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The Structure of Thorium(IV) Dititanium(IV) Oxide, $ThTi_2O_6$*

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The crystal structure of a modification of $ThTi_2O_6$, obtained from the melt at 1100 °C, has been analysed by X-ray diffraction and refined to the R value of 0.051. The crystals are monoclinic with $a = 1.0799(7)$, $b = 0.8570(6)$, $c = 0.5192(3)$ nm and $\beta = 115.29(3)°$, space group $C2/c$, $Z = 4$, $F(000) = 728$. The structure is based on a near-hexagonal close-packing of the oxygen atoms, with the thorium and titanium atoms in »octahedral sites«. The coordination polyhedron of Th is a distorted square antiprism with Th—O distances from 0.232 to 0.265 nm, that of Ti a distorted octahedron with Ti—O distances from 0.187 to 0.201 nm like those characteristic for TiO_2 polymorphs. The Ti coordination polyhedra form layers parallel to the (100) which are connected by zig-zag chains of the Th coordination polyhedra which run in the [001] direction. The relations to another $ThTi_2O_6$ polymorph structure[1] (isomorphous with brannerite) have been examined.

INTRODUCTION

The crystals of $ThTi_2O_6$ were prepared by one of us (Z. G.)[2] some 15 years ago in the Institute »Ruđer Bošković«, Zagreb, by crystallization from the melts: a stoichiometric mixture of TiO_2 and ThO_2, with Na_2MoO_4 and MoO_3 used as flux, was heated at 1100 °C in a platinum crucible and then cooled slowly (3.5—4 °C/hour) to 700 °C, quenched in air and then dissolved in hot water. The composition of the crystals obtained, as determined by chemical analysis, differed slightly from preparation to preparation, but always with excess of titanium (4—8 atomic %) and an equivalent deficit of thorium. The reason for this may be a submicroscopic intergrowth with one of the TiO_2 modifications.

Small, colourless crystals of greasy-diamond luster differed in their X-ray powder diagram and unit cell parameters from hitherto known modifications[1] of $ThTi_2O_6$.

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* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.

EXPERIMENTAL

The crystal used for the structure determination was of a short prismatic habit (6.21×10^{-3} mm^3) with well developed faces (Figure 1). The faces were indexed using an optical goniometer and the dimensions of the crystal were measured microscopically to an accuracy better than 0.01 mm. These data were used for the absorption correction.

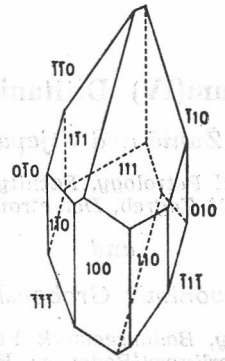

Figure 1. The shape of the $ThTi_2O_6$ crystal used in the structure analysis.

The intensities were collected with a Phillips PW1100 diffractometer using graphite monochromatized MoK$_\alpha$ radiation ($\lambda = 0.07107$ nm). Preliminary information obtained from Weissenberg photographs was used to collect and index 18 strong reflections in the range $8° < \Theta < 12°$ which were then used for the least-squares refinement of the unit cell parameters. The positions of these 18 reflections were re-measured once during the data collection, 15 times after the data collection and then averaged. The data collection yielded 623 symmetrically independent reflections in the range $0.05 < \sin\Theta < 0.5$. The systematic absences (also observed on the Weissenberg photographs):

$$hkl:\ h + k = 2n + 1$$

$$h0l:\ h,\ l = 2n + 1$$

indicated *C*2/*c* and *Cc* as possible space groups. The reflections were corrected for Lorentz-polarization factors using the program ZOAK5[3]. The absorption correction was made using the program ABSKOR[4] based on Thompa's analytical method. The linear absorption coefficient ($\mu = 385$ cm^{-1}) was calculated as the average of the values obtained with the observed ($\varrho_0 = 6.368$ gcm^{-3}) and calculated ($\varrho_x = 6.477$ gcm^{-3}) densities. Cutting or grinding of the crystal was not carried out because it would introduce structural defects[2]. The correction for the secondary extinction was applied in the last stage of the refinement using the CRYLSQ[5] program

STRUCTURE DETERMINATION AND REFINEMENT

The Wilson plot was calculated using the program NORMSF[5]. The obtained distribution of points showed nonsystematic discrepancies from the expected linear dependence over the whole range of $\sin^2\Theta/\lambda^2$. This may be due to a relatively low accuracy of data caused by a high absorption and/or to the presence of the heavy Th atom in a special position.

