

Crystal Structures of Some Niobium and Tantalum Oxides. Part V. CeTa₇O₁₉*

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CeTa₇O₁₉ crystallizes in the hexagonal system with unit-cell dimensions (from single crystal data) $a = 6.226(3)$, $c = 19.976(8)$ Å, and space group $P6_3/mcm$, $z = 2$. The structure was solved by conventional methods with 290 counter-measured reflections (MoK α radiation), and refined using Fourier and least-squares techniques to a conventional R of 0.067 ($R_w = 0.057$). CeTa₇O₁₉ has a structure that consists of double layers of tantalum polyhedra that may be described either as edge-shared pentagonal bipyramids or as corner-shared octahedra with a further long (2.48 Å) contact through one edge in the plane, separated by a layer of distorted bicapped trigonal antiprismatic sites. The latter polyhedra are edge-shared with the double layers and are fully occupied by two Ce(III) and two Ta(V) ions distributed randomly over the 4-fold site. The average Ta-O distance in the double layers is 2.06 Å and in the (Ce, Ta) layer is 2.34 Å.

Introduction

Rare earth niobates and tantalates have received attention recently in view of their potentially interesting physical properties (1). Three phases were shown to exist in the cerium oxide-tantalum oxide system, CeTa₇O₁₉, CeTa₃O₉, and CeTaO₄ (2); however, no single crystal studies were reported. We report here the single crystal structure determination of CeTa₇O₁₉.

Experimental

A small sample of the above compound was kindly supplied by Dr. R. S. Roth,

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National Bureau of Standards, Washington D.C., U.S.A. The crystals are light yellow to brown in color (probably as the result of being synthesized in a vanadium oxide flux (1)); a light yellow hexagonal prismatic crystal (0.025 mm across, 0.017 mm deep) was selected, checked for twinning or cracking using a polarizing microscope and mounted, using clear epoxy resin ('Resiweld') on a silica capillary. The crystal data were obtained using a Philips PW 1100 computer controlled diffractometer in a manner described earlier (3).

Crystal Data: CeTa₇O₁₉, $M = 1710.37$, $a = 6.226(3)$, $c = 19.976(8)$ Å. $U = 670.59$ Å³, $D_c = 8.47$ g cm⁻³, $z = 2$, insufficient material available to measure the density, $F(000) = 1442$, $\mu = 632.2$ cm⁻¹ for MoK α radiation ($\lambda = 0.7107$ Å). Space group $P6_3/mcm$, $P\bar{6}c2$ or $P6_3cm$; from absent reflections $h\bar{h}0l$, $l = 2n + 1$, and from Laue symmetry $6/mmm$; $P6_3/mcm$ (D_{6h}^3 , No. 193) by successful refinement. Insufficient material was

available for piezoelectric or second harmonic generation tests to be applied.

Intensity Measurements

Intensity measurements were made with the crystal described above using the diffractometer and MoK α radiation monochromated with a flat graphite monochromator crystal. A unique data set was collected out to 2θ (MoK α) = 60° using the ω scan technique with a symmetric scan range of $\pm 0.4^\circ$ in 2θ from the calculated Bragg angle with an allowance for dispersion, at a scan rate of $0.03^\circ \text{sec}^{-1}$. No reflection was sufficiently intense to require the insertion of an attenuation filter. Of the 391 independent reflexions measured 290 were considered to be significantly above the background ($I \geq 3\sigma(I)$) and only these were used during the refinement. Three standard reflexions measured at two hourly intervals showed no significant variations in intensity.

The data were processed in a manner described recently (3). An absorption correction was applied to the data following the indexing of the crystal faces and calculation of the direction cosines pertaining to each reflection. No extinction correction was applied. The atomic scattering factors used were Ce $^\circ$, Ta $^\circ$ (4) (corrected for anomalous dispersion (5)) and O $^\circ$ (4). All calculations were performed on the Monash University B6700 computer and the major program used was that of Sheldrick (6).

Structure Solution and Refinement

The structure was solved by conventional Patterson methods for the heavy atom positions, and the oxygen atoms were located in the subsequently calculated Fourier difference synthesis. Refinement of positional and thermal parameters (anisotropic for the metal atoms, isotropic for the oxygen atoms) resulted in a final R of 0.067 and R_w of 0.057, where $R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$ and $R_w = \frac{\sum w^{1/2} (|F_o| - |F_c|)}{\sum w^{1/2} |F_o|}$ where

F_o and F_c are observed and calculated structure factors respectively and $w (\propto 1/\sigma^2(F))$ is the weight of each individual reflexion. Attempts were made to refine the structure in space group $P\bar{6}c2$ in order to test the possibility that the Ce and Ta in site $\frac{1}{3}\frac{2}{3}0$ of $P6_3/mcm$ were ordered in pairs in the sites $\frac{2}{3}\frac{1}{3}0$ and $\frac{2}{3}\frac{1}{3}0$. Refinement resulted in large residuals at the Ce sites and negative thermal parameters for Ta and some of the oxygen atoms.

