This study has been stimulated by a fruitful interchange of ideas with other members of this Unit. In particular we are indebted to Dr F. H. C. Crick, who we hope will recognize his influence throughout the work.

The tabulation of the function $\mathfrak{g}(x, y, \omega)$ was made possible by the use of the University of Cambridge Mathematical Laboratory's electronic computer EDSAC 2.

References

Blow, D. M. (1958). *Proc. Roy. Soc.* A, **247**, 302.
Blow, D. M. & Crick, F. H. C. (1959). *Acta Cryst.* **12**, 794.
Blow, D. M. & Rossmann, M. G. (1960). *Acta Cryst.* **14** (In press).
Dickerson, R. E., Kendrew, J. C. & Strandberg, B. E. (1961). *Conference on Computing Methods and the Phase problem.* (Glasgow, 1960, London: Pergamon Press.)
Kendrew, J. C., Dickerson, R. E., Strandberg, B. E., Hart, R. G., Davies, D. R., Phillips, D. C. & Shore, V. C. (1960). *Nature, Lond.* **185**, 422.
Perutz, M. F., Rossmann, M. G., Cullis, A. F., Muirhead, H., Will, G. & North, A. C. T. (1960). *Nature, Lond.* **185**, 416.
Sim, G. A. (1959). *Acta Cryst.* **12**, 813.
Sim, G. A. (1960). *Acta Cryst.* **13**, 511.
Watson, G. N. (1922). *The theory of the Bessel Functions*, p. 77. Cambridge: University Press.
Wilson, A. J. C. (1949). *Acta Cryst.* **2**, 318.

Acta Cryst. (1961). **14**, 647

Preparation and Structure of $Ba_5Ta_4O_{15}$ and Related Compounds*

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The preparation and characterization of a new ternary oxide of tantalum, $Ba_5Ta_4O_{15}$, and isomorphous compounds, $Sr_5Ta_4O_{15}$ and $Ba_5Nb_4O_{15}$, are described. The barium tantalum compound was found to belong to the trigonal system; the axes of the primitive hexagonal cell are $a = 5{\cdot}79$, $c = 11{\cdot}75$ Å. Single crystals of $Ba_5Ta_4O_{15}$ grown in a lead II oxide flux were used in determining the structure. Anion deficiencies have been produced in these compounds by preparing them with tetravalent niobium and tantalum.

Introduction

In a general survey of the barium–tantalum–oxygen system, the existence of several phases have been noted. At a ratio of barium to tantalum of one half, two different phases have been reported, one a hexagonal phase, $Ba_{0.44}TaO_{2.92}$ (Galasso, Katz & Ward, 1958), and the other a tetragonal phase, $Ba_{0.5}TaO_3$ (Galasso, Katz & Ward, 1959*a*) with the tetragonal bronze structure (Magnéli, 1949). When the Ba/Ta ratio was increased to three, the phase $Ba(Ba_{0.5}Ta_{0.5})O_{2.75}$ was obtained with an ordered cubic perovskite structure (Brixner, 1958; Galasso, Katz & Ward, 1959*b*). At an intermediate ratio, the compound $Ba_5Ta_4O_{15}$ has been identified. The preparation and structure of this compound and isomorphous phases is the subject of this paper.

Experimental

Preparation of $Ba_5Ta_4O_{15}$

The best preparation of $Ba_5Ta_4O_{15}$ resulted from mixing barium carbonate in 2% excess of the amount indicated in the reaction

$$5\ BaCO_3 + 2\ Ta_2O_5 \rightarrow Ba_5Ta_4O_{15} + 5\ CO_2$$

and heating in air at 1150 °C. for 24 hr. The white product obtained gave an X-ray powder pattern which was indexed with the aid of single crystal data on the basis of a hexagonal cell with $a = 5{\cdot}79$ Å and $c = 11{\cdot}75$ Å.

The density was found pycnometrically to be $7{\cdot}9$ g.cm.$^{-3}$, and using the above parameters the unit cell content weight was calculated to be 1622, as compared to 1650 for the formula $Ba_5Ta_4O_{15}$. Analysis gave 44·04% Ta, 42·70% Ba, as compared to the theoretical 43·85% Ta, 41·64% Ba for $Ba_5Ta_4O_{15}$.

