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Crystal Structure of Orthorhombic $CaTa_2O_6$

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The crystal structure of the orthorhombic modification of $CaTa_2O_6$ has been studied using X-ray data from a single crystal. The cell dimensions are $a = 11.068$, $b = 7.505$ and $c = 5.378$ Å. The space-group is *Pnma*. The structure may be described as built up of distorted TaO_6 octahedra sharing edges and corners. The calcium atoms are situated in tunnels running through the structure. A comparison is made with the perovskite structure and the calcium coordination is discussed.

In a previous paper [1] the polymorphism of $CaTa_2O_6$ was reported. It was stated that this substance exists in three different structural modifications, *viz.* a perovskite-type structure with cubic symmetry and a random distribution of the calcium atoms if prepared at low temperatures, an orthorhombic modification above approximately 700°C and finally a structure of deformed perovskite-type in samples rapidly cooled from the melt. The crystal structure of the orthorhombic modification has now been determined.

EXPERIMENTAL

The sample of $CaTa_2O_6$ used in this investigation was prepared from Ta_2O_5 (Fansteel Metallurgical Corporation) and $CaCO_3$ (Mercks reagent, *pro analysi*). An intimate mixture of stoichiometric amounts of the substances was pressed into tablets, melted in an electric arc furnace in an argon atmosphere, and then heat-treated in air at 1300°C for six days and at 1500°C for about ten hours. The product was pale yellow and crystalline. Weissenberg photographs were taken of a rod-shaped crystal, 0.12 mm in length with cross section edges 0.04, 0.04, 0.03, and 0.01 mm long, using Cu*K* radiation. The crystal was rotated around both the *b* axis, lying almost in the rod-direction, and the *c* axis. All the layer lines thus obtainable were registered using multiple film techniques. The relative intensities of the reflections were visually estimated by comparison with an intensity scale prepared by registering accurately defined exposures with a suitable reflection from the crystal. The intensities were corrected for absorption by a numerical integration procedure in which the volume of the crystal was divided into 125 volume elements. Most of the calculations involved in the crystal structure determination were facilitated by the use of the electronic computers BESK and FACIT EDB with the help of several computer programs.[2]

DERIVATION OF THE STRUCTURE

The Weissenberg photographs showed orthorhombic symmetry. Guinier powder photographs, registered with strictly monochromatized Cu$K\alpha_1$ radiation and using potassium chloride (a = 6.2919 Å at 20°C) as an internal standard, gave the following cell dimensions:

$$a = 11.068, \qquad b = 7.505, \qquad c = 5.378 \text{ Å *}$$

Table 1. Powder pattern of $CaTa_2O_6$ (orthorhombic)

I	$\sin^2\Theta_{obs}$	$h\,k\,l$	$\sin^2\Theta_{calc}$	I	$\sin^2\Theta_{obs}$	$h\,k\,l$	$\sin^2\Theta_{calc}$
v w	0.01941	2 0 0	0.01937	v w	0.19618	2 3 2	0.19621
v st	0.02541	1 0 1	0.02535	st	0.20165	4 2 2	0.20166
v w	0.02991	2 1 0	0.02991	w	0.20319	5 0 2	0.20312
v w	0.03101	0 1 1	0.03104	w	0.20397	2 0 3	0.20397
w	0.03589	1 1 1	0.03589	w	0.20839	2 4 1	0.20841
m	0.03986	2 0 1	0.03988	w	0.21647	6 2 0	0.21648
v st	0.04219	0 2 0	0.04213	w	0.22820	3 0 3	0.22819
m	0.06147	2 2 0	0.06150	st	0.23269	3 4 1	0.23263
v st	0.06418	3 0 1	0.06410	v w	0.23649	5 3 1	0.23638
v st	0.06759	1 2 1	0.06749			6 2 1	0.23699
v w	0.07461	3 1 1	0.07463	st	0.24612	4 4 0	0.24602
st	0.07751	4 0 0	0.07749			2 2 3	0.24610
st	0.08208	2 2 1	0.08202	m	0.25054	0 4 2	0.25057
		0 0 2	0.08204	w	0.25542	1 4 2	0.25542
w	0.08688	1 0 2	0.08689	w	0.25627	6 0 2	0.25639
w	0.09800	4 0 1	0.09800	m	0.25785	7 0 1	0.25782
w	0.10138	2 0 2	0.10142	v w	0.26212	4 0 3	0.26209
st	0.10630	3 2 1	0.10623	m	0.27040	3 2 3	0.27032
v w	0.10845	4 1 1	0.10853	v w	0.28870	1 5 1	0.28868
v w	0.11185	2 1 2	0.11195	v w	0.29408	3 4 2	0.29416
v w	0.11407	2 3 0	0.11417	m	0.29987**	7 2 1	0.29995
v w	0.11527	0 3 1	0.11531	w	0.31001	8 0 0	0.30995
st	0.11986**	4 2 0	0.11962			5 4 1	0.31011
		1 3 1	0.12015	m	0.32810	4 4 2	0.32806
m	0.12416	0 2 2	0.12418			0 0 4	0.32818
w	0.12557	3 0 2	0.12563	w	0.33320	1 0 4	0.33302
w	0.12899	1 2 2	0.12902	w	0.34293	6 4 0	0.34288
v w	0.13611	3 1 2	0.13616	w	0.35207	8 2 0	0.35208
v w	0.14000	4 2 1	0.14013	w	0.35804**	1 4 3	0.35797
w	0.14152	5 0 1	0.14159	w	0.35918**	6 0 3	0.35895
w	0.14351	2 2 2	0.14355	w	0.37251	2 4 3	0.37250
v w	0.15211	5 1 1	0.15212	w	0.37539	1 2 4	0.37515
st	0.15952	4 0 2	0.15953	w	0.37910	0 6 0	0.37919
st	0.16849	0 4 0	0.16853	v w	0.39191	8 0 2	0.39200
w	0.17430	6 0 0	0.17435	w	0.39681	3 4 3	0.39671
w	0.18368	5 2 1	0.18372	v w	0.40116	6 2 3	0.40108
v w	0.18949	1 0 3	0.18944	w	0.40466	1 6 1	0.40454
m	0.19386	1 4 1	0.19388				