The structure was solved in the space group *C*2/*c*. An attempt to refine the structure in the space group *Cc* by releasing the constraints due to the two-fold axis did not improve the refinement but caused large deviations of the temperature factors for pairs of atoms symmetrically related in the space group *C*2/*c*.

The Patterson synthesis was calculated using the program FOURR[5]. The presence of a strong maximum at 0, 0.38, 0.5 indicated the special position (0, y, 1/4) of the Th atom. From the Patterson map the tentative position of the Ti atom was derived as: 0.273, 0.081, 0.065. The Fourier map calculated with Th and Ti revealed the positions of all oxygen atoms.

TABLE I

Fractional Coordinates and Temperature Factors with Standard Deviations

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Th	0	0.1909(1)	0.25	0.0019(6)	0.0091(7)	0.0082(6)	0	0.0015(4)	0
Ti	0.2691(3)	0.0819(4)	0.0598(6)	0.004(1)	0.010(1)	0.010(1)	—0.001(1)	0.002(1)	—0.000(1)
O(1)	0.363(1)	0.459(1)	0.347(3)	0.002(5)	0.007(5)	0.010(5)	0.001(4)	0.004(4)	—0.002(4)
O(2)	0.360(1)	0.088(2)	0.470(3)	0.007(5)	0.011(5)	0.012(5)	—0.002(4)	0.004(4)	0.002(4)
O(3)	0.140(1)	0.257(2)	0.030(3)	0.004(5)	0.011(6)	0.018(6)	0.001(4)	0.005(5)	0.001(5)

The obtained atomic parameters were then refined by the full matrix least-squares method using the CRYLSQ[5] program. The final R-value calculated with the correction for the secondary extinction, the anomalous dispersion correction for all atoms and with unit weight for all reflections was 0.051. The atomic parameters are listed in table I.*

STRUCTURE DESCRIPTION AND DISCUSSION

The structure of $ThTi_2O_6$ is shown in Figure 2. The oxygen atoms form layers parallel to the (100), building up approximately a hexagonal close packing while the thorium and titanium atoms, occupying its octahedral sites, form the alternating layers. Two additional O atoms approach the Th atom, realizing thus an eightfold coordination around the Th atom with a distorted square antiprism as the coordination polyhedron (Figure 3). The coordination of the Ti atom is a distorted octahedron of dimensions close to those found in TiO_2 polymorphs[6].

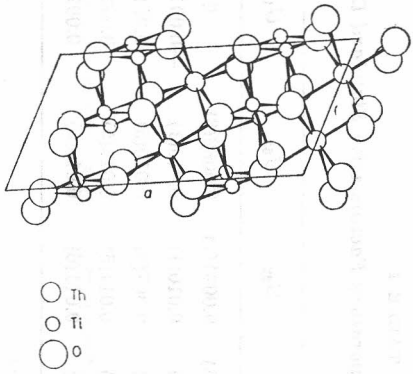

Figure 2. The projection of the structure of $ThTi_2O_6$ parallel to the b axis.