Preparation of $Ba_5Ta_4^{IV}O_{13}$

The compound $Ba_5Ta_4^{IV}O_{13}$ was prepared in an evacuated sealed silica capsule using tantalum pentoxide and tantalum metal as a source of tantalum IV, and barium oxide as the source of barium. As is frequently the case with oxygen deficient compounds, the powder pattern of the reduced (blue) phase could be indexed using the same parameters as for the oxidized phase.

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Preparation of $Ba_5Nb_4O_{15}$ *and* $Ba_5Nb_4^{IV}O_{13}$

The analogous phases, $Ba_5Nb_4O_{15}$ and $Ba_5Nb_4O_{13}$, were prepared using niobium pentoxide as a source of niobium V and niobium dioxide as a source of niobium IV. The X-ray powder photographs were the same, and the lines matched the tantalum compound in spacing but not in intensity.

Preparation of $Sr_5Ta_4O_{15}$

The strontium–tantalum compound $Sr_5Ta_4O_{15}$ was never obtained pure. Attempts to prepare this compound resulted in two phases. The X-ray powder pattern showed evidence for $Sr(Sr_{\frac{1}{2}}Ta_{\frac{1}{2}})O_{2.75}$ and the rest of the lines could be indexed on the basis of a hexagonal cell with the parameters $a = 5{\cdot}67$ Å and $c = 11{\cdot}42$ Å. No evidence for an analogous strontium–niobium compound was found. The possible identity of this compound was reported previously (Galasso, Katz & Ward, 1958).

Structure determination

Single crystals were grown by heating $Ba_5Ta_4O_{15}$ with lead II oxide in a platinum crucible at 1200 °C., and cooling the mixture slowly. Some of the clear hexagonal plates that were obtained were ground to a powder. The X-ray diffraction pattern of this powder was identical with that of the original $Ba_5Ta_4O_{15}$. Precession photographs showed the crystal to be trigonal, Laue group $\bar{3}m$. First photographs of the $hk0$, $hk3$, and $h0l$ nets showed absences which indicated a rhombohedral lattice in which the hexagonal cell had $c = 3{\cdot}92$ Å; however longer exposures and a rotation photograph showed that the lattice type was not rhombohedral and the c axis had to be tripled (11·75 Å). Since no general absences were observed, the probable space group is one of $\begin{pmatrix}P3m1\\P31m\end{pmatrix}$, $\begin{pmatrix}P321\\P312\end{pmatrix}$ or $\begin{pmatrix}P\bar{3}m1\\P\bar{3}1m\end{pmatrix}$. Optical observations and a negative pyroelectric test indicated that the crystal could be centrosymmetric. Of the two centrosymmetric possibilities, the mirror plane orientation is that of $P\bar{3}m1$. This was the space group assumed.

The volume and dimensions of the unit cell strongly suggest a five layer closest packing of oxygen and barium ions. One may compare the cell dimensions with those of hexagonal barium titanate (Burbank & Evans, 1948) in which there is a six layer repetition in the c direction: a for $BaTiO_3$, 5·735 Å; a for $Ba_5Ta_4O_{15}$, 5·79 Å; c for $BaTiO_3$, 14·05 Å; c for $Ba_5Ta_4O_{15}$, 11·75 Å. Five layers estimated from the $BaTiO_3$ value for c would be 11·72 Å. Since there are five barium ions in the unit cell, it is logical to assume that the unit cell contains a sequence of five close-packed layers with each layer containing one barium and three oxygen ions, thus accounting for the five bariums and fifteen oxygens in the unit cell. There is no problem in deciding how these layers should follow one another, because, with the restriction that superposing layers cannot be adjacent to each other, there is only one sequence possible (see, e.g., Burbank & Evans, 1948). Designating the close-packed layers A, B, and C, the five layer repeat sequence might be written $ABCBC$, $ABABC$, $ABACB$; $ABCAB$, or $ABCAC$, but these all describe the same sequence. The different letter combinations merely represent the five possible ways in which the first layer might be chosen. The tantalum ions, as were the titanium ions in barium titanate, will be located in the octahedral holes between the layers. However, although there are five such holes, there are only four tantalum ions, so that between one pair of layers the tantalum ion is missing. The obvious choice is to omit a tantalum ion from the position which would force face sharing among the TaO_6 octahedra. The unusual feature of the Ti_2O_9 groups in hexagonal barium titanate, then, would have no counterpart in $Ba_5Ta_4O_{15}$. Fig. 1 illustrates the five layer repeat sequence. This figure shows the ions which lie in the (11·0) plane, and is essentially an extension of the same sequence illustrated in the Burbank & Evans paper. A choice of unit cell consistent with the positions of $P\bar{3}m1$ as given in the *International Tables for X-ray Crystallography*, Vol. I, is outlined in the figure. An examination of the space group positions shows that the five octahedral holes in the unit cell involve two 2-fold positions and one 1-fold position. It is clear that if one of these holes is to remain unoccupied in a regular way, it must correspond to the 1-fold position. This is the one we