* The parameters have been calculated by the method of least squares and differ sligthly from those given in the previous paper.[1]

** Line overlaps line of KCl.

The powder pattern of $CaTa_2O_6$ is given in Table 1. Reflections with indices $hk0$ were observed only for $h = 2n$ and $0kl$ only for $k + l = 2n$ which is characteristic of the space-groups *Pnma* and $Pna2_1$. It was first tested whether a reasonable structure could be derived assuming the former symmetry. As this turned out to be the case, the latter space-group was not taken into account. The observed density was 7.32 g cm^{-3}. Four formula units $CaTa_2O_6$ correspond to a calculated density 7.40 g cm^{-3}.

In *Pnma* there are four point positions:

8(*d*) 1 $x,y,z;\ \frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}-z;\ \bar{x},\frac{1}{2}+y,\bar{z};\ \frac{1}{2}-x,\bar{y},\frac{1}{2}+z;$
$\bar{x},\bar{y},\bar{z};\ \frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}+z;\ x,\frac{1}{2}-y,z;\ \frac{1}{2}+x,y,\frac{1}{2}-z.$
4(*c*) *m* $x,\frac{1}{4},z;\ \bar{x},\frac{3}{4},\bar{z};\ \frac{1}{2}-x,\frac{3}{4},\frac{1}{2}+z;\ \frac{1}{2}+x,\frac{1}{4},\frac{1}{2}-z.$
4(*b*) $\bar{1}$ $0,0,\frac{1}{2};\ 0,\frac{1}{2},\frac{1}{2};\ \frac{1}{2},0,0;\ \frac{1}{2},\frac{1}{2},0.$
4(*a*) $\bar{1}$ $0,0,0;\ 0,\frac{1}{2},0;\ \frac{1}{2},0,\frac{1}{2};\ \frac{1}{2},\frac{1}{2},\frac{1}{2}.$

The positions 4(*a*) and 4(*b*) require that a vector ends in the point $u = \frac{1}{2}$, $w = \frac{1}{2}$ of the projection along [010] of the Patterson function. This projection (Fig. 1) shows no high maximum in this point, so the tantalum atoms could

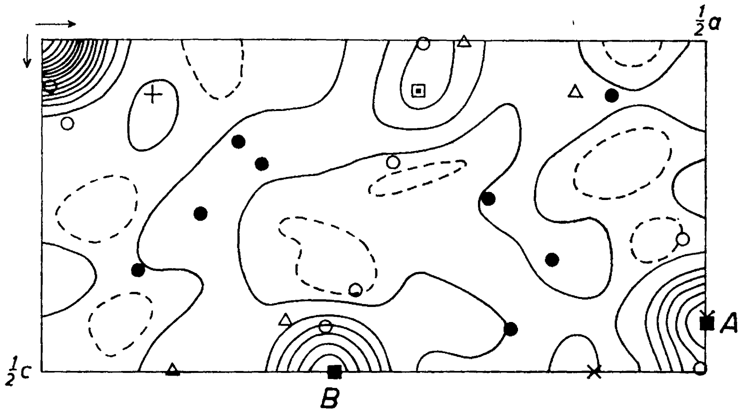


Fig. 1. Patterson projection along [010] and corresponding vectors obtained from the final atomic coordinates. Negative contours are dotted and represent only half the increments of the positive contours.

