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The Structures of the Reduced and Oxidized Forms of Barium Silicon Tantalum Oxide, $Ba_3Si_4Ta_6O_{23}$ and $Ba_3Si_4Ta_6O_{26}$

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The compound once reported as $Ba_{0.5-x}TaO_{3-x}$ has now been shown to be $Ba_3Si_4Ta_6O_{23}$. The silicon is readily introduced from the silica reaction capsule if fluoride is present. The symmetry is hexagonal, space group $P\bar{6}2m$, $a = 8.997 \pm 0.003$, $c = 7.745 \pm 0.005$ Å. The structure contains layers with tantalum coordinated by a square pyramid of oxygens and silicon coordinated tetrahedrally by oxygens. These layers are mirrored to form double layers which are interleaved with barium ions. The oxidized phase, $Ba_3Si_4Ta_6O_{26}$, which may be formed by oxidation of the reduced phase, has the same space group, and cell dimensions $a = 8.99 \pm 0.01$, $c = 7.79 \pm 0.01$ Å. The additional oxygens complete octahedra about the tantalum atoms.

Introduction

A previous attempt at the determination of the structure of $Ba_3Si_4Ta_6O_{23}$ was made on the assumption that the formula was $Ba_{0.5-x}TaO_{3-x}$ (*1*). Some discussion is offered in succeeding sections of this paper to explain how it was possible for members of a chemistry department to have made this error in the composition. In the earlier work a trial structure was obtained with a unit cell formula of $Ba_3Ta_6O_{18}$. Although there was fair agreement between calculated and observed structure factors for the available data, the following points were cited as disturbing: (1) There were marked deviations from Pauling's electrostatic valency rules. (2) There was no explanation for the observed Ba:Ta ratio of 0.44. (3) The maximum of 18 oxygens left considerable unfilled volume. (4) The X-ray density was lower than the observed range of values. It was indicated that at some future time a systematic effort would, hopefully, be undertaken to resolve the difficulties. This has now been accomplished. In addition the oxidized phase has also been studied and the locations of the added oxygens have been found.

Experimental

Reduced Phase

The reduced phase was first prepared by using BaO, a Fairmount sample of Ta_2O_5, and Ta metal in the mole ratios 5:4:2 and heated at 1250°C in an evacuated, sealed, silica capsule for 24 h. A blue product covered with blue hexagonal crystals was formed. The size of the crystals could be increased by wrapping the sample in Ta foil before heating. However, when new samples of Fansteel and Fairmount Ta_2O_5 were used, the hexagonal compound was not obtained. Instead a tetragonal compound was found. It seemed the hexagonal phase could only be prepared when Ta_2O_5 from a particular bottle was used, and when that source was exhausted, only the tetragonal phase could be prepared. Eventually, it was found that with very long heating at 1250°C or by using Ta_2O_5 dissolved by sodium hydroxide fusion and reprecipitated some of the hexagonal phase could be obtained. A still more successful preparation involved the use of $BaCl_2$ as a flux, but the product was still not homogeneous.

Suspicion that the original Ta_2O_5 had contained a fluoride impurity led us to add some BaF_2 to the reaction mixture. When this was done the hexagonal phase was obtained much more readily and with greater homogeneity.

The sample of reduced phase from which the crystal studied was taken was prepared by mixing $5BaO:4Ta_2O_5:1Ta$ with 5% BaF_2 by weight. The mixture was pressed into pellets, wrapped in Ta foil, sealed in evacuated silica capsules, and heated for three days at 1250°C. Clear blue flat crystals were found on the surface of the pellet, on the foil, and on the capsule. Another heating cycle improved the

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TABLE I

Representative Absorption Corrections

hkl	*I* measured	Transmission factor	Relative FOBS
400	112	0.085	249
$\bar{4}40$	97	0.071	274
$0\bar{4}0$	190	0.145	265
310	64	0.090	113
$\bar{4}30$	86	0.085	117
$1\bar{4}0$	112	0.139	106
611	17	0.093	82
$\bar{7}61$	13	0.085	75
$1\bar{7}1$	20	0.140	73
442	179	0.113	256
$\bar{8}42$	154	0.098	254
$4\bar{8}2$	183	0.110	262
324	132	0.113	192
$\bar{5}34$	130	0.180	195
$2\bar{5}4$	154	0.137	188
507	25	0.124	97
$\bar{5}57$	37	0.174	122
$0\bar{5}7$	34	0.143	100
4110	7	0.193	57
$\bar{5}410$	6	0.160	53
$1\bar{5}10$	6	0.154	48

homogeneity of the sample. Although most of the crystals were twinned, a thin plate was found to be single and was cut to an approximately rectangular parallelepiped, 0.055 × 0.055 × 0.042 mm.

Precession photography of the zero and first levels with the X-ray beam normal to the plate showed the crystal to be hexagonal, Laue group 6/*mmm*. Further examination revealed no systematic absences, so the probable space group was one of *P*622, *P*6*mm*, ($P\bar{6}m2$, $P\bar{6}2m$), or *P*6/*mmm*. Structure considerations eliminated the space groups with sixfold axes almost immediately and later established the probable space group as $P\bar{6}2m$. Cell dimensions were calculated from measurements on a G.E. single crystal orienter: $a = 8.997(3)$, $c = 7.745(5)$ Å.

All reflections for which $k \geqq 0$, $h \geqq k$ for $l = 0$ through $l = 12$ up to $2\theta = 60°$ were measured on a G.E. single-crystal orienter with Zr filtered Mo radiation, pulse height discrimination, 2° take off angle, and scintillation counter. The θ, 2θ scan technique was used at 2° 2θ/min for 80 sec. Background was measured by stationary counting at both ends of the 2.67° range. The total number of reflections measured was 1527 which yielded 509 independent reflections of which 254 were greater than 2σ for the background.

Because μ_l is about 478 for Mo radiation and μR is about 2.6, serious absorption problems are encountered. Symmetry related intensities were found in some cases to differ by as much as a factor of two. To correct for absorption, the crystal was measured with a travelling microscope and its shape described by six bounding planes. The absorption corrections were then made using Prewitt's program ACACA (*2*) by integration over an 8 × 8 × 4 grid. Table I shows representative absorption corrections and illustrates how dramatic the absorption effect can sometimes be. The reflections in the table are symmetry related in sets of three, but this isn't always obvious from the raw intensities.

Oxidized Phase

Crystals of the oxidized phase were clear colorless plates formed by heating crystals of the reduced phase in air at 1000°C for 1 h. The only single crystals obtained were thin plates. One of these was cut to a rectangle 0.2 × 0.2 × 0.003 mm and mounted with a^* parallel to the fiber. To obtain a measurable intensity and small absorption for low values of l this orientation was much better than one with c in the fiber direction because of the shape of the crystal.