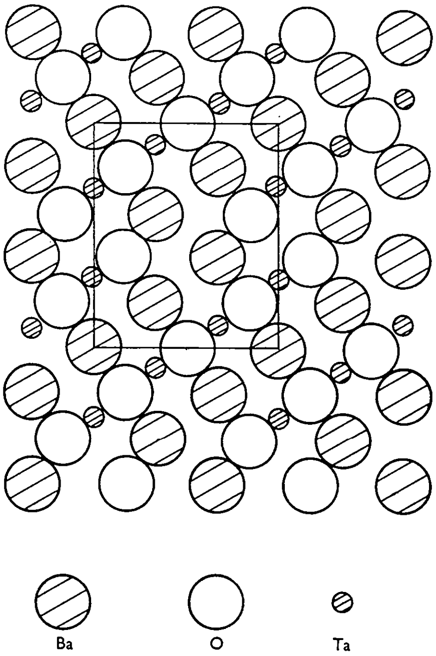

Fig. 1. The five layer repeat sequence in $Ba_5Ta_4O_{15}$. Ions shown lie in the (11·0) plane.

have already decided must be left empty in order to avoid face sharing of the TaO_6 octahedra. Approximate values for the three Ba z parameters, the two Ta z parameters, and the four O parameters can be obtained from the packing model. Our intention was to refine these parameters using $h0l$ data. Unfortunately even our longest exposure (a precession photograph which ran for 22 days) showed less than half of the $h0l$ reflections possible with a 30° precession angle and molybdenum radiation. The Fourier projection prepared with these data showed peaks corresponding to the expected atomic positions, but it also showed a number of lesser, unexplained peaks, and gave no indication of the oxygen positions. Because of the amount of time needed to acquire additional intensity data, it was decided not to attempt further refinement of the structure at this time. The atomic coordinates, with the accuracy we feel justified for the variable parameters implied, are given in Table 1.

The reliability factors are 0·10 for the six observed $hk0$ reflections, 0·06 for nine $hk3$ reflections, and 0·16 for 73 observed $h0l$ reflections. Without oxygens the reliability factor for the observed $h0l$ reflections was slightly higher, about 0·17.

Table 1. *Atomic coordinates*

1 Ba_I	in (a)	0, 0, 0		
2 Ba_{II}	in (d)	1/3, 2/3, z; 2/3, 1/3$\bar{z}$	$z=0{\cdot}79_3$	
2 Ba_{III}	in (d)		$z=0{\cdot}42_5$	
2 Ta_I	in (d)		$z=0{\cdot}31_3$	
2 Ta_{II}	in (c)	0, 0, z; 0, 0, $\bar{z}$	$z=0{\cdot}10_4$	
3 O_I	in (e)	1/2, 0, 0; 0, 1/2, 0; 1/2, 1/2, 0		
6 O_{II}	in (i)	$x, \bar{x}, z$; $x, 2x, z$; $2\bar{x}, \bar{x}, z$		x about 1/6
		$\bar{x}, x, z$; $\bar{x}, 2\bar{x}, \bar{z}$; $2x, x, \bar{z}$		z about 1/5
6 O_{III}	in (i)			x about 1/6
				z about 3/5