■	Ta–Ta	(Multiplicity 8)
⊡	Ta–Ta	(» 4)
△	Ta–Ca	(» 4)
●	Ta–O	(» 8)
○	Ta–O	(Multiplicity 4)
×	Ca–Ca	(» 2)
+	Ca–Ca	(» 1)

not be placed in these positions. The position 4(*c*), as well as 8(*d*), requires vectors to occur in points $u = \frac{1}{2}-2x$, $w = \frac{1}{2}$ and $u = \frac{1}{2}$, $w = \frac{1}{2}-2z$. Since there is only one high maximum (A in Fig. 1) for $u = \frac{1}{2}$ and one (B in Fig. 1) for $w = \frac{1}{2}$, the 8 tantalum atoms could not be placed in two 4(*c*) positions, but in 8(*d*) with $x = 0.142$ and $z = 0.038$. An electron density projection along [010] (Fig. 2) gave approximate x and z parameters for 4 calcium atoms in 4(*c*) and also indication of 16 oxygen atoms in two 8(*d*) positions. The remaining 8 oxygens were tentatively placed in 4(*c*) positions, with the

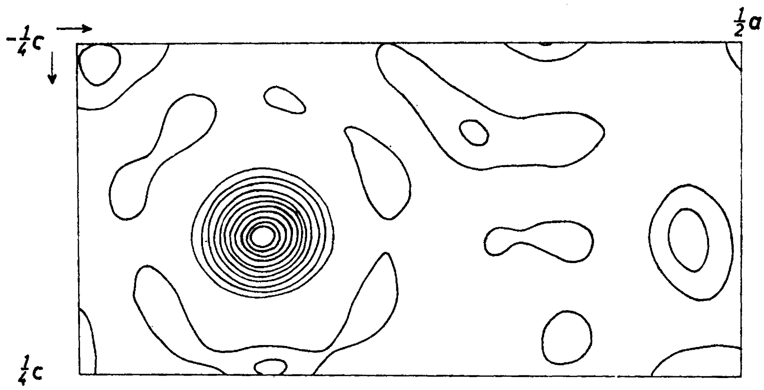


Fig. 2. Electron density projection along [010]. The figure is on an arbitrary scale and only every second contour is drawn for the tantalum peak.

same x and z parameters as Ta, in order to get an octahedral oxygen coordination for the tantalum atoms. The projection along [001] of the Patterson function (Fig. 3) gave $y = 0$ for the tantalum position. The y parameters for the

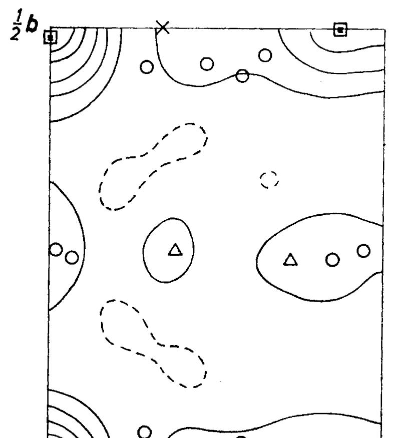


Fig. 3. Patterson projection along [001] and corresponding vectors obtained from the final atomic coordinates. Negative contours are dotted.

▣ Ta—Ta (Multiplicity 4)	○ Ta—O (Multiplicity 4)
□ Ta—Ta (» 2)	× Ca—Ca (» 2)
△ Ta—Ca (» 4)	

oxygen atoms in 8(d) positions were tentatively put equal to 0. The small shifts from 0 in the y parameters could not be obtained from the electron density projection because of the difficulty in determining the signs of the very

Table 2. Observed and calculated *F*-values.

