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Crystal Structures of $Na_2Nb_4O_{11}$ and $CaTa_4O_{11}$

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The crystal structures of $Na_2Nb_4O_{11}$ and $CaTa_4O_{11}$ have been determined from three-dimensional single-crystal data. The space group of the former is $C2/c$ and the cell dimensions $a = 10.840$, $b = 6.162$, $c = 12.745$ Å, and $\beta = 106.22°$. The symmetry of the latter is $P6_322$ ($a = 6.213$ and $c = 12.265$ Å). Both structures contain layers of pentagonal niobium (tantalum) oxygen bipyramids sharing edges. These layers are connected to form a three-dimensional network by octahedrally coordinated niobium (tantalum) atoms and by sodium (calcium), the coordination figures of which are flattened octahedra with one (two) oxygen(s) outside the large face(s).

Introduction

The knowledge of the structural chemistry of niobium oxides is largely due to the studies by Wadsley (*1*). The crystal structures of the alkali titanum niobates $KTiNbO_5$ and KTi_3NbO_9 were published by him (*2*). Another alkali niobate and a closely related tantalate will be reported in this paper.

During studies of the system CaO–$n$$Ta_2O_5$ ($n \geqslant 1$) the compound $CaTa_4O_{11}$ with hexagonal symmetry was found, besides the earlier reported $CaTa_2O_6$ (*3*), (*4*). The same phase was reported by Gasperin (*5*), who also gave the positions of the tantalum atoms. During the study of the system $NaNbO_3$–Nb_2O_5 a phase with composition $Na_2Nb_4O_{11}$ was prepared by Andersson (*6*). Although it is monoclinic, the strong reflections of the Weissenberg photographs around [010] showed a strong resemblance to the reflections around [100] of the hexagonal compound. The two structures have been determined and will be described below.

Experimental

$Na_2Nb_4O_{11}$ was prepared hydrothermally from $NaNbO_3$ and Nb_2O_5 by Andersson (*6*). The amount of sample obtained was quite small and no chemical analysis was made. The composition which was concluded from the starting composition and from the observed density has been essentially confirmed from the structure determination described below. The method of preparation, however, does not exclude the possibility of hydroxide partly substituting for oxygen with a corresponding deficiency in the content of sodium (v. inf.).

Weissenberg films were taken around the monoclinic axis with an integrating camera using CuKα radiation. The $h0l$, $h1l$, $h2l$, and $h3l$ reflections were recorded. The unit cell dimensions as obtained by Andersson (*6*) from Guinier CuKα photographs are $a = 10.840$, $b = 6.162$, $c = 12.745$ Å, and $\beta = 106.22°$.

$CaTa_4O_{11}$ was prepared from $CaCO_3$ (Merck's Reagent, p.a., 99.7%) and Ta_2O_5 (Koch-Light Laboratories Ltd., 99.9%). An intimate mixture was pressed into a tablet and melted in an electric arc furnace in an argon atmosphere. The crystals obtained from this sample were rather irregular and attempts to correct the data for absorption were not very successful. Crystals were later made according to the method described by Gasperin (*5*). Ta_2O_5 and $CaCO_3$ were mixed with melted and powdered boric acid and heated in air in a platinum crucible at about 1100°C. Hexagonal plates of $CaTa_4O_{11}$ were formed at the surface of the melt.

The density of the crystals was determined from the apparent loss of weight in benzene.

Weissenberg photographs were taken of an irregular crystal of the first sample, using CuK radiation and multiple film technique. The intensities were visually estimated with a standard scale.

TABLE I

POWDER PATTERN OF $CaTa_4O_{11}$

I	$\sin^2\theta_{obs}$	$h\ k\ l$	$\sin^2\theta_{calc}$
st	0.01575	0 0 2	0.01578
st	0.02046	1 0 0	0.02049
m	0.02440	1 0 1	0.02444
w	0.03624	1 0 2	0.03627
w	0.05592	1 0 3	0.05599
m	0.06305	0 0 4	0.06310
vst	0.06538	1 1 1	0.06542
vst	0.07726	1 1 2	0.07725
w	0.08356	1 0 4	0.08359
vw	0.08590	2 0 1	0.08591
m	0.09689	1 1 3	0.09697
vw	0.09767	2 0 2	0.09774
vw	0.11747	2 0 3	0.11746
w	0.14197	0 0 6	0.14198
vw	0.14346	2 1 0	0.14344
m	0.14739	2 1 1	0.14739
m	0.16003	1 1 5	0.16007
w	0.17890	2 1 3	0.17894
st	0.18440	3 0 0	0.18443
w	0.20019	3 0 2	0.20020
m	0.20350	1 1 6	0.20345
vw	0.20649	2 1 4	0.20654
vw	0.21373	1 0 7	0.21375
vw	0.22392	2 0 6	0.22395
w	0.24197	2 1 5	0.24204
st	0.24756	3 0 4	0.24753
m	0.24989	2 2 1	0.24985
w	0.25244	0 0 8	0.25241
m	0.25478	1 1 7	0.25472
m	0.26174	2 2 2	0.26168
vw	0.26649	3 1 0	0.26639
w	0.27026	3 1 1	0.27034
w	0.28139	2 2 3	0.28140
vw	0.30188	3 1 3	0.30189

The symmetry was found to be hexagonal and exposures were made with the crystal rotated both around the *a* and the *c* axis. The cell dimensions

$$a = 6.213 \pm 1 \quad \text{and} \quad c = 12.265 \pm 1\ \text{Å}$$

were derived from a Guinier powder pattern registered with monochromatized $CuK\alpha_1$ ($\lambda = 1.54050$ Å) radiation and with potassium chloride ($a = 6.2930$ Å) as an internal standard. The indexed powder pattern is given in Table I.