The probable space group is the same as for the reduced phase, $P\bar{6}2m$. Cell dimensions are $a = 8.99$ (1), $c = 7.79$ (1) Å. Reflections were measured in the same way as for the reduced phase, for $l = 0$ through $l = 4$ and $2\theta \leqq 60°$. A total of 518 measurements yielded 258 independent reflections of which 179 were greater than 2σ for the background. Absorption corrections were applied (as for the reduced phase) with the crystal described by six bounding planes and integration performed over an 8 × 8 × 4 grid.

Structure Determination

Reduced Phase

Three bariums and six tantalums were placed in the positions postulated in the earlier structure work (*1*). Four cycles of least-squares refinement (*3*) lowered the *R* factor from 33.0 to 12.8%. Inclusion of the oxygens in the positions of the trial structure lowered *R* to 10.7%, but when atom multipliers for the oxygens were varied, the multiplier for the oxygen at 0.24, 0, and 0.5 became negative. This oxygen completes an octahedron around tantalum, so its absence would mean that there are only five oxygens coordinated to tantalum. A difference

Fourier (*4*) based on phases determined by barium and tantalum not only confirmed the absence of this oxygen but produced a sharp peak at $\frac{1}{3}$, $\frac{2}{3}$, 0.24 and a broader peak at $\frac{1}{3}$, $\frac{2}{3}$, 0. The first of these sites was a reasonable location for additional tantalum, but previous attempts to place tantalum there had led to worsened structure factor agreement (*5*). Nevertheless, because of the sharp peak produced on the difference map, tantalum was again tried at this position, but with a variable atom multiplier in a least-squares refinement. The multiplier converged to 0.063 (full occupancy = 0.333) which corresponds very nearly to atomic number 14 and immediately suggested silicon. The other, broader, peak suggested oxygen. Isotropic refinement with these additional atoms in the structure (anomalous dispersion corrections included) reduced R to 8.4%. Changing the sign of $\Delta f''$ and refining increased R to 9.3%, which indicated the original choice of indexing to be correct. A Hughes-type weighting scheme (*6*) with $\sqrt{w} = 1$ for $|F_{\text{obs}}| \leqq 4|F_{\text{min}}|$ and $\sqrt{w} = 4|F_{\text{min}}|/|F_{\text{obs}}|$ for $|F_{\text{obs}}| > 4|F_{\text{min}}|$ with $F_{\text{min}} = 50$ was then introduced, and isotropic refinement led to a final value for $R \equiv \Sigma||F_0| - k|F_c||/\Sigma|F_0| = 0.077$ and weighted $R \equiv [\Sigma\omega(|F_0| - k|F_c|)^2/\Sigma\omega|F_0|^2]^{1/2} = 0.100$. Anisotropic refinement yielded position parameters which were not significantly different from the isotropic results and thermal parameters which were physically improbable, so the results of the anisotropic refinement are not reported here. A final difference Fourier showed no peaks greater than $\frac{1}{8}$ of an oxygen peak. A final attempt to place another oxygen in the position which would complete the octahedron around tantalum was tested by least squares with a variable atom multiplier; the multiplier actually became somewhat negative, emphasizing the absence of any atom at this position.

Scattering factors for O^{1-} and Si^{2+} (by interpolation) were obtained from the International Tables (*7*). The values for Ba^{1+} and Ta^{2+} were obtained from Thomas and Umeda (*8*). Anomalous dispersion corrections were obtained from Cromer (*9*).

Final atomic positions and temperature factors are listed in Table II, observed and calculated structure factors in Table III.

Oxidized Phase

Refinement of the oxidized phase began with the parameters of the reduced phase. It was found that R was reduced from 8.6–7.6% by making $\Delta f''$ negative; accordingly the *hkl* data were reindexed as $\bar{h}\bar{k}\bar{l}$. The possible positions for the additional oxygen of the oxidized phase were 0.21, 0, $\frac{1}{2}$ and $\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{2}$; both gave about the same R factor. However, the temperature factor for the first position was better behaved, since it remained low, whereas after four cycles it increased to about 7 for the second position. The Fourier evidence was stronger; a difference Fourier assuming oxygen in the 0.21, 0, $\frac{1}{2}$ position but absent from the $\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{2}$ position showed no peaks greater than $\frac{1}{10}$ of an oxygen peak.

Weights for the least-squares refinement were then assigned as with the reduced phase but with $F_{\text{min}} = 58$. The final conventional R was 7.3% (weighted $R = 9.6\%$).

TABLE II

ATOMIC POSITIONS AND THERMAL PARAMETERS FOR $Ba_3Si_4Ta_6O_{23}$[a] SPACE GROUP NO. 189, $P\bar{6}2m$

Atom	Position	x	y	z	$B \times 10^2$
Ba	3*g*	0.6016 (8)	0	$\frac{1}{2}$	49 (9)
Ta	6*i*	0.2384 (3)	0	0.2428 (4)	36 (4)
Si	4*h*	$\frac{1}{3}$	$\frac{2}{3}$	0.2046 (31)	16 (33)
O(I)	2*c*	$\frac{1}{3}$	$\frac{2}{3}$	0	154 (204)
O(II)	3*f*	0.2919 (111)	0	0	93 (163)
O(III)	6*i*	0.8191 (59)	0	0.2363 (68)	22 (72)
O(IV)	12*l*	0.4939 (48)	0.1773 (46)	0.2802 (36)	33 (57)

Position 2*c*: $\frac{1}{3}, \frac{2}{3}, 0; \frac{2}{3}, \frac{1}{3}, 0$. 3*f*: $x, 0, 0; 0, x, 0; \bar{x}, \bar{x}, 0$. 3*g*: $x, 0, \frac{1}{2}; 0, x, \frac{1}{2}; \bar{x}, \bar{x}, \frac{1}{2}$. 4*h*: $\frac{1}{3}, \frac{2}{3}, z$: $\frac{1}{3}, \frac{2}{3}, \bar{z}; \frac{2}{3}, \frac{1}{3}, z; \frac{2}{3}, \frac{1}{3}, \bar{z}$. 6*i*: $x, 0, z; 0, x, z; \bar{x}, \bar{x}, z; x, 0, \bar{z}; 0, x, \bar{z}; \bar{x}, \bar{x}, \bar{z}$. 12*l*: $x, y, z; \bar{y}, x - y, z; y - x, \bar{x}, z; x, y, \bar{z}; \bar{y}, x - y, \bar{z}; y - x, \bar{x}, \bar{z}; y, x, z; \bar{x}, y - x, z; x - y, \bar{y}, z; y, x, \bar{z}; \bar{x}, y - x, \bar{z}; x - y, \bar{y}, z$.

[a] Standard deviations, as calculated by ORFLS, are given in parentheses.