Description of the Structure and Discussion

The structure of CeTa $_7$ O $_{19}$, perhaps more explicitly written as (Ce, Ta)Ta $_6$ O $_{19}$, consists of two types of polyhedra. The Ce Ta polyhedron is a distorted bicapped trigonal antiprism; the top of the prism is rotated 21° relative to the base towards being a regular trigonal prism. The bond lengths within the prism itself are all 2.24 Å, with the oxygens above and below the prism along the 3-fold axis being 2.62 Å from the Ce or Ta atoms. Thus the coordination of Ta(V) would seem to be satisfied with six oxygen atoms at 2.24 Å, and that of Ce(III) with the six oxygens at 2.24 Å plus two further oxygen contacts at 2.62 Å. In the structure of Ce $_6$ (MoO $_4$) $_8$ Mo $_2$ O $_7$ determined recently (7) the forty-eight Ce–O distances of the six independent Ce(III) ions ranged from 2.33 to 2.90 Å with an average distance of 2.52 Å. Figure 1 shows a pair of the (Ce, Ta) sites in the CeTa $_7$ O $_{19}$ structure drawn in projection along [001].

The second polyhedron, that of Ta(2), may be described in two ways. As a distorted pentagonal bipyramid it has six Ta–O bonds between 1.89 and 2.06 Å and a long bond of 2.48 Å. As a distorted octahedral site it has a seventh bond through the middle of an octahedron edge (2.48 Å). A layer of these polyhedra is drawn in Fig. 2, in projection along [001]. It is felt that perhaps the description in terms of distorted octahedra may allow a discussion of the derivation of the structure from a basic framework such as

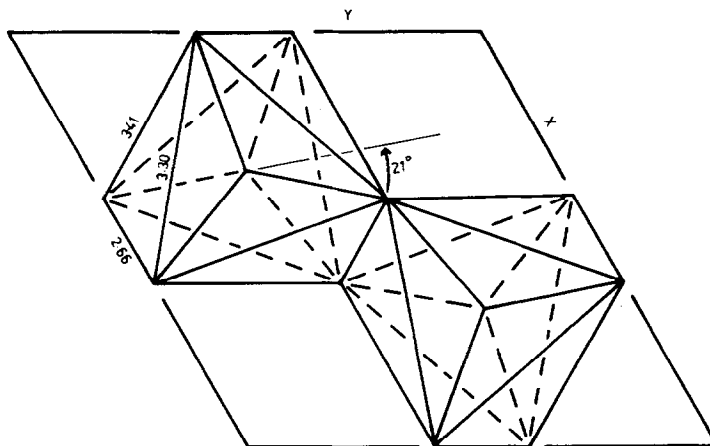


FIG. 1. Two edge-shared trigonal antiprismatic sites that contain (Ce, Ta) are shown, with their oxygen-oxygen distances, in projection along [001].

that of ReO_3 to be made more easily. A summary of a number of interatomic distances in tantalum compounds, some of which have pentagonal bipyramidal coordination was published recently (8).

The bicapped trigonal antiprisms of the Ce, Ta atoms are edge-shared to one another (Fig. 1) and form hexagonal rings in the structure. These polyhedra are edge-shared

to the layers of pentagonal bipyramids above and below (Fig. 3 shows a stereoscopic view of part of the contents of the unit-cell with pentagonal bipyramids drawn for Ta(2), Fig. 4 has the Ta(2) sites drawn as octahedra). The sheets of pentagonal bipyramids (or distorted octahedra) are corner shared with another sheet to form the double layer mentioned earlier.

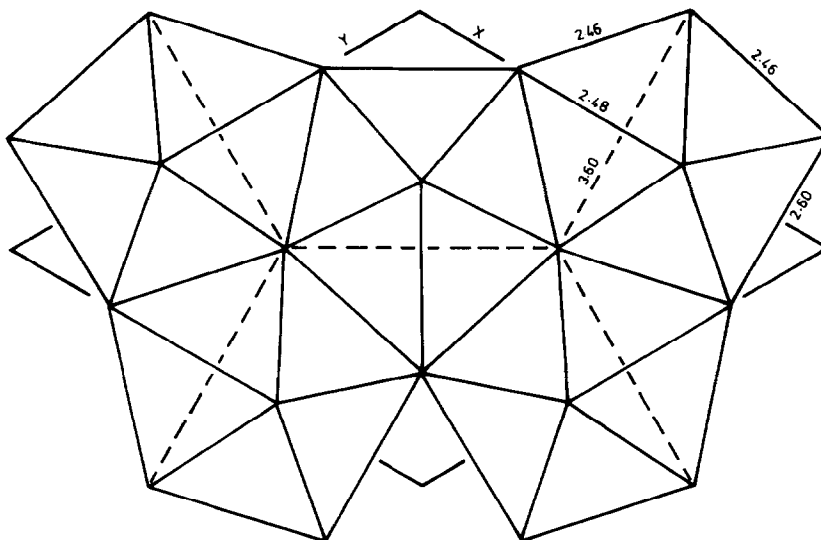


FIG. 2. The pentagonal bipyramidal or distorted octahedral sites of Ta(2) with oxygen-oxygen distances are illustrated in an [001] projection.