In the final structural refinement use was made of single-crystal data from an almost quadratic piece of an hexagonal plate from the second preparation. The size was approximately 0.05 × 0.05 × 0.006 mm^3. The $h0l$–$h4l$ reflections were collected with $CuK\alpha$ radiation and an integrating Weissenberg camera using multiple film technique. The intensities were visually estimated with a standard scale and corrected for absorption by a numerical integrating procedure.

Scattering factor curves for Nb^{5+} and Ta^{5+} were taken from Cromer and Waber (*7*). For Na^+ and Ca^{2+} values from the Int. Tab. (Boys, and Thomas and Umeda, respectively) (*8*) were used and for O^{2-}, values given by Suzuki (*9*). The calculations were executed with the computers FACIT EDB, CD 3600, and IBM 1800.

Derivation of the Structures

Weissenberg photographs of $CaTa_4O_{11}$ around the *c* axis showed the Laue symmetry to be $6/mmm$. With $00l$ reflections existing only for $l = 2n$ this gave the space group $P6_322$. The observed density was 7.58 g cm^{-3}. Two formula units $CaTa_4O_{11}$ correspond to a calculated density of 7.61 g cm^{-3}. From Patterson projections tantalum positions were derived which were in agreement with those given by Gasperin (*5*). The positions

$$6(g){:}\ x,0,0;\ 0,x,0;\ \bar{x},\bar{x},0;\ \bar{x},0,\tfrac{1}{2};\ 0,\bar{x},\tfrac{1}{2};\ x,x,\tfrac{1}{2}$$

and

$$2(c){:}\ \tfrac{1}{3},\tfrac{2}{3},\tfrac{1}{4};\ \tfrac{2}{3},\tfrac{1}{3},\tfrac{3}{4}$$

in $P6_322$ were chosen for the eight tantalum atoms. The combination of the conditions limiting possible reflections for these two positions was present in the data. An electron density projection along [100] gave $x = 0.35$. The tantalum positions thus derived in the planes $z = 0$ and $z = \frac{1}{2}$ showed a great resemblance to the metal atom positions of U_3O_8 (*10*). The length of the *c* axis (12.27 Å) corresponded to the sum of two O–Ta–O distances (ca. 2 × 4 Å) and two distances between opposite faces of TaO_6 octahedra (ca. 2 × 2.3 Å). It was found to be likely that the structure contained layers of pentagonal TaO_7 bipyramids sharing edges, and that these layers were connected by octahedrally coordinated Ta. The structure could not be quite confirmed with the data available.

At this point the compound $Na_2Nb_4O_{11}$ was discovered to have a great similarity to $CaTa_4O_{11}$. The symmetry was monoclinic with $h + k = 2n$ for hkl reflections and $l = 2n$ for $h0l$ reflections. This is characteristic of the space groups Cc and $C2/c$. The observed density was 4.75 g cm^{-3} and the calculated, 4.82 g cm^{-3} with four formula units $Na_2Nb_4O_{11}$ (*6*). The cell parameters resembled those of the *C*-centered orthohexagonal unit cell with four formula units that could be chosen for $CaTa_4O_{11}$.

TABLE II

ATOMIC PARAMETERS IN $Na_2Nb_4O_{11}$—SPACE GROUP $C2/c$ $(0,0,0;\frac{1}{2},\frac{1}{2},0)+$

Atom	Position	x	y	z	B
8Nb(I)	8(f)	0.1825 ± 2	0.5658 ± 9	0.2499 ± 2	1.14 ± 6
4Nb(II)	4(e)	0	0.1140 ± 13	$\frac{1}{4}$	0.93 ± 7
4Nb(III)	4(d)	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$	1.58 ± 9
8Na	8(f)	0.082 ± 2	0.253 ± 3	0.996 ± 2	3.3 ± 4
8O(I)	8(f)	0.233 ± 2	0.512 ± 5	0.407 ± 2	1.0 ± 3
8O(II)	8(f)	0.157 ± 2	0.601 ± 4	0.090 ± 1	0.6 ± 3
8O(III)	8(f)	0.081 ± 2	0.135 ± 4	0.410 ± 2	0.8 ± 3
8O(IV)	8(f)	0.125 ± 2	0.880 ± 5	0.251 ± 2	1.0 ± 4
8O(V)	8(f)	0.159 ± 2	0.254 ± 6	0.218 ± 2	1.2 ± 4
4O(VI)	4(e)	0	0.505 ± 9	$\frac{1}{4}$	1.8 ± 7

$Na_2Nb_4O_{11}$: $a = 10.84$, $b = 6.162$, $c = 12.75$ Å, $\beta = 106.2°$ (*6*).

$CaTa_4O_{11}$: $a = 10.76$, $b = 6.213$, $c = 12.27$ Å.