TABLE III. Observed and Calculated Structure Factors, Reduced Phase (The columns are h, k, $|F_0|$, and $|F_c|$)

**** L= 0 ****

1	0	121	99
2	0	115	95
3	0	147	169
4	0	265	299
5	0	237	256
6	0	< 58	16
7	0	< 64	41
8	0	223	226
9	0	155	141
10	0	< 80	37
1	1	177	195
2	1	261	338
3	1	113	89
4	1	175	171
5	1	193	189
6	1	218	212
7	1	95	100
8	1	108	99
9	1	57	79
10	1	157	156
2	2	182	190
3	2	208	223
4	2	145	153
5	2	167	161
6	2	169	171
7	2	128	122
8	2	< 73	72
9	2	158	177
10	2	102	90
3	3	257	296
4	3	52	48
5	3	135	130
6	3	170	176
7	3	206	206
8	3	88	78
9	3	< 78	65
10	3	< 81	38
4	4	211	215
5	4	113	111
6	4	74	73
7	4	< 73	22
8	4	134	128
9	4	104	108
10	4	< 82	27
5	5	124	123
6	5	196	166
7	5	89	77
8	5	145	158
9	5	< 81	52
6	6	< 75	80
7	6	< 78	54
8	6	< 81	99
7	7	128	136

**** L= 1 ****

0	0	73	105
1	0	< 29	36
2	0	99	98
3	0	46	33
4	0	< 48	39
5	0	117	105
6	0	< 59	22
7	0	71	40
8	0	< 69	37
9	0	< 75	31
10	0	< 80	67
1	1	131	147
2	1	46	39
3	1	105	104
4	1	80	45
5	1	< 58	13
6	1	77	83
7	1	< 69	39
8	1	< 73	60
9	1	< 77	15
10	1	< 80	15
2	2	81	77
3	2	80	82
4	2	77	77
5	2	< 62	44
6	2	66	39
7	2	< 70	40
8	2	< 74	32
9	2	< 77	44
10	2	< 80	35
3	3	< 51	33
4	3	< 56	40
5	3	69	55
6	3	< 67	62
7	3	< 71	41
8	3	< 75	22
9	3	< 78	28
10	3	< 81	33
4	4	87	85
5	4	< 64	17
6	4	< 70	8
7	4	< 73	65
8	4	< 77	31
9	4	< 80	41
10	4	< 82	18
5	5	79	65
6	5	< 72	6
7	5	< 76	31
8	5	< 79	23
9	5	< 81	8
6	6	< 75	52
7	6	< 78	25
8	6	< 81	36
7	7	< 81	33

**** L= 2 ****

0	0	378	360
1	0	159	162
2	0	200	205
3	0	48	26
4	0	322	323
5	0	78	53
6	0	< 60	9
7	0	66	50
8	0	118	132
9	0	173	165
10	0	86	87
1	1	291	311
2	1	196	197
3	1	166	145
4	1	171	190
5	1	156	139
6	1	253	255
7	1	< 70	50
8	1	141	138
9	1	73	65
10	1	146	143
2	2	115	118
3	2	227	237
4	2	148	147
5	2	204	198
6	2	116	113
7	2	182	168
8	2	127	115
9	2	90	69
10	2	112	122
3	3	209	206
4	3	< 58	38
5	3	< 63	60
6	3	< 68	50
7	3	223	231
8	3	< 75	26
9	3	107	99
10	3	< 82	55
4	4	259	258
5	4	161	152
6	4	< 71	44
7	4	79	78
8	4	139	139
9	4	133	141
5	5	107	101
6	5	144	143
7	5	< 76	57
8	5	100	87
9	5	< 82	54
6	6	139	133
7	6	99	88
8	6	< 81	20

**** L= 3 ****

0	0	162	145
1	0	< 42	5
2	0	58	51
3	0	89	90
4	0	< 68	9
5	0	132	123
6	0	< 61	24
7	0	< 65	32
8	0	74	64
9	0	< 75	19
10	0	< 80	43
1	1	102	103
2	1	112	91
3	1	129	80
4	1	< 56	18
5	1	< 60	23
6	1	76	67
7	1	< 69	39
8	1	< 72	58
9	1	< 77	17
10	1	< 80	24
2	2	< 46	36
3	2	< 52	41
4	2	99	87
5	2	60	50
6	2	< 67	45
7	2	< 70	31
8	2	< 74	47
9	2	77	68
10	2	< 80	24
3	3	74	69
4	3	73	52
5	3	< 64	45
6	3	69	66
7	3	< 72	27
8	3	< 75	32
9	3	< 78	21
10	3	< 81	27
4	4	78	68
5	4	< 65	3
6	4	< 71	32
7	4	< 74	45
8	4	< 77	23
9	4	< 79	32
5	5	95	81
6	5	< 73	31
7	5	< 76	29
8	5	< 79	52
6	6	< 76	42
7	6	< 79	17
8	6	< 81	49

**** L= 4 ****

0	0	547	542
1	0	123	93
2	0	83	59
3	0	141	126
4	0	277	252
5	0	254	232
6	0	< 61	39
7	0	< 65	43
8	0	210	212
9	0	128	121
10	0	< 79	35
1	1	188	167
2	1	285	276
3	1	64	63
4	1	142	125
5	1	173	154
6	1	180	182
7	1	96	83
8	1	95	90
9	1	87	69
10	1	151	148
2	2	164	150
3	2	194	182
4	2	134	124
5	2	173	149
6	2	152	144
7	2	116	106
8	2	< 73	69
9	2	163	160
10	2	50	83
3	3	276	261
4	3	< 59	50
5	3	132	118
6	3	170	160
7	3	191	183
8	3	86	72
9	3	< 77	52
10	3	< 80	39
4	4	193	185
5	4	111	105
6	4	< 70	65
7	4	< 73	26
8	4	126	122
9	4	113	102
5	5	117	105
6	5	152	148
7	5	< 75	72
8	5	141	138
6	6	86	85
7	6	< 78	47

**** L= 5 ****

0	0	< 51	27
1	0	< 49	44
2	0	88	92
3	0	< 52	6
4	0	59	60
5	0	77	60
6	0	< 62	11
7	0	< 65	37
8	0	< 69	5
9	0	70	66
10	0	< 78	79
1	1	116	120
2	1	53	49
3	1	92	92
4	1	66	71
5	1	< 61	22
6	1	91	97
7	1	< 69	39
8	1	< 72	53
9	1	< 75	24
10	1	< 78	20
2	2	94	72
3	2	99	93
4	2	< 59	60
5	2	64	54
6	2	< 67	34
7	2	< 70	54
8	2	< 73	33
9	2	< 76	19
10	2	< 78	50
3	3	< 56	20
4	3	< 60	24
5	3	< 64	48
6	3	< 68	50
7	3	< 71	59
8	3	< 74	15
9	3	< 77	39
4	4	116	113
5	4	< 66	31
6	4	< 70	11
7	4	69	68
8	4	< 75	45
5	5	< 69	50
6	5	< 72	29
7	5	< 75	26
8	5	< 77	4
6	6	< 75	54
7	6	< 77	32