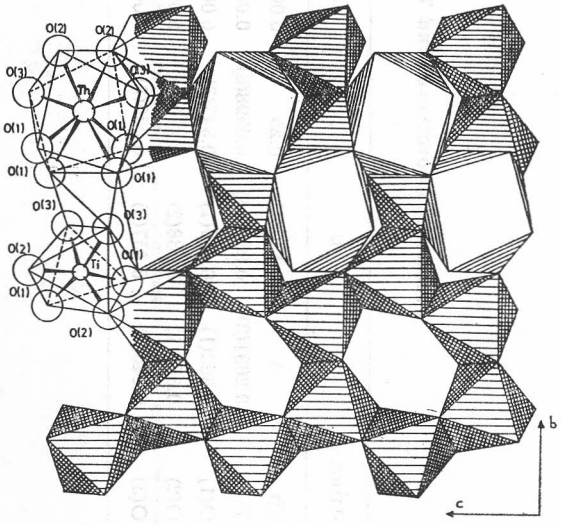

Figure 3. Part of a ∞ [TiO_3] layer with part of one ∞ [ThO_6] chain.

* A list of Fo and Fc values is available, on request, from the first author.

TABLE II

Interatomic Distances and Angles in $ThTi_2O_6$

Th — $O(3)_{1,2}$	0.232(2) nm	Ti — $O(3)_7$	0.187(2) nm
— $O(1)_{3,4}$	0.236(1)	— $O(2)_8$	0.192(2)
— $O(2)_{3,4}$	0.247(1)	— $O(2)_1$	0.193(1)
— $O(1)_{5,6}$	0.265(1)	— $O(1)_6$	0.199(1)
		— $O(1)_7$	0.201(1)
		— $O(3)_1$	0.201(1)

$O(3)_1$ — Th — $O(2)_4$	83.4(5)°	$O(3)_7$ — Ti — $O(3)_1$	81.6(7)°
$O(2)_4$ — — $O(2)_3$	79.9(4)	$O(3)_7$ — — $O(1)_7$	94.6(6)
$O(2)_3$ — — $O(3)_2$	83.4(5)	$O(3)_7$ — — $O(2)_8$	96.8(7)
$O(3)_2$ — — $O(1)_3$	89.4(5)	$O(3)_7$ — — $O(2)_1$	100.5(6)
$O(1)_3$ — — $O(1)_5$	67.1(4)	$O(1)_6$ — — $O(2)_1$	80.0(6)
$O(1)_5$ — — $O(1)_6$	82.8(4)	$O(1)_6$ — — $O(2)_8$	98.8(6)
$O(1)_6$ — — $O(1)_4$	67.1(4)	$O(1)_6$ — — $O(1)_7$	84.3(5)
$O(1)_4$ — — $O(3)_1$	89.4(5)	$O(1)_6$ — — $O(3)_1$	82.3(6)
		$O(3)_1$ — — $O(2)_1$	94.3(6)
		$O(2)_1$ — — $O(2)_8$	102.5(6)
		$O(2)_8$ — — $O(1)_7$	79.7(5)
		$O(1)_7$ — — $O(3)_1$	83.8(5)

Symmetry Operations:

1. x, y, z	5. x — 1/2, y — 1/2, z
2. —x, y, 1/2 — z	6. 1/2 — x, y — 1/2, 1/2 — z
3. 1/2 — x, 1/2 — y, 1 — z	7. 1/2 — x, 1/2 — y, z
4. x — 1/2, 1/2 — y, z — 1/2	8. x, —y, z — 1/2

The Ti coordination polyhedra form $^{2}_{\infty}[TiO_3]$ layers parallel to (100) in which each octahedron shares three edges with the adjacent octahedra. One third of the octahedral sites in the $^{2}_{\infty}[TiO_3]$ layers, around the inversion center at 1/4, 1/4, 1/2, are unfilled. The layers are connected by $^{1}_{\infty}[ThO_6]$ zig-zag chains which extend in the [001] direction. The Th coordination polyhedra are located between the empty octahedral sites of the neighbouring $^{2}_{\infty}[TiO_3]$ layers (looking along the [100] direction). In Figure 3 a cut out of $^{2}_{\infty}[TiO_3]$ layer is shown together with a cut out of a $^{1}_{\infty}[ThO_6]$ chain overlying it. The bond distances and angles are listed in Table II. The Th—O distances range from 0.232 to 0.265 nm, the Ti—O distances from 0.187 to 0.201 nm (the distances in ThO_2 are 0.242 nm while those in TiO_2 polymorphs vary from 0.187 to 0.204 nm[6]).