For the strong reflections of $Na_2Nb_4O_{11}$ a mirror plane corresponding to orthorhombic symmetry could be traced and the intensity distribution for these reflections was similar to that of $CaTa_4O_{11}$. From these facts it was concluded that the transition metal atom arrangement should be almost the same in both structures. The following positions in $C2/c$ were used to describe the tantalum atom positions of $CaTa_4O_{11}$ in the monoclinic symmetry:

$(0,0,0;\frac{1}{2},\frac{1}{2},0)+$

$8(f)$: $x, y, z;\ \bar{x}, \bar{y}, \bar{z};\ \bar{x}, y, \frac{1}{2}-z;\ x, \bar{y}, \frac{1}{2}+z\ (x \approx \frac{1}{6}, y \approx \frac{7}{12}, z \approx \frac{1}{4})$,

$4(e)$: $0, y, \frac{1}{4}; 0, \bar{y}, \frac{3}{4}\ (y \approx \frac{1}{12})$,

$4(d)$: $\frac{1}{4}, \frac{1}{4}, \frac{1}{2}; \frac{3}{4}, \frac{1}{4}, 0$.

These values were adopted as starting parameters for the niobium atom arrangement of $Na_2Nb_4O_{11}$. An electron density projection along [010] confirmed these positions and also gave approximate x and z parameters for 8Na and 24O in 8(f). The rest of the O-atom coordinates were derived geometrically from a suggested structure. This trial structure which gave a rather good agreement for the strong reflections but too low values for the weak ones, was refined by the method of full-matrix least squares. Six very strong reflections were excluded in the final stages of refinement. These were measured with low accuracy and also likely to suffer from extinction. The atomic coordinates and temperature factors thus obtained are given in Table II. The R value for the observed reflections was 7.2%. Observed and calculated structure factors are given in Table III, and interatomic distances in Table VI.

It was stated above that the difficulty to perform a chemical analysis of the $Na_2Nb_4O_{11}$ sample and the hydrothermal conditions employed in the synthesis left open the possibility of some deviation from the stoichiometric formula, with a partial substitution of hydroxide for oxygen. The composition $Na_{2-x}Nb_4O_{11-x}(OH)_x$, corresponding to a slightly lower content of sodium than the ideal formula used in this paper, cannot be excluded by the present structure determination. In this connection it may be stated that the B parameter of the sodium atom is somewhat high. This might be due to a deficiency in the occupancy of the sodium sites but in consideration of the low accuracy of the "thermal parameter," such an interpretation is not a conclusive one.

The new set of integrated data around [100] was now used for the calculations on $CaTa_4O_{11}$. An electron density projection along this axis derived from phase angles given by the tantalum atoms only was not easily interpreted, but some peaks indicated calcium and oxygen positions in agreement with those geometrically derived. The parameters were refined by the method of least squares with a program for the computer CD 3600 which allowed hexagonal symmetry and a full matrix to be used. However, the strongest reflections systematically showed too low values of F_{obs} which suggested the presence of secondary extinction. An effort was made to correct for this effect according to Zachariasen's (*11*) formula. It was not successful since there was probably too much error in the estimation of these strong reflections. They were therefore excluded in the final refinement. The number of reflections to be excluded was chosen so as to give a weight analysis without visible trend. The parameters and standard deviations derived from this refinement with 134 independent reflections are given in Table IV. The R value obtained was 3.9%. All observed reflections (177) gave an R value of 10.5%. Observed and calculated structure factors are given in Table V, and interatomic distances in Table VI. In a refinement with all observed reflections the standard deviations were approximately doubled. Only the Ta coordinate shifted a little more than the value of the standard deviation.

Description and Discussion of the Structures

The structures contain layers of pentagonal MeO_7 bipyramids (Me = Nb or Ta) sharing edges equatorially. The layers which contain three-quarters of the Me atoms are repeated with an interval of $c/2$ by the glide plane and the 6_3 axis, respectively. Figure 1 shows the atoms in the planes $z = 0.25$ and $z = 0.75$ for $Na_2Nb_4O_{11}$. One oxygen atom position [O(V)] deviates from the $z = 0.25$ plane by about 0.4 Å. These oxygens are marked with a plus or minus in Fig. 1, indicating whether they are above or below the planes. [The corresponding position in $CaTa_4O_{11}$ is O(III).] One of the five metal–oxygen distances in the pentagons is longer than the other four: around 2.40 Å compared with 1.96–2.07 Å for the Nb–O distances, and 2.46 Å compared with 1.98 and 2.04 Å for the Ta–O distances. Thus, the layers could also be regarded as consisting of very deformed octahedra sharing corners. The oxygen–oxygen distances are short for the common edges of the pentagonal bipyramids, 2.39–2.43 Å. Remaining oxygen–oxygen distances are 2.60–3.06 Å.

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $Na_2Nb_4O_{11}$

Asterisk reflections were not included in the refinement. The columns give h, k, l, $|F_{obs}|$ and $|F_{calc}|$. For all nonobserved reflections, $|F_{calc}|$ < min. observable $|F_{obs}|$.