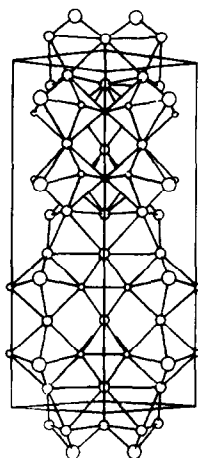


FIG. 3. Part of the unit-cell contents with the Ta(2) sites drawn as pentagonal bipyramids illustrated as a stereoscopic pair.

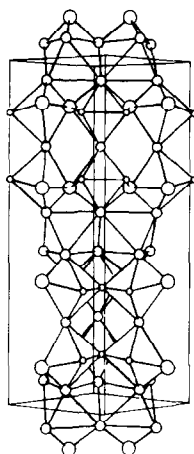
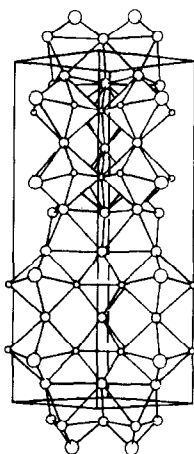
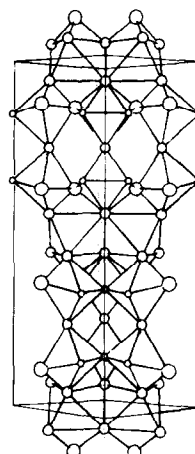


FIG. 4. As for Fig. 3, with the Ta(2) sites drawn as distorted octahedra.



In a report dealing with 'hexa- and hepta-coordination in niobium and tantalum oxides and oxide fluorides and structurally related compounds', Jahnberg (9) drew attention to a hypothetical structure for the compound $\text{YT}_a_7\text{O}_{19}$ (unit-cell dimensions $a = 6.203$, $c = 19.863 \text{ \AA}$) and its relationship to the structures of $\text{Na}_2\text{Nb}_4\text{O}_{11}$ and $\text{CaTa}_4\text{O}_{11}$ (10). With the exception that Jahnberg considered the sites, called Ta(2) here, only as pentagonal bipyramids, and the Ce, Ta sites as octahedra the hypothetical structure is that found here for $\text{CeTa}_7\text{O}_{19}$. The relationship of the layers of pentagonal bipyramids in $\text{Na}_2\text{Nb}_4\text{O}_{11}$ and $\text{CaTa}_4\text{O}_{11}$ to those in $\alpha\text{-U}_3\text{O}_8$ was also discussed by Jahnberg (9).

TABLE II

BOND LENGTHS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Cerium(tantalum)-oxygen < 3.50 Å	
Ce(Ta)-O(2)	2.24(2) [6] ^a
O(3)	2.62(6) [2]
Tantalum(pbp)-oxygen < 3.50 Å.	
Ta(2)-O(4)	1.886(6)
O(2)	1.97(4)
O(1)	1.981(6) [2]
O(3)	2.06(2) [2]
O(1)	2.48(3)

^aNumber of these particular bonds.

TABLE I

FINAL POSITIONAL PARAMETERS (METALS $\times 10^4$, OXYGEN $\times 10^3$) AND THERMAL PARAMETERS (METALS $\times 10^4$, OXYGEN $\times 10^3$) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ce, Ta	3333	6667	0	20(9)	20(9)	19(13)	0	0	10(5)
Ta(2)	6394(2)	0	3438(1)	20(6)	18(7)	34(6)	0	15(6)	9(4)
O(1)	241(5)	0	156(2)	14(6)					
O(2)	398(6)	0	559(2)	38(9)					
O(3)	3333	6667	131(3)	66(16)					
O(4)	604(8)	0	2500	32(13)					

We have determined the structure of a cerium niobium oxide, $CeNb_5O_{14}$ (11) and will be examining the possibility of the formation of compounds related to $CeTa_7O_{19}$ but with different ordering of layers of the two types observed here.

The indexed X-ray powder pattern of $CeTa_7O_{19}$ was reported recently (12) and the unit cell dimensions determined.

Acknowledgments

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