**** L= 6 ****

0	0	194	171
1	0	129	127
2	0	133	126
3	0	< 55	25
4	0	244	247
5	0	68	55
6	0	< 63	33
7	0	< 66	29
8	0	121	121
9	0	125	127
10	0	< 77	73
1	1	218	215
2	1	151	148
3	1	129	126
4	1	122	119
5	1	94	100
6	1	197	202
7	1	< 69	23
8	1	110	117
9	1	61	56
10	1	135	128
2	2	76	93
3	2	165	171
4	2	108	107
5	2	181	177
6	2	82	78
7	2	134	135
8	2	101	107
9	2	< 76	55
3	3	163	168
4	3	< 62	29
5	3	< 65	49
6	3	< 69	39
7	3	176	183
8	3	< 74	22
9	3	80	77
4	4	186	194
5	4	130	133
6	4	< 70	37
7	4	88	64
8	4	119	127
5	5	90	96
6	5	115	116
7	5	< 74	44
6	6	< 75	118

**** L= 7 ****

0	0	174	149
1	0	< 56	12
2	0	< 56	17
3	0	78	78
4	0	< 59	31
5	0	107	114
6	0	< 64	29
7	0	< 67	26
8	0	75	80
9	0	109	39
10	0	< 77	27
1	1	53	56
2	1	92	100
3	1	67	46
4	1	< 62	31
5	1	< 64	32
6	1	66	60
7	1	< 70	37
8	1	< 73	44
9	1	< 75	21
2	2	< 55	25
3	2	< 59	38
4	2	74	70
5	2	< 66	47
6	2	< 68	47
7	2	< 71	27
8	2	< 73	43
9	2	< 75	75
3	3	71	84
4	3	< 63	44
5	3	< 67	43
6	3	76	67
7	3	< 72	39
8	3	< 74	34
4	4	< 65	73
5	4	< 68	16
6	4	< 71	37
7	4	< 73	33
5	5	76	67
6	5	< 73	47
6	6	< 75	39

**** L= 8 ****

0	0	290	291
1	0	80	77
2	0	< 59	24
3	0	58	70
4	0	174	180
5	0	177	181
6	0	< 66	59
7	0	< 68	43
8	0	161	173
9	0	< 74	86
1	1	128	132
2	1	187	188
3	1	< 61	40
4	1	64	66
5	1	106	100
6	1	136	128
7	1	73	59
8	1	72	69
9	1	< 75	52
2	2	101	105
3	2	123	123
4	2	81	79
5	2	128	121
6	2	89	96
7	2	< 71	76
8	2	< 73	61
3	3	189	193
4	3	< 65	47
5	3	93	91
6	3	117	125
7	3	130	136
4	4	135	134
5	4	87	88
6	4	< 72	50
7	4	< 73	32
5	5	< 71	74
6	5	< 73	112

**** L= 9 ****

0	0	< 63	13
1	0	< 62	47
2	0	67	47
3	0	< 62	2
4	0	< 64	79
5	0	< 65	19
6	0	< 67	7
7	0	< 70	22
8	0	< 72	25
1	1	< 58	93
2	1	< 62	50
3	1	< 64	72
4	1	< 66	56
5	1	< 68	31
6	1	< 70	91
7	1	< 72	22
8	1	< 74	49
2	2	< 61	39
3	2	77	76
4	2	< 67	50
5	2	< 69	68
6	2	< 70	27
7	2	< 72	56
3	3	< 65	36
4	3	< 67	16
5	3	< 70	26
6	3	< 71	24
4	4	< 69	101
5	4	< 71	44
6	4	< 72	14
5	5	< 72	49

**** L=10 ****

0	0	72	82
1	0	76	91
2	0	69	75
3	0	< 65	22
4	0	165	167
5	0	< 67	46
6	0	< 69	43
7	0	< 71	15
1	1	131	142
2	1	87	99
3	1	78	93
4	1	< 68	68
5	1	< 69	63
6	1	126	141
2	2	79	68
3	2	100	111
4	2	45	70
5	2	132	136
6	2	< 72	47
3	3	114	118
4	3	< 68	22
5	3	< 71	34
4	4	91	133

**** L=11 ****

0	0	98	120
1	0	< 66	25
2	0	< 67	7
3	0	< 67	42
4	0	< 68	57
5	0	75	98
1	1	< 64	54
2	1	66	84
3	1	< 68	24
4	1	< 70	21
5	1	< 71	33
2	2	< 66	39
3	2	< 68	44
3	3	< 68	84

**** L=12 ****

0	0	159	172
1	0	< 69	52
2	0	< 69	13
3	0	< 69	47
4	0	< 76	115
5	0	122	124
1	1	85	87
2	1	87	124
2	2	< 68	63

TABLE IV

ATOMIC POSITIONS AND THERMAL PARAMETERS FOR $Ba_3Si_4Ta_6O_{26}$
SPACE GROUP NO. 189, $P\bar{6}2m$

Atom	Position	x	y	z^a	$B \times 10^{2a}$
Ba	$3g$	0.6022 (10)	0	$\frac{1}{2}$	77 (13)
Ta	$6i$	0.2379 (3)	0	0.2452 (11)	36 (5)
Si	$4h$	$\frac{1}{3}$	$\frac{2}{3}$	0.2137 (81)	52 (54)
O(I)	$2c$	$\frac{1}{3}$	$\frac{2}{3}$	0	2 (184)
O(II)	$3f$	0.2767 (86)	0	0	−16 (142)
O(III)[b]	$6i$	0.8332 (97)	0	0.2112 (171)	50
O(IV)	$12l$	0.4881 (39)	0.1809 (38)	0.2903 (62)	−67 (52)
O(V)	$3g$	0.2217 (111)	0	$\frac{1}{2}$	65 (157)

[a] Large errors, particularly in z and B, are due to the limited data in z direction. See text.

[b] Multiplicity reduced to 0.7 of full occupancy value and B held fixed at 0.5. See text.

Final atomic positions and temperature factors are listed in Table IV, observed and calculated structure factors in Table V.