h k l	F_{obs}	F_{calc}	*h k l*	F_{obs}	F_{calc}
2 0 0	46	41	10 0 4	107	113
4 0 0	304	340	11 0 4	39	36
6 0 0	234	236	1 0 5	83	71
8 0 0	243	209	2 0 5	199	185
10 0 0	250	229	3 0 5	102	85
12 0 0	125	116	4 0 5	132	104
14 0 0	123	152	5 0 5	<58	10
1 0 1	239	259	6 0 5	202	189
2 0 1	109	118	7 0 5	83	73
3 0 1	336	419	8 0 5	104	101
4 0 1	93	97	9 0 5	<30	5
5 0 1	146	145	0 0 6	<51	30
6 0 1	100	95	1 0 6	190	164
7 0 1	257	365	2 0 6	<51	8
8 0 1	<49	8	3 0 6	111	86
9 0 1	<51	22	4 0 6	<49	38
10 0 1	<51	25	5 0 6	174	151
11 0 1	171	179	6 0 6	<32	13
12 0 1	72	61	2 1 0	23	20
13 0 1	118	108	4 1 0	19	26
0 0 2	368	399	6 1 0	56	66
1 0 2	109	116	8 1 0	18	19
2 0 2	86	83	10 1 0	<20	3
3 0 2	127	136	12 1 0	<17	5
4 0 2	308	320	0 1 1	25	26
5 0 2	160	157	1 1 1	36	31
6 0 2	178	157	2 1 1	10	11
7 0 2	<56	9	3 1 1	39	40
8 0 2	132	145	4 1 1	33	31
9 0 2	120	129	5 1 1	42	47
10 0 2	183	201	6 1 1	<17	1
11 0 2	<49	37	7 1 1	26	30
12 0 2	76	73	8 1 1	<19	6
13 0 2	63	64	9 1 1	<20	23
1 0 3	144	126	10 1 1	<20	11
2 0 3	241	225	11 1 1	<17	12
3 0 3	273	275	12 1 1	<16	8
4 0 3	100	108	13 1 1	<13	12
5 0 3	56	58	1 1 2	<13	2
6 0 3	155	141	2 1 2	37	40
7 0 3	222	193	3 1 2	51	50
8 0 3	97	102	4 1 2	39	38
9 0 3	<51	11	5 1 2	<19	10
10 0 3	83	88	6 1 2	30	36
11 0 3	118	125	7 1 2	<22	12
12 0 3	90	95	8 1 2	29	26
0 0 4	181	192	9 1 2	<20	18
1 0 4	192	183	10 1 2	<20	15
2 0 4	<53	12	11 1 2	<17	2
3 0 4	137	128	12 1 2	<15	2
4 0 4	141	134	13 1 2	<11	9
5 0 4	178	163	0 1 3	46	46
6 0 4	120	98	1 1 3	<10	10
7 0 4	<60	18	2 1 3	39	34
8 0 4	107	87	3 1 3	<18	14
9 0 4	165	181	4 1 3	<19	1

h k l	F_{obs}	F_{calc}	h k l	F_{obs}	F_{calc}
5 1 3	29	28	4 2 2	311	327
6 1 3	<23	10	5 2 2	210	176
7 1 3	<24	25	6 2 2	170	138
8 1 3	<22	1	7 2 2	35	25
9 1 3	<20	10	8 2 2	166	169
10 1 3	<18	24	9 2 2	84	100
11 1 3	<15	3	10 2 2	150	145
12 1 3	<11	14	11 2 2	38	52
1 1 4	21	22	12 2 2	33	37
2 1 4	<12	12	13 2 2	53	55
3 1 4	30	24	1 2 3	208	187
4 1 4	32	18	2 2 3	269	246
5 1 4	<24	2	3 2 3	245	217
6 1 4	<24	5	4 2 3	84	61
7 1 4	<24	15	5 2 3	73	59
8 1 4	<21	13	6 2 3	121	99
9 1 4	<17	9	7 2 3	186	175
10 1 4	<15	3	8 2 3	137	135
11 1 4	<10	11	9 2 3	<46	24
0 1 5	40	32	10 2 3	91	96
1 1 5	<24	0	11 2 3	135	152
2 1 5	<24	15	12 2 3	88	96
3 1 5	<16	12	0 2 4	155	150
4 1 5	<24	6	1 2 4	168	178
5 1 5	<23	7	2 2 4	<51	20
6 1 5	<22	6	3 2 4	106	97
7 1 5	<18	6	4 2 4	161	146
8 1 5	<15	10	5 2 4	245	219
9 1 5	<12	8	6 2 4	97	88
1 1 6	<20	18	7 2 4	<51	32
2 1 6	<19	4	8 2 4	102	101
3 1 6	25	23	9 2 4	157	156
4 1 6	<14	2	10 2 4	77	83
5 1 6	<16	10	11 2 4	35	39
6 1 6	<13	6	1 2 5	77	76
2 2 0	150	128	2 2 5	245	223
4 2 0	250	306	3 2 5	55	63
6 2 0	203	207	4 2 5	55	61
8 2 0	205	207	5 2 5	<53	5
10 2 0	152	165	6 2 5	177	149
12 2 0	64	53	7 2 5	71	63
1 2 1	250	301	8 2 5	130	133
2 2 1	104	88	9 2 5	<24	7
3 2 1	265	269	0 2 6	<42	13
4 2 1	64	65	1 2 6	163	150
5 2 1	93	92	2 2 6	<44	10
6 2 1	42	51	3 2 6	75	57
7 2 1	263	295	4 2 6	<40	25
8 2 1	<46	32	5 2 6	181	190
9 2 1	68	64	6 2 6	<24	11
10 2 1	<49	20	2 3 0	54	59
11 2 1	188	210	4 3 0	47	52
12 2 1	62	61	6 3 0	<19	7
13 2 1	66	67	8 3 0	75	83
0 2 2	263	268	10 3 0	19	22
1 2 2	106	93	12 3 0	<15	17
2 2 2	152	138	0 3 1	74	73
3 2 2	75	70	1 3 1	49	50

