_2Te is +3 and +4 respectively. Assuming that in $\text{U}_4\text{O}_4\text{Te}_3$ the individual uranium atoms have the very same electronic configurations as their counterparts in the above two oxytellurides one can rationalize the chemical formula of this compound as $\text{U}(1)_2^{+4}\text{U}(2)_2^{+3}\text{O}_4^{2-}\text{Te}_3^{2-}$. It is worthwhile noting that this formulation gives a full charge compensation and in consequence one should expect the semiconducting electrical properties of this compound. Also the possibility of ferrimagnetic properties of $\text{U}_4\text{O}_4\text{Te}_3$, considered in our recent magnetic studies [4], may find an explanation just by assuming the presence of two different electronic states of the uranium atoms in this oxytelluride, in accordance with the presence of two positions U(1) and U(2) in its unit cell. The results of magnetic and electrical transport investigations of $\text{U}_4\text{O}_4\text{Te}_3$ single crystals will be presented in our forthcoming paper [4].

Acknowledgements

We thank Dr. R. Pöttgen for a helpful discussion. This work was partly (L.S., D.K. and R.T.) supported by the Committee for Scientific Research (Poland) under Grant 202969101.

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