The refinement of the oxidized phase was in some respects unsatisfactory. Neither the temperature factor nor the x parameter of O(III) converged after eight cycles of isotropic refinement. In order to obtain convergence for the x parameter, the temperature factor was held fixed at 0.5 and the atom multiplier allowed to vary, with the results shown in Table IV. Other oxygen temperature factors are also unsatisfactory, and the errors in the z parameters are large. All of these difficulties are attributable to the limited data in z. This was established by calculating an electron density map with calculated structure factors as coefficients; this calculated Fourier showed wide variation in electron density at the oxygen positions with the lowest density at O(III). By extending the range of calculated structure factors to $l = 12$ instead of $l = 4$ the oxygen densities become equal and the map was altogether normal. The effect of the series truncation on the Fourier calculation suggests that the difficulties with the least squares refinement are also due to the limited data.

Chemical Evidence for Composition

The detection of silicon during the structure determination and a report of its presence in a commercial analysis (though no analysis was made for silicon) led to trying the following syntheses:

$$2.9BaO + 3Ta_2O_5 + 0.1BaF_2 \overset{\text{air}}{\underset{\Delta}{}} \text{tetragonal phase}$$

$$3.0BaO + 3Ta_2O_5 + 4SiO_2 \overset{\text{air}}{\underset{\Delta}{}} 70\%\ \text{hexagonal phase} + 30\%\ \text{tetragonal phase}$$

$$2.9BaO + 3Ta_2O_5 + 4SiO_2 + 0.1BaF_2 \overset{\text{air}}{\underset{\Delta}{}} \text{hexagonal phase}$$

It was thus clear that the phase can be prepared with just the oxides of barium, tantalum, and silicon; that the fluoride is not essential to the preparation when SiO_2 is intimately mixed with the BaO and Ta_2O_5 (indeed, when care was taken to insure that the reactants were especially finely ground, by using agate mortar grinding and a SPEX mixer/mill, the hexagonal phase was formed with only minor impurities); but that even under these conditions, the fluoride aids the formation of the hexagonal compound. (The tetragonal phase was known from earlier work (*10*) and has the tetragonal tungsten bronze structure.)

Chemical analysis of the compound proved very difficult, particularly since the product was never completely homogeneous. The best analyses were probably those reported originally by Galasso in his thesis (*11*), but they were carried out at a time when the presence of silicon was not realized. In these analyses, SiO_2 would have come down with Ta_2O_5 and the total weight used (incorrectly, of course) to deduce the percentage of tantalum. The values calculated for $Ba_3Si_4TaO_{26}$: Ba, 20.34; Si, 5.55; Ta, 53.58. If the weighing forms for Ta and Si, Ta_2O_5, and SiO_2, respectively, were together mistakenly used to calculate Ta, the values calculated would be: Ba, 20.34, "Ta," 63.34. The found values: Ba, 20.98, "Ta," 61.64.

The difficulties in working with somewhat inhomogeneous products of course extended to the density determinations. These were performed on

TABLE V. OBSERVED AND CALCULATED STRUCTURE FACTORS, OXIDIZED PHASE (The columns are h, k, $|F_0|$, and $|F_c|$)

h	k	$\lvert F_0\rvert$	$\lvert F_c\rvert$
**** L= 0 ****			
1	0	124	119
2	0	99	96
3	0	148	162
4	0	294	299
5	0	236	254
6	0	< 31	11
7	0	49	34
8	0	207	224
9	0	131	146
10	0	52	35
1	1	220	209
2	1	338	350
3	1	93	93
4	1	178	174
5	1	178	183
6	1	194	201
7	1	94	114
8	1	102	114
9	1	60	58
10	1	150	156
2	2	207	216
3	2	228	228
4	2	164	158
5	2	182	174
6	2	170	179
7	2	123	116
8	2	53	63
9	2	162	159
10	2	92	86
3	3	306	311
4	3	54	65
5	3	122	135
6	3	158	151
7	3	208	214
8	3	71	82
9	3	80	72
10	3	< 53	29
4	4	229	208
5	4	120	107
6	4	75	70
7	4	< 46	28
8	4	131	132
9	4	116	95
10	4	< 56	23
5	5	135	134
6	5	168	160
7	5	78	72
8	5	163	159
9	5	< 56	54
6	6	95	82
7	6	56	51
8	6	101	87
7	7	142	129
**** L= 1 ****			
0	0	165	134
1	0	32	35
2	0	87	85
3	0	37	36
4	0	30	19
5	0	110	110
6	0	< 31	18
7	0	< 35	28
8	0	43	35
9	0	< 41	25
10	0	58	67
1	1	144	135
2	1	50	59
3	1	87	89
4	1	38	33
5	1	< 31	9
6	1	68	78
7	1	47	43
8	1	46	45
9	1	< 44	12
10	1	< 47	13
2	2	87	100
3	2	70	80
4	2	66	70
5	2	< 33	33
6	2	44	41
7	2	< 43	40
8	2	< 46	25
9	2	< 47	39
10	2	< 51	26
3	3	51	43
4	3	37	43
5	3	57	57
6	3	68	57
7	3	50	34
8	3	< 47	20
9	3	< 50	25
10	3	< 53	29
4	4	77	66
5	4	< 40	7
6	4	< 44	7
7	4	61	55
8	4	< 50	29
9	4	< 53	31
10	4	< 56	13
5	5	66	64
6	5	< 46	5
7	5	< 50	20
8	5	< 53	22
6	6	50	44
7	6	< 53	22
8	6	< 56	28
7	7	< 56	27
**** L= 2 ****			
0	0	311	323
1	0	150	150
2	0	140	192
3	0	< 24	22
4	0	317	304
5	0	56	38
6	0	< 32	8
7	0	58	42
8	0	122	129
9	0	159	161
10	0	63	76
1	1	337	323
2	1	171	179
3	1	127	137
4	1	176	177
5	1	130	135
6	1	233	250
7	1	54	62
8	1	126	137
9	1	60	57
10	1	136	139
2	2	121	105
3	2	224	234
4	2	134	142
5	2	187	182
6	2	113	112
7	2	152	148
8	2	107	106
9	2	75	69
10	2	116	104
3	3	208	211
4	3	< 37	24
5	3	53	53
6	3	< 52	37
7	3	225	229
8	3	< 47	36
9	3	100	94
10	3	59	57
4	4	275	256
5	4	151	142
6	4	< 46	41
7	4	63	60
8	4	122	127
9	4	126	135
5	5	95	93
6	5	154	139
7	5	< 56	56
8	5	94	96
6	6	149	143
7	6	80	73
7	7	168	160
**** L= 3 ****			
0	0	142	142
1	0	< 21	16
2	0	46	60
3	0	84	83
4	0	< 30	33
5	0	< 32	121
6	0	< 34	11
7	0	< 37	33
8	0	56	55
9	0	< 43	19
10	0	< 46	31
1	1	149	109
2	1	105	76
3	1	80	89
4	1	< 32	24
5	1	< 35	5
6	1	50	53
7	1	< 40	37
8	1	51	58
9	1	< 46	9
10	1	< 48	10
2	2	42	19
3	2	46	34
4	2	89	80
5	2	< 37	50
6	2	< 40	36
7	2	< 43	42
8	2	< 46	52
9	2	65	43
10	2	< 51	17
3	3	68	56
4	3	53	62
5	3	< 40	27
6	3	54	41
7	3	< 46	18
8	3	< 50	38
9	3	< 52	24
10	3	< 54	30
4	4	66	72
5	4	< 44	13
6	4	< 46	32
7	4	< 50	36
8	4	< 52	16
9	4	< 54	16
5	5	84	76
6	5	< 50	22
7	5	< 54	24
8	5	< 56	42
6	6	< 53	33
7	6	< 56	21
7	7	< 58	23
**** L= 4 ****			
0	0	487	518
1	0	70	92
2	0	84	64
3	0	131	132
4	0	250	254
5	0	218	229
6	0	< 37	47
7	0	< 39	26
8	0	203	209
9	0	120	133
10	0	< 49	28
1	1	115	174
2	1	374	298
3	1	77	59
4	1	133	130
5	1	148	150
6	1	175	183
7	1	80	90
8	1	92	96
9	1	< 49	58
10	1	129	150
2	2	215	161
3	2	200	172
4	2	< 39	129
5	2	150	161
6	2	142	147
7	2	108	103
8	2	64	62
9	2	140	147
10	2	93	89
3	3	294	263
4	3	67	67
5	3	136	118
6	3	143	141
7	3	178	180
8	3	70	71
9	3	< 54	58
10	3	< 57	34
4	4	203	187
5	4	110	111
6	4	60	65
7	4	< 52	29
8	4	121	124
9	4	82	95
5	5	114	111
6	5	137	146
7	5	72	63
8	5	123	134
6	6	98	89
7	6	< 58	49