*0	0	2	234	281
*0	0	4	459	580
0	0	6	319	350
0	0	8	407	437
0	0	10	103	110
0	0	12	328	318
0	0	14	112	116
2	0	-12	91	84
2	0	-8	106	115
2	0	-4	132	133
2	0	-2	84	71
2	0	0	217	192
2	0	2	89	87
4	0	-16	68	67
4	0	-12	91	93
4	0	-8	168	180
4	0	-4	124	117
4	0	0	123	115
4	0	2	109	96
4	0	4	133	146
4	0	8	74	77
4	0	12	83	78
6	0	-14	211	204
6	0	-12	73	79
6	0	-10	298	300
6	0	-8	154	156
6	0	-6	372	381
6	0	-4	177	165
*6	0	-2	532	512
6	0	0	158	147
6	0	2	404	401
6	0	4	161	169
6	0	6	289	295
6	0	8	82	88
6	0	10	238	216
8	0	-14	92	98
8	0	-6	113	112
8	0	-2	181	174
8	0	6	88	77
10	0	-12	69	65
10	0	-10	167	180
10	0	-8	103	98
10	0	-6	175	172
10	0	-4	106	92
10	0	-2	206	197
10	0	2	154	161
10	0	6	111	120
12	0	-8	143	136
12	0	-4	152	147
12	0	0	156	175
1	1	-3	83	89
1	1	-1	178	188
1	1	1	79	74
1	1	3	119	137
1	1	7	120	114
1	1	11	97	91
3	1	-16	80	88
3	1	-15	144	137
3	1	-14	174	150
3	1	-12	137	153
3	1	-11	195	192
3	1	-10	132	144
3	1	-8	222	252
3	1	-7	274	321
3	1	-6	231	256
3	1	-4	163	164
3	1	-3	286	314
3	1	-2	316	323
3	1	0	315	324
3	1	1	308	316
3	1	2	160	163
3	1	4	236	256
3	1	5	301	320
3	1	6	231	254
3	1	8	142	143
3	1	9	211	191
3	1	10	159	152
3	1	12	137	153
3	1	13	127	140
3	1	14	81	88
5	1	-14	81	70
5	1	-9	105	108
5	1	-8	111	119
5	1	-6	140	132
5	1	-5	124	123
5	1	-2	160	151
5	1	-1	91	89
5	1	0	164	166
5	1	1	69	68
5	1	2	59	59
5	1	3	100	96
5	1	4	106	99
5	1	5	71	77
5	1	6	120	114
5	1	12	72	63
7	1	-15	82	70
7	1	-8	121	111
7	1	-7	105	91
7	1	-6	88	74
7	1	-4	96	93
7	1	-3	178	167
7	1	-2	134	130
7	1	0	97	84
7	1	1	133	131
7	1	2	90	79
7	1	4	110	104
7	1	5	112	118
7	1	9	101	98
9	1	-14	87	81
9	1	-13	123	113
9	1	-12	115	111
9	1	-10	132	127
9	1	-9	147	130
9	1	-8	112	117
9	1	-6	159	144
9	1	-5	168	165
9	1	-4	157	160
9	1	-2	147	133
9	1	-1	158	149
9	1	0	137	140
9	1	2	149	145
9	1	3	136	132
9	1	4	121	113
9	1	6	105	102
9	1	7	125	117
9	1	8	107	100
11	1	-10	62	71
11	1	-2	92	93
13	1	-8	88	90
13	1	-6	88	76
13	1	-5	90	98
13	1	-4	90	95
13	1	-2	92	96
13	1	-1	92	110
*0	2	1	213	315
*0	2	2	254	327
0	2	3	147	155
0	2	5	239	253
0	2	6	321	328
0	2	7	256	248
0	2	9	120	139
0	2	10	195	194
0	2	11	149	153
0	2	13	154	150
0	2	14	140	141
0	2	15	72	84
2	2	-14	99	83
2	2	-6	140	146
2	2	-4	91	92
2	2	-2	119	111
2	2	2	119	123
2	2	6	178	170
2	2	10	98	92
2	2	14	74	68
4	2	-15	72	72
4	2	-9	107	119
4	2	-7	105	109
4	2	-6	87	88
4	2	-5	56	61
4	2	-4	76	78
4	2	-3	176	166
4	2	-2	98	83
4	2	-1	162	159
4	2	1	52	59
4	2	2	136	116
4	2	3	141	137
4	2	5	110	124
4	2	6	117	103
4	2	11	82	77
6	2	-15	112	109
6	2	-13	130	126
6	2	-12	142	144
6	2	-11	137	139
6	2	-9	167	173
6	2	-8	209	214
6	2	-7	195	190
6	2	-5	214	189
6	2	-4	241	226
6	2	-3	232	217
6	2	-1	253	218
6	2	0	241	220
6	2	1	197	189
6	2	3	208	189
6	2	4	222	215
6	2	5	193	175
6	2	7	148	139
6	2	8	152	142
6	2	9	131	124
6	2	11	120	111
8	2	-12	84	81
8	2	-8	112	129
8	2	-4	121	123
8	2	-1	93	88
8	2	0	123	122
8	2	4	137	143
8	2	8	81	88
10	2	-13	64	69
10	2	-11	87	91
10	2	-9	101	101
10	2	-8	91	103
10	2	-7	94	95
10	2	-5	104	110
10	2	-4	112	102
10	2	-3	112	119
10	2	-1	96	99
10	2	0	95	100
10	2	1	100	103
10	2	3	110	102
10	2	4	101	111
10	2	5	80	80
12	2	-10	66	74
12	2	-9	79	68
12	2	-7	101	109
12	2	-6	86	87
12	2	-5	87	95
12	2	-3	76	71
12	2	-2	75	69
12	2	-1	93	106
12	2	1	87	93
12	2	2	76	77
1	3	-14	66	68
1	3	-8	125	115
1	3	-7	81	84
1	3	-6	105	104
1	3	-5	86	90
1	3	-4	58	59
1	3	-3	60	70
1	3	-2	149	166
1	3	-1	84	81
1	3	0	132	143
1	3	2	50	58
1	3	3	114	121
1	3	4	123	126
1	3	5	54	62
1	3	6	127	119
1	3	7	121	105
1	3	10	87	71
1	3	12	87	73
3	3	-15	57	68
3	3	-13	208	213
3	3	-11	79	84
3	3	-9	283	285
3	3	-7	159	165
3	3	-5	343	393
3	3	-3	151	142
*3	3	-1	401	511
3	3	1	167	164
3	3	3	330	381
3	3	5	165	165
3	3	7	296	303
3	3	9	87	80
3	3	11	218	211
3	3	13	72	78
5	3	-14	64	63
5	3	-13	93	90
5	3	-9	113	108
5	3	-8	98	103
5	3	-6	77	76
5	3	-5	136	131
5	3	-4	82	87
5	3	-2	130	126
5	3	-1	172	166
5	3	0	105	95
5	3	2	75	78
5	3	3	90	85
5	3	4	95	106
5	3	6	95	78
5	3	7	95	74
5	3	10	70	65
5	3	11	63	61
7	3	-13	82	91
7	3	-9	152	148
7	3	-5	120	123
7	3	-4	96	87
7	3	-1	127	126
7	3	3	125	130
7	3	7	89	77
9	3	-11	149	152
9	3	-7	206	199
9	3	-5	87	67
9	3	-3	224	206
9	3	-1	87	66
9	3	1	213	206
9	3	5	151	155
11	3	-11	55	65
11	3	-10	61	64
11	3	-7	89	98
11	3	-6	73	66
11	3	-4	81	77
11	3	-3	86	105
11	3	0	70	59
11	3	2	59	71