h k l	F_{obs}	F_{calc}	*h k l*	F_{obs}	F_{calc}
2 3 1	18	17	4 3 6	<15	4
3 3 1	30	31	5 3 6	<11	9
4 3 1	25	26	2 4 0	28	25
5 3 1	63	70	4 4 0	203	284
6 3 1	<19	3	6 4 0	143	180
7 3 1	19	26	8 4 0	166	170
8 3 1	<21	1	10 4 0	187	200
9 3 1	<21	7	12 4 0	85	91
10 3 1	<19	4	1 4 1	189	191
11 3 1	<17	11	2 4 1	92	81
12 3 1	<15	14	3 4 1	284	326
13 3 1	14	14	4 4 1	60	51
1 3 2	15	18	5 4 1	97	98
2 3 2	73	64	6 4 1	78	77
3 3 2	<18	6	7 4 1	254	280
4 3 2	<20	6	8 4 1	<46	21
5 3 2	30	23	9 4 1	<46	12
6 3 2	<23	14	10 4 1	<39	22
7 3 2	<22	15	11 4 1	141	155
8 3 2	38	33	12 4 1	48	47
9 3 2	<21	6	0 4 2	300	314
10 3 2	<20	17	1 4 2	143	115
11 3 2	22	21	2 4 2	55	48
12 3 2	25	27	3 4 2	104	88
0 3 3	<19	14	4 4 2	258	242
1 3 3	<19	16	5 4 2	134	116
2 3 3	<20	0	6 4 2	159	131
3 3 3	<20	9	7 4 2	<51	4
4 3 3	<21	22	8 4 2	125	123
5 3 3	71	63	9 4 2	108	105
6 3 3	<25	15	10 4 2	154	170
7 3 3	33	32	11 4 2	30	27
8 3 3	21	25	12 4 2	58	64
9 3 3	<20	12	1 4 3	122	104
10 3 3	<16	1	2 4 3	168	171
11 3 3	13	15	3 4 3	219	209
1 3 4	52	50	4 4 3	101	82
2 3 4	47	43	5 4 3	74	53
3 3 4	<23	3	6 4 3	166	132
4 3 4	<23	0	7 4 3	180	169
5 3 4	<25	2	8 4 3	101	89
6 3 4	<25	11	9 4 3	<42	12
7 3 4	<22	11	10 4 3	65	66
8 3 4	<18	19	11 4 3	83	104
9 3 4	<16	9	0 4 4	159	163
10 3 4	27	28	1 4 4	159	153
0 3 5	<25	3	2 4 4	<51	5
1 3 5	<16	2	3 4 4	106	103
2 3 5	41	37	4 4 4	120	109
3 3 5	<24	6	5 4 4	175	139
4 3 5	39	35	6 4 4	88	78
5 3 5	<22	16	7 4 4	<46	14
6 3 5	<19	4	8 4 4	74	70
7 3 5	<15	2	9 4 4	129	153
8 3 5	18	20	1 4 5	51	53
1 3 6	18	22	2 4 5	182	161
2 3 6	<12	0	3 4 5	85	70
3 3 6	<17	2	4 4 5	115	91

$h\ k\ l$	F_{obs}	F_{calc}	$h\ k\ l$	F_{obs}	F_{calc}
5 4 5	<44	17	1 4 6	127	135
6 4 5	180	156	2 4 6	<32	7
7 4 5	55	68	3 4 6	71	82
0 4 6	<32	29			

Table 3. Interatomic distances (Å).