the reduced phase: $d_{\text{calc}} = 6.05$ g/cm^3; $d_{\text{obs}} = 6.21$ g/cm^3. The observed value reported here was a measurement on what appeared optically to be the cleanest preparation. However, we have obtained values as low as 5.74 g/cm^3 and as high as 6.29 g/cm^3. These values straddle the theoretical one and attest to the difficulty of obtaining a single, clean, phase. In earlier work, presumably because particles of unreacted tantalum metal were present, some much higher densities were observed.

It is clear from the above that the chemical analyses and density information do not by themselves establish the formula. However, given the uncertainties involved, they are consistent with the results of the structure determination.

Discussion

Now that it is known that the phase originally written as $Ba_{0.44}TaO_{3-x}$ is, per unit cell, $Ba_3Si_4Ta_6O_{23-26}$, the troublesome questions previously left unanswered (*1*) can be explained. The X-ray density is now in the range of observed values; there is no longer considerable unfilled volume, but indeed quite efficient packing; and there are no longer any unreasonably large deviations from Pauling's electrostatic valency rules. A comparison of sums of electrostatic bond strengths from adjacent cations for the oxidized model without silicon (idealized cell formula $Ba_3Ta_6O_{18}$), for the reduced compound (cell formula $Ba_3Si_4Ta_6O_{23}$), and for the oxidized compound (cell formula $Ba_3Si_4Ta_6O_{26}$) is presented in Table VI.

The early, but quite reproducible, chemical analyses resulting in the formula $Ba_{0.44}TaO_{3-x}$ deserve discussion. A great many complex metal oxides, including some of barium and tantalum, have been prepared in silica capsules without the silica behaving as a reagent. The present analyses were carried out assuming only barium, tantalum, and oxygen in the structure. The procedure used was fusion with potassium hydroxide in a silver crucible, cooling, immersion in dilute hydrochloric acid, at which time hydrous tantalum pentoxide precipitated out. Sulfuric acid was added to the solution and the barium determined as barium sulfate. Unfortunately, at the same time that the hydrous tantalum pentoxide precipitated, some hydrated silica would also precipitate (*12*). The result would be the calculation of a too high percentage of tantalum in the sample.

The question as to why silica should have reacted in these cases when in so many other preparations of complex metal oxides carried out in evacuated

TABLE VI

ELECTROSTATIC VALENCE SUMS FOR $Ba_3Ta_6O_{18}$, $Ba_3Si_4Ta_6O_{23}$, AND $Ba_3Si_4Ta_6O_{26}$

Contribution from		Ba	Si	Ta	Total
2O	I	—	—	—	—
	II	—	2	—	2
	III	—	2	—	2
3O(II)	I	—	—	$1\frac{2}{3}$	$1\frac{2}{3}$[a]
	II	—	—	$1\frac{3}{5}$	$1\frac{3}{5}$
	III	—	—	$1\frac{2}{3}$	$1\frac{2}{3}$
6O(III)	I	$\frac{1}{5}$	—	$1\frac{2}{3}$	$1\frac{13}{15}$[a]
	II	$\frac{1}{5}$	—	$1\frac{3}{5}$	$1\frac{4}{5}$
	III	$\frac{1}{5}$	—	$1\frac{2}{3}$	$1\frac{13}{15}$
12O(IV)	I	$\frac{2}{5}$	—	$\frac{5}{6}$	$1\frac{7}{30}$[a]
	II	$\frac{2}{5}$	1	$\frac{4}{5}$	$2\frac{1}{5}$
	III	$\frac{2}{5}$	1	$\frac{5}{6}$	$2\frac{7}{30}$
3O(V)	I	—	—	$1\frac{2}{3}$	$1\frac{2}{3}$[a]
	II	—	—	—	—
	III	—	—	$1\frac{2}{3}$	$1\frac{2}{3}$

I, $Ba_3Ta_6O_{18}$; II, $Ba_3Si_4Ta_6O_{23}$; II, $Ba_3Si_4Ta_6O_{26}$.

[a] Only 18 oxygens would be available to distribute among the 24 sites of these positions.

silica capsules it did not is of considerable interest. It has already been mentioned that this was dependent on the sample of Ta_2O_5 used. It is suspected now that the Ta_2O_5 used by Galasso in his initial preparations contained a fluoride impurity which resulted in the transport of silica from the capsule walls. Certainly, as reported in the experimental section, the addition of fluoride to the preparation mixture makes it easy to prepare the compound. Fluoride could well have been present, since, in the separation of niobium from tantalum, the dissolution of Nb_2O_5–Ta_2O_5 mixtures in 70% HF is a common first step (*13*). Indeed, spectroscopically pure Nb_2O_5 has been shown in a dramatic way to sometimes contain fluoride impurity, since the structure of Nb_3O_7F was carried out on a crystal taken from a bottle of "spectroscopically pure" Nb_2O_5 (*14*)! It is reasonable to conclude that some samples of Ta_2O_5 would also contain fluoride impurity, introduced, ironically enough, in the process designed to purify the compound.