TABLE IV

ATOMIC PARAMETERS IN $CaTa_4O_{11}$—SPACE GROUP $P6_322$

Atom	Position	x	y	z	B
6Ta(I)	6(*g*)	0.3592 ± 3	0	0	0.64 ± 5
2Ta(II)	2(*c*)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	0.60 ± 6
2Ca	2(*d*)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$	1.5 ± 2
12O(I)	12(*i*)	0.375 ± 4	0.945 ± 3	0.156 ± 2	0.8 ± 3
6O(II)	6(*g*)	0.754 ± 4	0	0	0.9 ± 4
4O(III)	4(*f*)	$\frac{1}{3}$	$\frac{2}{3}$	0.966 ± 2	0.7 ± 4

TABLE V

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $CaTa_4O_{11}$

Asterisk reflections were not included in the final refinement. The columns give *h*, *k*, *l*, $|F_{obs}|$ and $|F_{calc}|$. For all nonobserved reflections, $|F_{calc}|$ < min. observable $|F_{obs}|$.

*0	0	2	172	251
*0	0	4	327	483
*0	0	6	236	262
*0	0	8	320	394
0	0	10	113	117
*0	0	12	241	294
0	0	14	109	109
0	1	0	122	131
0	1	1	81	84
0	1	2	53	54
0	1	3	85	82
0	1	4	87	82
0	1	5	40	39
0	1	6	34	31
0	1	7	68	69
0	1	8	67	69
0	1	9	51	49
0	1	10	36	39
0	1	11	54	58
0	1	12	51	51
0	1	13	40	40
0	1	14	22	22
0	1	15	34	32
0	2	1	56	57
0	2	2	98	99
0	2	3	78	79
0	2	4	40	36
0	2	5	57	57
0	2	6	113	122
0	2	7	74	72
0	2	9	41	41
0	2	10	75	72
0	2	11	44	47
0	2	13	40	37
0	2	14	72	65
*0	3	0	247	425
*0	3	2	140	159
*0	3	4	252	363
*0	3	6	133	144
*0	3	8	248	294
0	3	10	98	92
*0	3	12	206	222
0	3	14	75	74
0	4	0	105	119
0	4	1	69	71
0	4	3	61	55
0	4	4	92	93
0	4	7	47	45
0	4	8	84	81
0	4	9	42	44
0	4	11	54	54
0	4	12	67	65
0	5	0	72	76
0	5	1	50	49
*0	5	2	131	144
0	5	3	48	49
0	5	4	67	58
0	5	5	37	34
*0	5	6	151	141
0	5	7	43	45
0	5	8	58	58
0	5	9	36	34
0	5	10	108	106
*0	6	0	153	182
0	6	2	65	58
*0	6	4	171	185
0	6	6	40	39
1	1	0	38	36
*1	1	1	199	287
*1	1	2	207	281
*1	1	3	170	207
*1	1	5	191	240
*1	1	6	228	272
*1	1	7	198	232
*1	1	9	156	169
*1	1	10	178	193
*1	1	11	146	158
1	1	12	34	31
*1	1	13	153	150
*1	1	14	146	150
1	1	15	108	110
1	2	0	82	77
1	2	1	110	111
1	2	2	55	53
1	2	3	98	96
1	2	4	68	67
1	2	5	101	99
1	2	6	51	49
1	2	7	108	105
1	2	8	57	48
1	2	9	60	60
1	2	10	46	42
1	2	11	63	63
1	2	12	33	32
1	2	13	63	61
1	2	14	34	32
1	3	0	119	124
1	3	1	106	105
1	3	3	82	82
1	3	4	97	96
1	3	5	81	75
1	3	7	91	89
1	3	8	83	82
1	3	9	60	61
1	3	11	66	67
1	3	12	67	64
1	3	13	61	59
*1	4	1	139	154
*1	4	2	156	169
*1	4	3	147	155
*1	4	5	134	142
*1	4	6	143	150
1	4	7	127	129
1	4	9	120	121
1	4	10	125	132
1	4	11	105	106
1	5	1	75	78
1	5	2	42	43
1	5	3	77	79
1	5	4	41	27
1	5	5	75	76
1	5	6	45	40
1	5	7	71	77
1	5	8	27	21
1	5	9	52	57
1	6	0	83	86
1	6	1	86	88
1	6	2	33	30
1	6	3	82	85
1	6	4	78	87
*2	2	1	179	213
*2	2	2	195	216
*2	2	3	192	199
*2	2	5	178	190
*2	2	6	181	201
*2	2	7	163	175
*2	2	9	140	152
*2	2	10	155	159
*2	2	11	137	134
2	2	13	115	118
2	3	0	31	29
2	3	1	62	66
2	3	2	108	107
2	3	3	71	70
2	3	5	63	58
2	3	6	111	109
2	3	7	59	63
2	3	9	43	47
2	3	10	82	73
2	3	11	53	49
2	3	12	21	23
2	4	0	96	90
2	4	1	99	99
2	4	3	98	98
2	4	4	73	71
2	4	5	94	96
2	4	7	94	94
2	4	8	64	63
2	4	9	73	73
2	5	1	95	101
2	5	2	116	110
2	5	3	104	109
2	5	5	97	96
2	5	6	99	101
*3	3	0	184	230
3	3	2	78	78
*3	3	4	195	225
3	3	6	57	59
*3	3	8	174	184
3	3	10	55	53
3	4	0	85	89
3	4	1	75	70
3	4	2	28	26
3	4	3	64	62
3	4	4	88	88
3	4	5	53	56
3	4	7	61	61