It is interesting to compare our structure with that of the $ThTi_2O_6$ polymorph[1] isomorphous with brannerite (UTi_2O_6). In this structure the O atoms form a near-cubic-close-packing and the structure consists of anatase-like portions connected by the Th coordination polyhedra. The Th atom is located between the two »tetrahedral« sites forming a very flattened octahedral coordination. The two additional O atoms are at the significantly longer distances of 0.296 nm.

Although the structure described here is based on a near-hexagonal-close--packing like the rutile structure, the connection of the Ti coordination

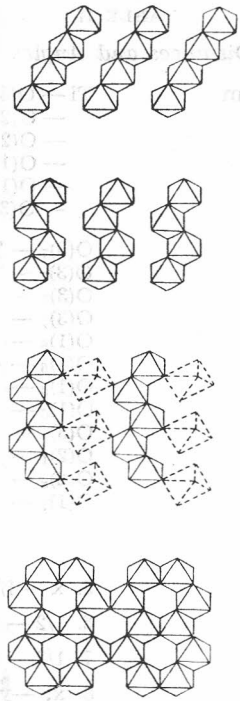

Figure 4. The »octahedral-site-occupancy« of Ti between the two near-close-packed layers of oxygen in:

a) rutile, projection parallel to [100];

b) anatase, projection parallel to [112] or brookite, projection parallel to [100];

c) the brannerite polymorph of $ThTi_2O_6$, projection perpendicular to $(\bar{1}12)$ (the coordination polyhedra of Th are shown by dashed lines);

d) $ThTi_2O_6$ described in the present work, projection perpendicular to (100).

polyhedra is significantly different. It shows anatase-like chains of the Ti polyhedra like the brannerite polymorph but they are interconnected in a different way (Figure 4).

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REFERENCES

1. R. Ruh, A. D. Wadsley, *Acta Cryst.* **21** (1966) 974.
2. Z. Grobenski, *MSc Thesis,* University of Zagreb (1971).
3. I. Vicković, *MSc Thesis,* University of Zagreb (1977).
4. P. Engel, Z. *Kristallogr.* **146** (1977) 137.
5. J. M. Stewart, P. A. Machin, C. W. Dickinson, H. Heck, H. Flack, *The X-ray system, technical report TR-446.* Computer Science Center, Univ. of Maryland, College park, Maryland (1976).
6. *Crystal Structures,* Vol. **1**, W. G. Wyckoff, New York, John Wiley & Sons, 1963, Ch. IV.

SAŽETAK

Struktura $ThTi_2O_6$

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Kristalna struktura jedne od modifikacija $ThTi_2O_6$, dobivene iz taljevine na 1100 °C, određena je rendgenskom difrakcijom i utočnjena do $R = 0.051$. Kristali su monoklinski s jediničnom ćelijom $a = 1.0799(7)$, $b = 0.8570(6)$, $c = 0.5192(3)$ nm i $\beta = 115.29(3)°$, prostorna grupa $C2/c$, $Z = 4$ formulske jedinice, $F(000) = 728$. U osnovi strukture leži približna heksagonska gusta slagalina atoma kisika unutar koje Th i Ti atomi zauzimaju oktaedarske praznine. Koordinacijski poliedar oko atoma Th je deformirana Arhimedova antiprizma s razmacima Th—O od 0.232 do 0.265 nm, a oko atoma Ti deformirani oktaedar s razmacima Ti—O od 0.187 do 0.201 nm, karakterističnim za polimorfne modifikacije TiO_2. Koordinacijski poliederi oko atoma titana tvore slojeve paralelne (100) koji su povezani cik-cak lancima, sačinjenim od koordinacijskih poliedara oko atoma torija, koji se pružaju smjerom [001]. Istražen je i odnos prema drugoj poznatoj modifikaciji $ThTi_2O_6$ koja je izomorfna s branneritom.[1]