$Ta-O_I$	2.11 ± 0.02
$Ta-O'_I$	1.93 ± 0.02
$Ta-O_{II}$	2.06 ± 0.03
$Ta-O'_{II}$	1.85 ± 0.03
$Ta-O_{III}$	1.96 ± 0.01
$Ta-O_{IV}$	1.96 ± 0.02
$2 \times Ca-O_I$	2.45 ± 0.03
$2 \times Ca-O''_I$	2.49 ± 0.03
$2 \times Ca-O_{II}$	2.56 ± 0.03
$(Ca-O_{III}$	$3.28 \pm 0.05)$
$Ca-O'_{III}$	2.57 ± 0.05
$Ca-O'_{IV}$	2.43 ± 0.04
$O_I-O'_I$	2.53 ± 0.03
$O_I-O''_I$	3.05 ± 0.03
O_I-O_{II}	2.75 ± 0.03
$O'_I-O'_{II}$	2.98 ± 0.03
O''_I-O_{II}	3.04 ± 0.04
O_I-O_{III}	2.83 ± 0.05
O'_I-O_{III}	2.73 ± 0.04
O_I-O_{IV}	2.70 ± 0.03
O'_I-O_{IV}	2.85 ± 0.04
$2 \times O_{II}-O'_{II}$	2.91 ± 0.04
$O_{II}-O''_{II}$	3.01 ± 0.04
$O_{II}-O_{III}$	2.79 ± 0.05
$O'_{II}-O_{III}$	2.78 ± 0.04
$O_{II}-O_{IV}$	2.73 ± 0.04
$O'_{II}-O_{IV}$	2.81 ± 0.04
$O'_{III}-O'_{IV}$	3.04 ± 0.06
$O'_{III}-O''_{IV}$	3.05 ± 0.06

weak reflections with odd k. These shifts were found by (F_o-F_c)-synthesis in the [001] projection. The parameters were refined, with three-dimensional data from the b axis, by the method of least squares. An overall "temperature factor" exp $(-\beta/\lambda^2 \cdot \sin^2\Theta)$ was approximately determined by plotting log F_o/F_c against $\sin^2\Theta/\lambda^2$, the slope of the graph giving the value of β. This value was then refined individually for each atomic position by the method of least squares.

The following parameters were obtained:

8 Ta in 8(d): $x = 0.1412 \pm 0.0002$, $y = -0.0056 \pm 0.0004$,
$z = 0.0376 \pm 0.0004$, $\beta = 0.93 \pm 0.04$

4 Ca in 4(c): $x = 0.042 \pm 0.001$, $y = \frac{1}{4}$, $z = 0.540 \pm 0.002$, $\beta = 1.0 \pm 0.2$

8 O_I in 8(d): $x = -0.024 \pm 0.002$, $y = 0.035 \pm 0.003$, $z = 0.225 \pm 0.005$
$\beta = 0.0 \pm 0.4$
8 O_{II} in 8(d): $x = 0.213 \pm 0.002$, $y = 0.049 \pm 0.004$, $z = 0.383 \pm 0.006$
$\beta = 0.6 \pm 0.5$
4 O_{III} in 4(c): $x = 0.146 \pm 0.004$, $y = \frac{1}{4}$, $z = -0.033 \pm 0.010$
$\beta = 3.2 \pm 1.2$
4 O_{IV} in 4(c): $x = 0.122 \pm 0.003$, $y = -\frac{1}{4}$, $z = 0.162 \pm 0.008$
$\beta = 1.5 \pm 0.8$