The atomic arrangement in these layers is almost identical with the one present in U_3O_8, as given by Loopstra (*12*). In the latter structure, however, the unit cell is only one layer high and the pentagonal bipyramids share vertex atoms. This is not the case in $Na_2Nb_4O_{11}$ and $CaTa_4O_{11}$. Here the rest of the Me atoms are situated between the layers, octahedrally surrounded by six oxygens which are vertex atoms of the pentagonal bipyramids, viz., three in the layer below and three in the layer above. Also, the Na and Ca atoms are situated between the layers and surrounded by six vertex oxygens which form a very distorted octahedron. Hence, the structures could be described as consisting of layers of pentagonal bipyramids alternating with layers of octahedra (Fig. 2). The Nb octahedron is quite regular, the Nb–O distances being 1.95–2.00 Å and the O–O distances 2.75–2.85 Å. The Nb–O distances are in very good agreement with those reported by Gatehouse and Wadsley (*13*) for octahedral coordination. In $CaTa_4O_{11}$ the Ta–O bond-lengths of the octahedron are all 1.98 Å but the O–O distances vary a little more: 2.60–3.04 Å. This is not surprising since the Nb octahedron is surrounded by six Na polyhedra while there are only three polyhedra containing Ca around Ta. The edges in common with these are shorter (2.60 Å) than the other edges.

In addition to the six vertex oxygens the sodium atoms in $Na_2Nb_4O_{11}$ also have a seventh close oxygen neighbour situated outside one of the large faces of the flattened octahedron (cf. Fig. 2). This

TABLE VI

INTERATOMIC DISTANCES (Å) FOR $Na_2Nb_4O_{11}$ AND $CaTa_4O_{11}$

$Na_2Nb_4O_{11}$		$CaTa_4O_{11}$	
Nb(I) pentagonal bipyramid		Ta(I) pentagonal bipyramid	
Nb(I)–O(I)	1.96 ± 2	2 × Ta(I)–O(I)	1.96 ± 2
Nb(I)–O(II)	1.99 ± 2	2 × Ta(I)–O(II)	1.98 ± 1
Nb(I)–O(IV)	2.04 ± 3	Ta(I)–O(II)	2.46 ± 3
Nb(I)–O(IV)	2.38 ± 2	2 × Ta(I)–O(III)	2.04 ± 1
Nb(I)–O(V)	1.96 ± 3		
Nb(I)–O(V)	2.02 ± 3		
Nb(I)–O(VI)	2.01 ± 1		
O(I)–O(IV)	3.04 ± 4	2 × O(I)–O(II)	2.92 ± 3
O(I)–O(IV)	2.97 ± 3	2 × O(I)–O(II)	3.05 ± 2
O(I)–O(V)	2.81 ± 3	2 × O(I)–O(II)	2.78 ± 2
O(I)–O(V)	2.69 ± 3	2 × O(I)–O(III)	2.64 ± 2
O(I)–O(VI)	2.76 ± 2	2 × O(I)–O(III)	2.84 ± 3
O(II)–O(IV)	2.77 ± 3	O(II)–O(II)	2.64 ± 5
O(II)–O(IV)	2.98 ± 3	4 × O(II)–O(III)	2.43 ± 2
O(II)–O(V)	2.69 ± 4		
O(II)–O(V)	2.85 ± 3		
O(II)–O(VI)	3.06 ± 2		
2 × O(IV)–O(V)	2.39 ± 3		
O(IV)–O(V)	2.39 ± 4		
O(IV)–O(VI)	2.68 ± 5		
O(V)–O(VI)	2.43 ± 4		
Nb(II) pentagonal bipyramid			
2 × Nb(II)–O(III)	1.99 ± 2		
2 × Nb(II)–O(IV)	1.98 ± 3		
2 × Nb(II)–O(V)	2.07 ± 3		
Nb(II)–O(VI)	2.41 ± 6		
2 × O(III)–O(IV)	2.71 ± 3		
2 × O(III)–O(IV)	3.02 ± 3		
2 × O(III)–O(V)	2.89 ± 3		
2 × O(III)–O(V)	2.76 ± 3		
2 × O(III)–O(VI)	3.02 ± 5		
O(IV)–O(IV)	2.71 ± 4		
2 × O(IV)–O(V)	2.39 ± 4		
2 × O(V)–O(VI)	2.43 ± 4		
Nb(III) octahedron		Ta(II) octahedron	
2 × Nb(III)–O(I)	1.98 ± 3	6 × Ta(II)–O(I)	1.98 ± 2
2 × Nb(III)–O(II)	1.95 ± 2		
2 × Nb(III)–O(III)	2.00 ± 2		
2 × O(I)–O(II)	2.79 ± 4	6 × O(I)–O(I)	2.80 ± 3
2 × O(I)–O(II)	2.76 ± 3	3 × O(I)–O(I)	2.60 ± 3
2 × O(I)–O(III)	2.85 ± 4	3 × O(I)–O(I)	3.04 ± 4
2 × O(I)–O(III)	2.77 ± 3		
2 × O(II)–O(III)	2.84 ± 2		
2 × O(II)–O(III)	2.75 ± 3		