Table 2. *Observed and calculated structure factors*

$hk0$

hk	F_o	F_c
10	(31)	+19
20	(42)	−6
30	403	+385
40	(56)	+4
50	(62)	+13
60	240	+314
11	430	+442
21	(41)	+18
31	(46)	+16
41	367	+328
51	(54)	+13
22	397	+430
32	(49)	+14
33	345	+307

$hk3$

hk	F_o	F_c
20	460	+489
30	(57)	+28
40	354	+380
50	288	+280
11	(43)	+23
21	361	+397
31	359	+341
41	(67)	+24
51	294	+277
22	(57)	+26
32	294	+314
42	321	+306
33	(69)	+21
43	251	+260

$h0l$

hl	F_o	F_c
01	(18)	+41
02	24	−33
03	30	+30
04	(35)	−41
05	(40)	+63
06	(43)	+33
07	58	+66
08	129	−115
09	258	+239
0,10	250	+283
0,11	(59)	−36
0,12	(61)	+24
0,13	(63)	−24
10	(32)	+19
11	(32)	−54
12	101	−57
13	(37)	−5
14	48	+51
15	105	+95
16	317	+340
17	161	+187
18	(52)	−48
19	(55)	+29
1,10	(58)	−26
1,11	73	+97
1,12	61	−69
1,13	63	+70
20	(43)	−6
21	(44)	+19
22	99	−65
23	446	+485
24	153	+149
25	78	−61
26	63	+42
27	(53)	−48
28	(55)	−58
29	(58)	+34
2,10	60	+63
2,11	102	−90
2,12	176	+123
2,13	220	+266
30	297	+385
31	64	+33
32	53	−28
33	53	27
34	54	−36
35	68	−45
36	(56)	−27
37	58	+56
38	99	−100
39	207	+211
3,10	170	+206
3,11	(62)	−31
40	(58)	+4
41	(58)	−17
42	(58)	−9
43	(59)	−4
44	(59)	+33
45	95	−84
46	250	+290
47	164	+180
48	(61)	−50
49	(61)	+23
4,10	(60)	−29
4,11	(60)	−1
50	(60)	+13
51	(60)	−2
52	(60)	−28
53	243	+291
54	105	+85
55	(60)	−35
56	(60)	−24
57	(60)	−13
58	(59)	−28
59	(57)	−41
5,10	(53)	+58
5,11	77	−80
60	236	+314
61	(57)	+25
62	(57)	+84
63	(56)	+20
64	(56)	−29
65	(54)	+2
66	(51)	−20
67	(45)	+42
68	54	−76

$\bar{h}0l$

$\bar{h}l$	F_o	F_c
11	(32)	−3
12	48	−46
13	396	+428
14	115	+115
15	60	−46
16	(46)	+29
17	(49)	+47
18	73	−47
19	68	−54
1,10	91	+76
1,11	120	−100
1,12	185	+136
1,13	210	+241
21	(44)	0
22	(45)	+18
23	(45)	−28
24	57	+32
25	109	−106
26	322	+352
27	195	+219
28	55	−60
29	(58)	+27
2,10	(60)	−34
2,11	(61)	+1
2,12	(62)	−40
2,13	76	+60
31	(53)	+33
32	(53)	+28
33	(53)	+27
34	(53)	−38
35	96	−45
36	(56)	−27
37	58	+56
38	108	−100
39	239	+211
3,10	181	+207
3,11	(62)	−31
41	(58)	+9
42	(58)	−44
43	336	+368
44	140	+116
45	73	−49
46	(60)	+34
47	(60)	−40
48	(61)	−5
49	(61)	−27
4,10	(60)	56
4,11	97	−80
4,12	165	+110
4,13	194	+236
51	(60)	−38
52	74	−39
53	(60)	−2
54	(60)	+25
55	86	−67
56	227	+246
57	147	+139
58	(59)	−37
59	(57)	+22
5,10	(53)	−25

Parentheses indicate non-observed reflection. F_o should be in the vicinity of the value given or less.