A commercial analysis of a sample prepared with fluoride deliberately added to facilitate the preparation showed about 1% fluoride. However, there is no evidence that the fluoride is actually incorporated in the structure.

A structural feature of interest is the value of the Si–O–Si angle (*15*)–(*17*). Since the oxygen positions are not accurately determined in the present studies, it would ordinarily be expected that the Si–O–Si angle would not be known accurately. However, in our model all three atoms lie on a $\bar{6}$ axis, so that the angle is required to be 180°. This result would follow for any hexagonal space group, so the question is are we really sure the crystal is hexagonal. Optical evidence with the polarizing microscope indicates that the crystals are uniaxial (*18*), so, unless we are dealing with one of the uncommon exceptions (a possibility of course), we may reinforce our conclusion that the crystals are hexagonal. Then the only way to avoid the conclusion that the Si–O–Si angle is 180° would be to hold that the symmetry is statistical in nature. If one relaxed the symmetry requirement altogether, one could, of course, change the value for the Si–O–Si angle too. An estimate of standard deviations for the non-absorption corrected data suggests that this angle error could be 10–15°, or the angle could be about 165°. We have no evidence for any such relaxation of symmetry nor for statistical symmetry, so we have no reason to report an angle different from 180°. The possibility of linearity in a Si–O–Si bond has been questioned by Liebau (*15*) and supported by Cruickshank (*16*). Linear bonds have been reported in hexagonal $CaAl_2Si_2O_8$ (*19*) and in thortveitite (*20*). In both of these cases linearity is fixed by symmetry, but of course the symmetry decision itself can be called into question.

In projection down the *c* axis $Ba_3Si_4Ta_6O_{23-26}$ is very similar to $K_3V_5O_{14}$ (*21*), with Ba, Si, and Ta in the K, V_1, and V_2 positions, respectively.† The coordination schemes are also similar, with trigonal pyramids around the V_1 atoms and square pyramids around the V_2 atoms. However, in the vanadium compound there are single layers interleaved with large cations (K^+), whereas in the tantalum compound there are double layers—one mirroring the other—and these double layers are interleaved with large cations (Ba^{++}). In the oxidized tantalum compound the square pyramids become octahedra with the addition of oxygens at the barium level. Tantalum–oxygen distances are in agreement with reported values. The tantalum atoms in the square pyramids lie very nearly at the base of the pyramid, whereas in $K_3V_5O_{14}$ the vanadium is reported to be markedly displaced towards the apex, although

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† Dr. F. Galasso and I (L. K.) discussed this problem with Dr. A. D. Wadsley on one of his visits to the University of Connecticut. On the basis of unit cell dimensions, probable cell contents, and an early Patterson map, Wadsley suggested that the structure should have much in common with that of $K_3V_5O_{14}$, as has now indeed been established.

in the latter case oxygens were placed from spatial considerations. Five coordinate tantalum has not been reported in the solid state, although trigonal bipyramidal coordination is reported for the vapor state pentahalides (*22*). Interatomic distances and angles are summarized in Table VII. Figures 1, 2, 3, 4, and 5 show, respectively, the tantalum environment in the reduced phase, the tantalum environment in the oxidized phase, a schematic drawing of four unit cells in *c* axis projection, and unit cell contents for the reduced and oxidized phases (*23*). The schematic drawing emphasizes the four connected net discussed by Wells (*24*). The rings of three tantalum polyhedra sharing corners, which are a feature of $Ba_3Si_4Ta_6O_{23-26}$, are also found in the

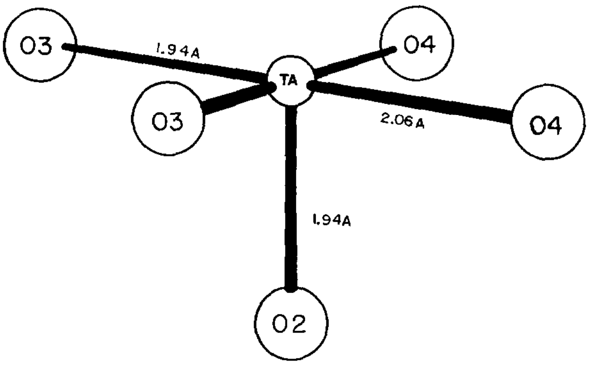

FIG. 1. Tantalum environment, reduced phase.

TABLE VII

DISTANCES AND ANGLES IN $Ba_3Si_4Ta_6O_{23}$

Distances

Ba-O(III)	2.83(5) Å	Ta-Ta	3.71(1); 3.76(1); 3.98(1)
Ba-O(IV)	2.82(4); 3.04(4)	O(I)-O(IV)	2.63(3)
Ta-O(II)	1.94(3)	O(II)-O(III)	2.94(7)
Ta-O(III)	1.94(2)	O(II)-O(IV)	2.77(5)
Ta-O(IV)	2.06(4)	O(III)-O(III)	2.82(9)
Si-O(I)	1.59(2)	O(III)-O(IV)	2.84(5)
Si-O(IV)	1.60(4)	O(IV)-O(IV)	2.57(6); 2.76(7)

Angles

O(I)-Si-O(IV)	111.5(14)°	O(III)-Ta-O(III)	90.9(17)
O(IV)-Si-O(IV)	107.3(15)	O(III)-Ta-O(IV)	84.2(22)
O(II)-Ta-O(III)	98.3(25)	O(IV)-Ta-O(IV)	93.3(30)
O(II)-Ta-O(IV)	87.4(23)		

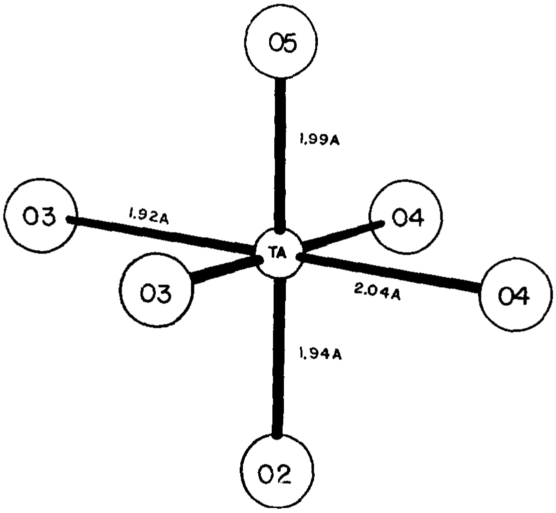

FIG. 2. Tantalum environment, oxidized phase.