TABLE VI (*continued*)

$Na_2Nb_4O_{11}$		$CaTa_4O_{11}$	
Na polyhedron		Ca polyhedron	
Na–O(I)	2.52 ± 3	6 × Ca–O(I)	2.46 ± 2
Na–O(I)	2.66 ± 3	2 × Ca–O(III)	2.65 ± 3
Na–O(II)	2.48 ± 3		
Na–O(II)	2.68 ± 2		
Na–O(III)	2.51 ± 2		
Na–O(III)	2.63 ± 3		
Na–O(V)	2.72 ± 3		

is the oxygen that deviates from the equatorial plane of the pentagonal bipyramids, which brings it closer to the sodium atom. This type of seven-coordination is found in the A–M_2O_3 structure type of La_2O_3 and other rare earth metal oxides (*14*), (*15*), and also in $NbOF_6^{3-}$ (*16*).

In $CaTa_4O_{11}$ there are two types of interstices corresponding to the sodium position in $Na_2Nb_4O_{11}$. One corresponds to a six-coordinated void while the other is eight-coordinated, with an oxygen atom outside both of the large faces of the deformed octahedron. The latter position is occupied by the calcium atoms. This structural difference between $Na_2Nb_4O_{11}$ and $CaTa_4O_{11}$ is due to the difference in the relative positions of the two layers of pentagonal bipyramids, which is reflected in the change of symmetry from one compound to the other. Figure 3 shows a projection, perpendicular to the *ab* plane, of two successive equatorial planes of pentagonal bipyramids for each structure. The arrangement of niobium and tantalum is approximately the same, but the oxygen pentagons are not arranged in the same way. The surroundings of the octahedrally coordinated Nb(Ta) atoms are similar in both structures but while sodium has a seventh oxygen either above or below calcium has both one above and one below since the positions of the O(III) atoms in the two layers always coincide in the projection (cf. Fig. 3). The coordination figures of sodium and calcium are shown in Fig. 4.

This type of symmetry variation, where two layers change their relative positions when cations between them demand different coordination numbers, has been described by Wilhelmi (*17*) for the MCr_3O_8 family, where M = Li, Na, K, Rb, Tl, and Cs.

The pentagonal bipyramid as a coordination figure around niobium is found in $LiNb_6O_{15}F$ (*18*), $NaNb_6O_{15}F$ and the isomorphous $NaNb_6O_{15}OH$

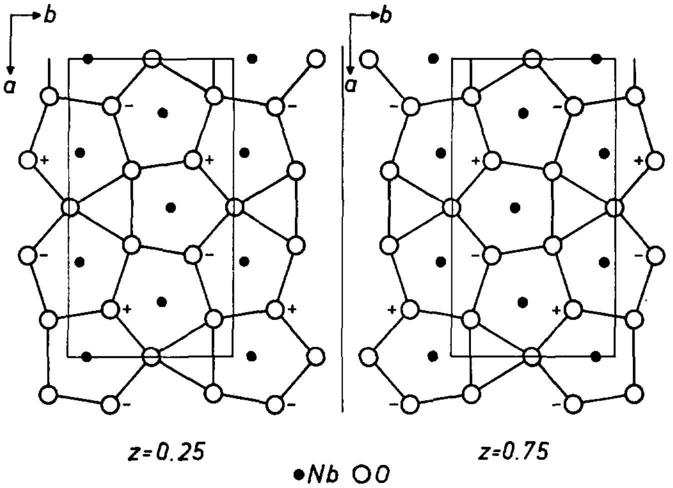

FIG. 1. The atoms in the planes $z = 0.25$ and $z = 0.75$ for $Na_2Nb_4O_{11}$. Atoms marked with + or − are situated about 0.4 Å above and below the planes, respectively.

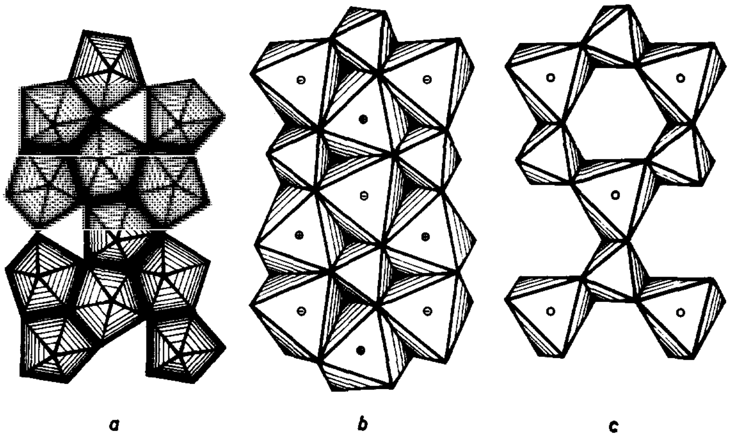

FIG. 2. (a) Layer of pentagonal bipyramids. (b) Layer of octahedra in $Na_2Nb_4O_{11}$. Small ones contain Nb and big ones Na. The circles represent the seventh close oxygen neighbour of Na. (c) The same type of layer for $CaTa_4O_{11}$. The circles represent the seventh and eighth close oxygen neighbours of Ca.