Discussion

The structure of $Ba_5Ta_4O_{15}$, Fig. 2, can be described as a five layer repeat closest packing of oxygens with a barium replacing one oxygen in each layer in the unit cell. The tantalum ions are in octahedral coordination with oxygen, and the octahedra share corners, except for the third and fourth layers of oxygens, which are not shared. All of the cations are arranged in strings along the $0, 0, z$; $\frac{1}{3}, \frac{2}{3}, z$; and $\frac{2}{3}, \frac{1}{3}, z$ lines.

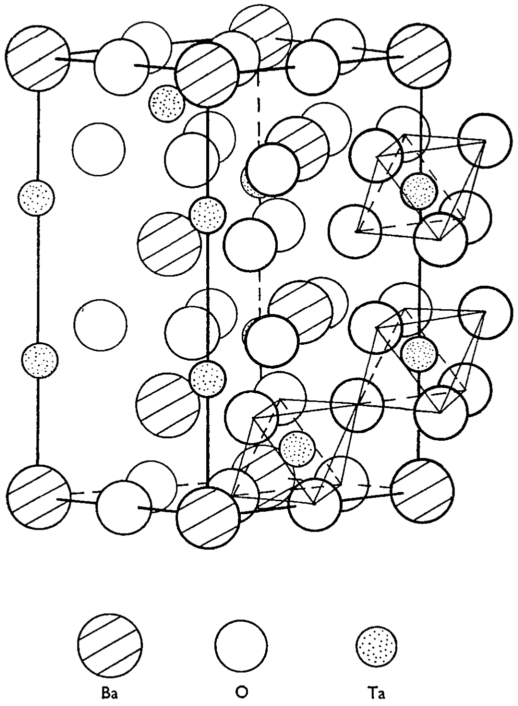

Fig. 2. Crystal structure of $Ba_5Ta_4O_{15}$.

The coordination scheme results in sums of electrostatic bond strengths from adjacent cations of $2\frac{1}{3}$ (O_{I}), $2\frac{1}{3}$ (O_{II}), and $1\frac{1}{2}$ (O_{III}). It is interesting to note that the barium compounds can be made oxygen deficient by introducing tantalum IV and niobium IV. It seems probable that the oxygens lost in the reduced phases are from the O_{III} group.

Barium to near neighbor oxygen distances range from 2·7 to 3·0 Å; tantalum to near neighbor oxygen distances vary from 2·0 to $2{\cdot}1_5$ Å. No significance can be attached to the variations because of the limited accuracy of the atomic parameters. However the reasonableness of the values obtained also testifies to the reasonableness of the structure.

The strontium–niobium analog could not be formed. Table 3 suggests that the strontium niobium oxides may be more generally non-typical.

Table 3. *$A_xB_yO_z$ compounds prepared*

	Sr	Ba
Nb	III, V	I, II, IV, V
Ta	I, II, IV, V	I, II, IV, V

A = Sr or Ba; B = Nb or Ta.

I: $x/y = 0{\cdot}5$, tetragonal phase.
II: $x/y = 0{\cdot}5$, hexagonal phase.
III: $x/y = 0{\cdot}7$ to $0{\cdot}9$, cubic perovskite phase (Ridgley & Ward, 1955).
IV: $x/y = 1{\cdot}25$.
V: $x/y = 3$.

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References

Brixner, L. H. (1958). *J. Amer. Chem. Soc.* **80**, 3214.
Burbank, R. D. & Evans, H. T. (1948). *Acta Cryst.* **1**, 330.
Galasso, F., Katz, L. & Ward, R. (1958). *J. Amer. Chem. Soc.* **80**, 1262.
Galasso, F., Katz, L. & Ward, R. (1959*a*). *J. Amer. Chem. Soc.* **81**, 5898.
Galasso, F., Katz, L. & Ward, R. (1959*b*). *J. Amer. Chem. Soc.* **81**, 820.
Magnéli, A. (1949). *Ark. Kemi*, **1**, 213.
Ridgley, D. & Ward, R. (1955). *J. Amer. Chem. Soc.* **77**, 6132.