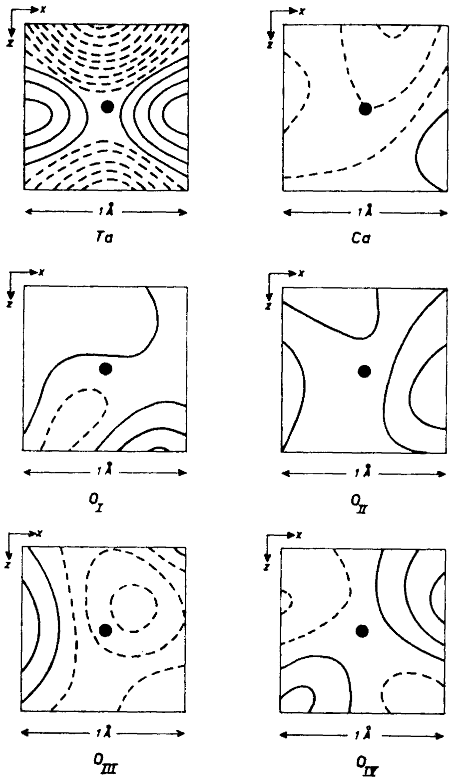


Fig. 4. $(F_o - F_c)$-synthesis showing sections through the atoms parallel to the xz-plane. Contours are drawn at an interval of 1.1 e/Å³. Negative contours are dotted. (The electron density of Ta was found to be equal to 197 e/Å³.)

Observed and calculated F-values are given in Table 2 and interatomic distances in Table 3. The R-value was 10.2 %. An $(F_o - F_c)$-synthesis was calculated for the surroundings of the atoms and was found to be satisfactorily low. It showed, however, that the tantalum atom has a distinct anisotropic temperature factor. Fig. 4 shows that the thermal vibration is greater in the x-direction. The y-direction showed no variations. Anisotropic thermal vibration is also indicated for the oxygen atoms. No correction was made for this anisotropy, however. The variation of the β-values for the oxygens shows that these "temperature factors" must be looked upon as mathematical correction factors which are only partially due to the temperature.

DESCRIPTION OF THE STRUCTURE

The structure is built up from TaO_6 octahedra sharing edges and corners. Fig. 5 shows a projection along [010]. Pairs of octahedra are formed by sharing

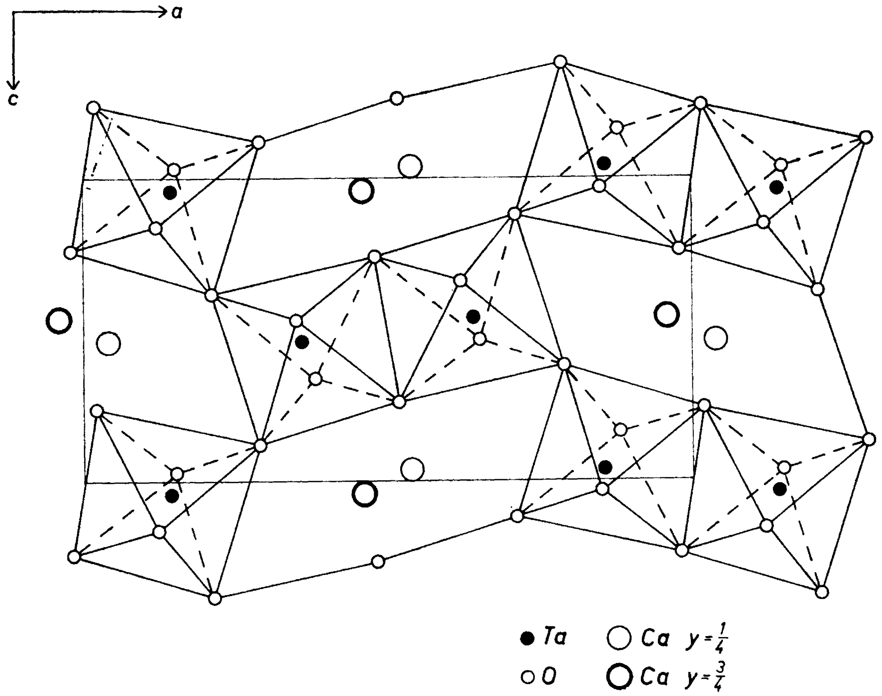
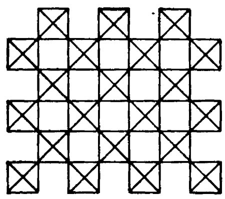


Fig. 5. Structure of $CaTa_2O_6$. Projection along [010]. The extension of the unit cell perpendicularly to the figure comprises two TaO_6 octahedra, the metal atoms of which are situated close to $y = 0$ and $\frac{1}{2}$, respectively.