(*19*) and in the region $Nb_2O_5 \cdot WO_3$–WO_3 (*20*), (*21*). In these structures the pentagonal bipyramids share edges with octahedra. The oxide fluorides are built up of blocks each consisting of a quite regular pentagonal bipyramid sharing edges with five octahedra. The building blocks are joined by sharing corners. The niobium wolfram oxides are closely related to the tetragonal potassium wolfram bronze structure (*22*), where niobium and oxygen atoms alternate inside pentagonal oxygen tunnels. Ta_3O_7F has one form isomorphous with $LiNb_6O_{15}F$ and another isomorphous with U_3O_8 (*23*).

Sevenfold coordination is also found in the ions NbF_7^{2-} and TaF_7^{2-} (*24*) the configuration being a triangular prism with one oxygen outside a prism face; and in $NbOF_6^{3-}$ (16) which has the coordination found in A–M_2O_3.

A compound $CaNb_4O_{11}$ analogous with $CaTa_4O_{11}$ does evidently not form (*25*). For the system Na_2O–Ta_2O_5 there are several pieces of information summarized by Whiston and Smith (*26*). According to this work, the compound $Na_2Ta_4O_{11}$ is reported as tetragonal by King, Schultz, Durbin, and Duckworth and by Whiston and Smith, and as orthorhombic by Reisman. A sample prepared from Na_2CO_3 and Ta_2O_5 in air at 1000°C gave a powder photograph which could not be indexed according to these reports, but had a distinct resemblance to the patterns of $Na_2Nb_4O_{11}$ and $CaTa_4O_{11}$. It could be indexed with the same monoclinic unit cell as $Na_2Nb_4O_{11}$ but this gave a lot of double-indexed lines which were sharp and suggested higher symmetry. Thus it was found to be rhombohedral, probable space group $R\bar{3}c$ with

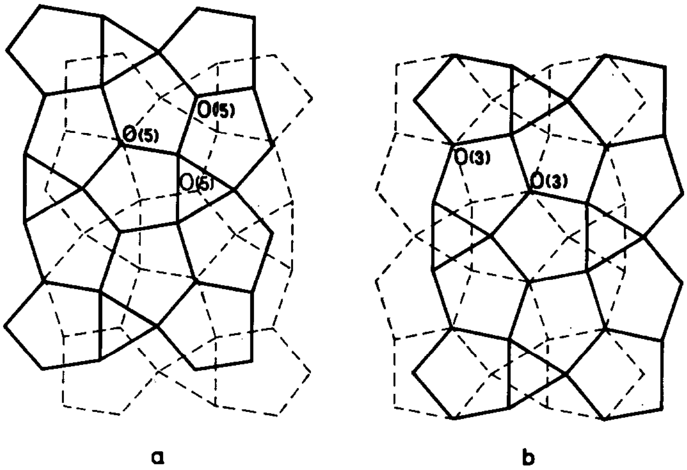

FIG. 3. Projection perpendicular to the *ab* plane of two successive equatorial planes of pentagonal bipyramids for (a) $Na_2Nb_4O_{11}$, and (b) $CaTa_4O_{11}$.

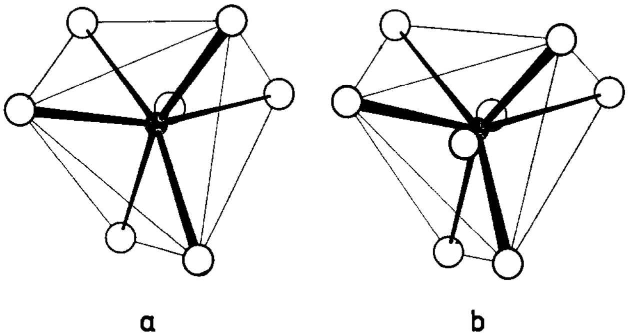

FIG. 4. Clinographic projection of (a) the sodium, and (b) the calcium coordination figure. The figures are rotated 5° around the *a* and *b* axes (orthohexagonal axes for $CaTa_4O_{11}$), starting from a view perpendicular to the *ab* plane.

hexagonal axes $a = 6.209 \pm 1$ and $c = 36.618 \pm 2$ Å (rhombohedral cell dimensions $a = 12.722$ Å and $\alpha = 28.25°$).

The approximately trigonal character of the $Na_2Nb_4O_{11}$ structure is obvious from Fig. 3. The inclination of the monoclinic *c* axis to the *ab* plane is such that the structure may be described as only moderately deviating from an hexagonal arrangement with unit cell dimensions corresponding to the *a* axis and three times the *c* axis of the $CaTa_4O_{11}$ unit cell. This indicates that the stacking of the layers of polyhedra is essentially the same in $Na_2Ta_4O_{11}$ and $Na_2Nb_4O_{11}$. The difference in symmetry, however, may make it appropriate to characterize the structure of the latter as a somewhat distorted version of the former. Further studies of $Na_2Ta_4O_{11}$ are in progress.

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