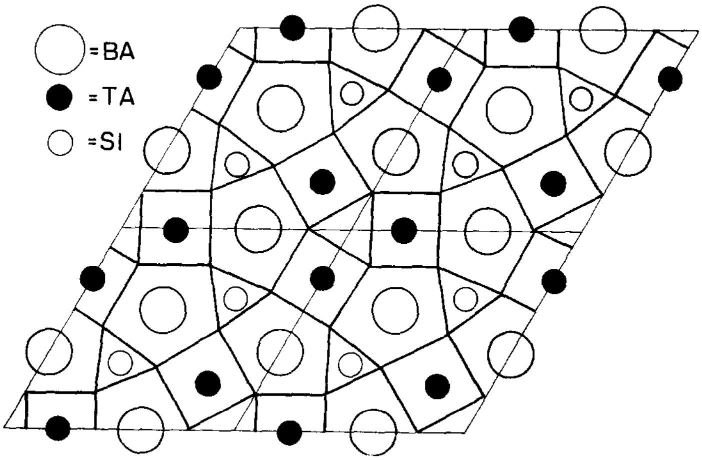

FIG. 3. Schematic projection down *c* axis.

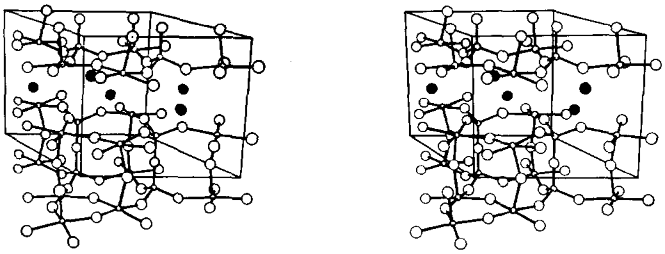

FIG. 4. Stereo view of unit cell contents, reduced phase.

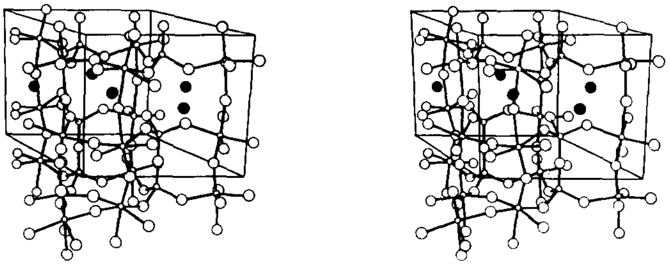

FIG. 5. Stereo view of unit cell contents, oxidized phase. Small open circles in tetrahedral environment are Si atoms; other small open circles are Ta atoms; large open circles are O atoms; large shaded circles are Ba atoms.

TABLE VIII

DISTANCES AND ANGLES IN $Ba_3Si_4Ta_6O_{26}$

		Distances	
Ba–O(III)	3.06(II) Å	Ta–Ta	3.71(1); 3.82(2);
Ba–O(IV)	2.84(4);		3.97(2)
	2.95(4)	O(I)–O(IV)	2.72(4)
Ba–O(V)	3.11(1);	O(II)–O(III)	2.72(9)
	3.42(10)	O(II)–O(IV)	2.88(5)
Ta–O(II)	1.94(2)	O(III)–O(III)	2.60(15)
Ta–O(III)	1.92(3)	O(III)–O(IV)	2.90(6)
Ta–O(IV)	2.04(3)	O(III)–O(V)	2.88(12)
Ta–O(V)	1.99(1)	O(III)–O(V)	2.88(12)
Ta–O(V)	1.99(1)	O(IV)–O(IV)	2.60(5);2.82(6)
Si–O(I)	1.66(6)	O(IV)–O(V)	2.68(7)
Si–O(IV)	1.61(4)	O(IV)–O(V)	2.68(7)

	Angles		
O(I)–Si–O(IV)	111.7(28)°	O(III)–Ta–O(III)	85.1(52)
O(IV)–Si–O(IV)	107.2(31)	O(III)–Ta–O(IV)	93.8(25)
O(II)–Ta–O(III)	89.7(42)	O(IV)–Ta–O(IV)	87.2(18)
O(II)–Ta–O(IV)	92.4(21)		

barium tantalum oxide, $B_{0.5}TaO_3$, with the tetragonal tungsten bronze structure, although in this latter compound there are four-membered and five-membered rings as well. Bond lengths and angles (*25*) are listed in Tables VII and VIII.

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References

1. F. GALASSO AND L. KATZ, *Nature* **188**, 1099 (1960).
2. C. T. PREWITT, *ACACA*, E. I. Dupont de Nemours and Co., Wilmington, Del., 1965.
3. W. R. BUSING, K. O. MARTIN, AND H. A. LEVY, ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee (1962) modified by W. C. Hamilton, Brookhaven National Laboratory, Upton, New York.
4. W. G. SLY AND D. P. SHOEMAKER, *MIFR1*, Massachusetts Institute of Technology, Cambridge, Mass., 1960.
5. L. DAVIS (née WATERS), unpublished work.
6. E. W. HUGHES, *J. Amer. Chem. Soc.* **63**, 1737 (1941).
7. "International Tables for X-ray Crystallography", Vol. III. Kynoch Press, Birmingham, 1962.
8. L. H. THOMAS and K. UMEDA, *J. Chem. Phys.* **26**, 239 (1957).
9. D. T. CROMER, *Acta Cryst.* **18**, 17 (1965).
10. F. GALASSO, L. KATZ, AND R. WARD, *J. Amer. Chem. Soc.* **81**, 5898 (1959).
11. F. GALASSO, Ph.D. Thesis, University of Connecticut, 1960.

12. H. Diehl and G. Frederick Smith, "Quantitative Analysis," p. 116, John Wiley and Sons, Inc., New York, 1952.

13. I. M. Kolthoff, P. J. Elving, and E. B. Sandell, "Treatise on Analytical Chemistry", Part II, Vol. 6, p. 1771, Interscience Publ. Inc., New York, 1962.

14. S. Anderson and A. Astrom, *Acta Chem. Scand.* **18**, 2233 (1964).

15. F. Liebau, *Acta Cryst.* **14**, 1103 (1962).

16. D. W. J. Cruickshank, *J. Chem. Soc.* 5486 (1961).

17. T. Zoltai and M. J. Buerger, *Z. Krist* **111**, 129 (1959).

18. J. Reffner, private communication.

19. Y. Takenchi and G. Donnay, *Acta Cryst.* **12**, 465 (1959).

20. D. W. J. Cruickshank, J. Lynton, and G. A. Barclay, *Acta Cryst.* **15**, 491 (1962).

21. A. M. Bystrom and H. T. Evans, *Acta Chem. Scand.* **13**, 377 (1959).

22. E. L. Muetterties and R. A. Schunn, *Quart. Rev.* **20**, 245 (1966).

23. C. K. Johnson, ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.

24. A. F. Wells, "Structural Inorganic Chemistry." Oxford University Press, New York/London, 1962.

25. W. R. Busing, K. O. Martin, and H. A. Levy, ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1964.