Xe$\cdots$F(1^I) 3·27 Å and Xe$\cdots$F(4^{II}) 3·26 Å, where I and II refer to atoms symmetry-related to those in Table 1 by the operations $(1+x,y,z)$ and $(x,\frac{1}{2}-y,\frac{1}{2}+z)$ respectively, are only slightly shorter than the non-bonded Xe$\cdots$F contact in XeF$_2$ (3·42 Å; Levy & Agron, 1963). The crystal structure therefore consists of fluorine-bridged molecules with weak intermolecular forces rather than of ions.

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Calcium Tetratantalate

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Abstract. CaTa$_4$O$_{11}$, hexagonal, $P6_3 22$, $a=6\cdot2173$ (3), $c=12\cdot271$ (2) Å, $Z=2$, $D_x=7\cdot60$ g cm^{-3}. Colourless transparent crystals of CaTa$_4$O$_{11}$ were synthesized from a 1:2 mixture of CaCO$_3$ and Ta$_2$O$_5$ by the floating-zone technique [Akashi, Matsumi, Okada & Mizutani. *IEEE Trans. Mag.* (1969). **5**, 285–289]. One of the two independent Ta atoms is surrounded by seven oxygen atoms in the form of a pentagonal bipyramid with the average distance 2·06 Å. The remaining Ta and Ca atoms are coordinated to six and eight oxygen atoms with average distances 1·97 and 2·52 Å, respectively.

Introduction. The systematic absence observed on Weissenberg photographs was 00*l* for *l* odd. The space group was uniquely determined to be $P6_3 22$ from the systematic absence and the Laue symmetry of 6/*mmm*. Cell dimensions were determined by the least-squares method from 11 reflexion data. For intensity measurements, a specimen was roughly ground into a sphere with average radius 0·04 mm. Intensities were collected on an automated four-circle diffractometer with Mo *K*α radiation monochromated by a graphite plate. The ω–2θ scan technique was employed with a scanning speed of 0·5° min^{-1} in ω. In all, 291 independent re-

flexion data, whose |*F*|'s were larger than $3\sigma(|F|)$, were obtained within the range $2\theta\leq75°$. The intensities were corrected for Lorentz, polarization and absorption factors.

The structure was solved by the heavy-atom method. The positions of the Ta atoms were obtained from the Patterson maps. Those of the remaining atoms were found on Fourier maps phased with the Ta atoms. The structure was refined with the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970) by assuming anisotropic temperature factors for Ta and Ca atoms and isotropic for oxygen atoms. At the final stage of the refinement, the isotropic secondary-extinction parameter was included in the calculation. The final *R* value was 0·032 for the 291 observed reflexions.* Unit weight was given to all the reflexions. The atomic scattering factors used were those given by Tokonami (1965) and Cromer & Waber (1965) for O^{2-} and Ta^{5+},

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respectively, and the values for Ca^{2+} in *International Tables for X-ray Crystallography* (1968). The final atomic parameters are given in Table 1. The interatomic distances and bond angles are given in Table 2.

Fig. 1. The structure of $CaTa_4O_{11}$ viewed along the *a* axis.

Discussion. A synthesis and crystallographic study of $CaTa_4O_{11}$ were reported by Gasperin (1963). On the basis of the Patterson function Gasperin gave a probable arrangement of Ta atoms. The present investigation was undertaken to elucidate the details of the structure and its relationship to the structures of the other members in the $CaO-Ta_2O_5$ system.

The structure viewed along the *a* and *c* axes is shown in Figs. 1 and 2, respectively. In Fig. 2, Ta(2) at $\frac{2}{3},\frac{1}{3},\frac{3}{4}$ and Ca at $\frac{1}{3},\frac{2}{3},\frac{3}{4}$ are omitted to avoid complexity. There are two independent Ta atoms. Ta(1) atoms lie on the planes at $z=0$ and $z=\frac{1}{2}$ and are surrounded by seven oxygen atoms in the form of a pentagonal bipyramid. The coordination polyhedra of Ta(1) are joined to each other by edge-sharing, forming two-dimensional networks parallel to (001). Ta(2) and Ca atoms are on the planes at $z=\frac{1}{4}$ and $z=\frac{3}{4}$. Ta(2) is octahedrally surrounded by six oxygen atoms, whereas Ca is surrounded by eight oxygen atoms in the form of a distorted cube. These two kinds of coordination polyhedra also form two-dimensional networks parallel to (001) by sharing edges. The layers of the $Ta(1)O_7$ pentagonal bipyramids alternate with the mixed layers of $Ta(2)O_6$ and CaO_8 polyhedra in the c direction. The former is linked with the latter by sharing edges with CaO_8 polyhedra to construct the whole structure. In the $Ta(1)O_7$ polyhedra the shortest edges are those shared by the neighbouring pentagonal bipyramids owing to the strong repulsion between Ta^{5+} cations with large positive charge. The edges shared by the neighbouring CaO_8 polyhedron are also shorter than the unshared edges. In the $Ta(2)O_6$ and CaO_8 polyhedra the shared edges are also significantly shorter than the unshared ones.