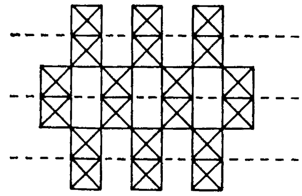
edges. The Ta—Ta distance in this pair is 3.15 Å and the O—O distance of the edge in common is 2.53 Å, as compared with the rest of the O—O distances which are not shorter than 2.70 Å. These pairs of octahedra are joined in the xz-plane by sharing corners (Ta—Ta distance 3.61 Å). The octahedra also share corners in the y-direction. The small shifts from 0 and $\frac{1}{2}$ for the tantalum atoms in this direction give two different Ta—Ta distances, *viz.* 3.67 and 3.84 Å. The oxygen atom joining the tantalum atoms with the shorter distance is displaced further from the ideal position than is the oxygen atom joining those with the longer distance. The Ta—O distances are both 1.96 Å. The framework of TaO_6 octahedra forms tunnels running in the y-direction. The calcium atoms are situated in these tunnels at the same heights as the top oxygens of the octahedra (*cf.* Fig. 5.) The calcium atoms are surrounded by eight oxygens at the distances 2.43—2.57 Å, six of them forming a triangular prism and two lying outside the prism faces.

DISCUSSION

Though the powder pattern of this structure is quite different from the pattern of the perovskite phases occurring at higher and lower temperatures, the structures have some features in common. The pairs of octahedra are mutually coupled in the same way as the single octahedra in perovskite (Fig. 6a, b) and in both cases the calcium atoms are in the holes between the octa-



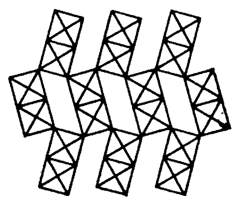
a



b

Fig. 6. Idealized coupling of octahedra in *a*) the perovskite phase

b) the orthorhombic phase (The broken lines indicate the projections of the shear planes of the perovskite blocks.)



c

c) the orthorhombic phase with angles of 60° and 120° instead of 90°.

hedra. The structure can be looked upon as built up from blocks of perovskite joined by pairs of octahedra sharing edges. This type of shear plane (indicated by broken lines in Fig. 6b) has been discussed by Magnéli.[3]

The oxygen coordination of the calcium atoms is different, however. In the low-temperature perovskite phase the calcium atoms are likely to be randomly distributed over the twelve-coordinated *A*-position of the ABO_3 structure.

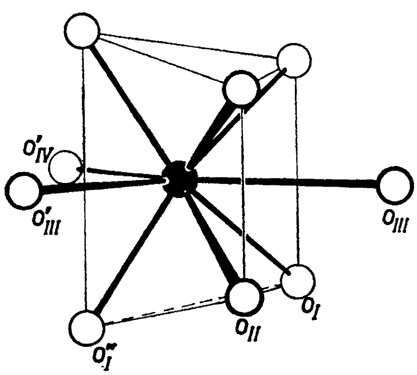


Fig 7. Clinographic projection of the coordination around Ca.

Calcium, however, often adopts an eight- or ninefold coordination in the form of a trigonal prism with two or three oxygens outside the prism faces. The orthorhombic structure corresponds to a deformation of the ideal structure in Fig. 6c towards such an environment around calcium. The calcium atoms thus have eight near neighbours, six at the distances 2.45—2.56 Å forming a trigonal prism and two outside the prism faces at the distances 2.43 and 2.57 Å. A ninth oxygen outside the third prism face has a much larger distance, 3.28 Å (Fig. 7).

A similar oxygen coordination around Ca is known in the three isomorphous oxides CaV_2O_4,[4] β-$CaCr_2O_4$[5,6] and $CaFe_2O_4$[5,6] and also in $CaTi_2O_4$.[7] The CaV_2O_4 structure type has an eightfold coordination with two oxygens close to the prism faces and the third at a larger distance. $CaTi_2O_4$ has a somewhat more symmetrical coordination polyhedron, but, in this compound also, one of the three oxygens outside the prism lies a little farther away than the other two.

The orthorhombic structure does not seem to occur if calcium is exchanged for strontium or barium. Galasso, Katz and Ward [8] have found that $SrTa_2O_6$ and $BaTa_2O_6$ prepared at 1100°C, have a tetragonal tungsten bronze structure. This structure has been described by Magnéli [9] for $K_{6-x}W_{10}O_{30}$ and consists of octahedra joined by corners forming rings of three, four or five octahedra with the K atoms situated in the interstices between adjacent tetragons and pentagons. The tantalum oxides are cation-deficient with respect to the numbers of A-cation sites available in the structure, the ideal formula being $A_6B_{10}O_{30}$. However, Ismailzade[10] has given a four times larger unit cell. This corresponds to the unit cell given by Magnéli [11] for a tetragonal sodium tungsten bronze, which is very closely related to the potassium tungsten bronze but possesses a superstructure.

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