Besides $CaTa_4O_{11}$, the following three phases have been reported in the $CaO-Ta_2O_5$ system: $CaTaO_3$, $CaTa_2O_6$ and $Ca_2Ta_2O_7$. The structure of $CaTaO_3$ is of the perovskite type (Gasperin, 1958) and that of $CaTa_2O_6$ is known to have a close relation to the perovskite structure (Jahnberg, 1963). $Ca_2Ta_2O_7$ is supposed to have a pyrochlore type structure (Ismailzade, 1958). In all these compounds, Ta atoms have octahedral coordinations of oxygen atoms. Pentagonal bipyramidal coordinations around Ta atoms have been found in the low-temperature form Ta_2O_5 (Stephenson & Roth, 1971a) and in a series of compounds in the

Table 1. *Positional and thermal parameters for* $CaTa_4O_{11}$

The anisotropic temperature factors are in the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$. The following constraints are required from the symmetry: $\beta_{11}=\beta_{22}$ and $\beta_{13}=-\beta_{23}$ for the Ta(1) atom, and $\beta_{11}=\beta_{22}=2\times\beta_{12}$ and $\beta_{13}=\beta_{23}=0$ for the Ta(2) and Ca atoms.

	x	y	z	$\beta_{11}\times10^5$ or B (Å^2)	$\beta_{22}\times10^5$	$\beta_{33}\times10^5$	$\beta_{12}\times10^5$	$\beta_{13}\times10^5$	$\beta_{23}\times10^5$
Ta(1)	0·3589 (2)	0·3589	$\frac{1}{2}$	360 (24)	360	67 (4)	240 (26)	1 (8)	−1
Ta(2)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	354 (44)	354	76 (10)	177	0	0
Ca	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{4}$	790 (242)	790	78 (47)	395	0	0
O(1)	0·371 (3)	0·430 (3)	0·344 (1)	0·3 (2)					
O(2)	0·750 (3)	0·750	$\frac{1}{2}$	0·5 (2)					
O(3)	$\frac{1}{3}$	$\frac{2}{3}$	0·538 (2)	0·7 (4)					

Table 2. *Interatomic distances* (Å) *and bond angles* (°) *with their estimated standard deviations in parentheses*

Ta(1) pentagonal bipyramid			Ta(2) octahedron		
Ta(1)–O(1)	1·96 (1)	2×	Ta(2)–O(1)	1·97 (2)	6×
O(2^{iv})	1·98 (3)	2×	O(1)—O(1^i)	2·62 (2)	3×
O(3)	2·05 (1)	2×	O(1^{ii})	2·77 (3)	6×
O(2)	2·43 (1)		O(1^i)–O(1^{ii})	3·02 (3)	3×
O(1)—O(2)	2·91 (2)	2×			
O(2^{iv})	3·06 (3)	2×	O(1)–Ta(2)–O(1^i)	83·0 (8)	3×
O(2^v)	2·77 (2)	2×	O(1)–Ta(2)–O(1^{ii})	89·3 (8)	6×
O(3)	2·86 (3)	2×	O(1^i)–Ta(2)–O(1^{ii})	99·6 (7)	3×
O(3^{vi})	2·64 (2)	2×			
O(2)—O(3)	2·41 (2)	4×			
O(2^{iv})–O(2^v)	2·70 (4)		Ca polyhedron		
O(2^{iv})–Ta(1)–O(2^v)	85·9 (9)		Ca—O(1)	2·48 (2)	6×
O(2)—Ta(1)–O(3)	64·7 (6)	2×	O(3^{vi})	2·61 (3)	2×
O(2^v)–Ta(1)–O(3)	73·5 (6)	2×	O(1)—O(1^i)	2·62 (2)	3×
O(1)—Ta(1)–O(2)	82·4 (4)	2×	O(1^i)—O(1^{iii})	3·82 (3)	3×
O(1)—Ta(1)–O(2^v)	89·2 (6)	2×	O(1)–O(1^{iii})	3·81 (3)	6×
O(1)—Ta(1)–O(2^{iv})	102·0 (5)	2×	O(3^{vi})	2·64 (2)	6×
O(1)—Ta(1)–O(3)	91·2 (9)	2×			
O(1)—Ta(1)–O(3^{vi})	82·3 (9)	2×	O(1)–Ca–O(1^i)	63·5 (5)	3×
			O(1)–Ca–O(1^{iii})	100·2 (7)	6×
			O(1^i)–Ca–O(1^{iii})	100·4 (6)	3×
			O(1)–Ca–O(3^{vi})	62·3 (3)	6×

Symmetry code

	x	y	z				
None	x	y	z	iv	$1-y$	$x-y$	z
i	$1-y$	$1-x$	$\frac{1}{2}-z$	v	$y-x$	$1-x$	z
ii	$1-y$	$1+x-y$	z	vi	y	x	$1-z$
iii	$1+y-x$	$1-x$	z				

system of Ta_2O_5–WO_3 with low WO_3 contents (Stephenson & Roth, 1971*b, c, d, e*).

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Fig. 2. The structure of $CaTa_4O_{11}$ viewed along the c axis. Ta(2) at $\frac{2}{3},\frac{1}{3},\frac{3}{4}$ and Ca at $\frac{1}{3},\frac{2}{3},\frac{3}{4}$ have been omitted for clarity.