Structural Systematics in the Binary System Ta₂O₅–WO₃. III. The Structure of 45Ta₂O₅.Al₂O₃.4WO₃

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The composition 45Ta₂O₅.Al₂O₃.4WO₃ has an orthogonal unit cell with dimensions $a = 6.182$, $b = 29.200$ and $c = 3.876$ Å. This unit cell contains one sixth of a formula unit and differs from $Ta_{30}W_2O_{81}$ in that it contains a whole number of atoms. The metal atoms are surrounded by either an octahedron or pentagonal bipyramid of oxygen atoms and distortions occur in the shapes of these polyhedra depending on their positions in the unit cell. Metal atoms lie in slightly puckered sheets parallel to (001) and the space group, selected after refinement in a number of plane groups and space groups, is *P*2. Atomic parameter interactions are shown to be minimized by the use of extensive three-dimensional data. However the interdependence of parameters is determined mainly by the model that is being refined, and the use of the maximum amount of data serves only to minimize rather than remove this intractability.

Introduction

The crystal structure of the compound $Ta_{30}W_2O_{81}$ is inexact in that the asymmetric unit which is refined using the X-ray data is a structural unit containing 8 metal (M) atoms and $20\frac{1}{4}$ oxygen (O) atoms. It represents an average structural unit and is a superposition of one quarter of an ideal cell *i.e.*, M_8O_{21} and three quarters of a real cell containing distortion planes *i.e.* M_8O_{20}. Certainly, a more favorable unit to examine from the standpoint of accurately determining the structural

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Fig. 1. Isothermal section of a portion of the ternary system Ta₂O₅–Al₂O₃WO₃ showing the sub-solidus phases existing in equilibrium at high temperatures. The 'single phase' region at the Ta₂O₅ corner has been contoured to show the compositions of equal multiplicities. The dashed line represents all compositions with cation:anion ratio of 2:5 and the large dot at the intersection of this line with the $m = 8$ contour is the composition of the crystal whose structure is described here.

features of a distortion plane would be M_8O_{20}, *i.e.* a unit cell containing 16 metal atoms and 40 oxygen atoms. Such a unit cell does not exist in the Ta₂O₅–WO₃ system but Fig. 1, which depicts a section of the phase diagram for the ternary system Ta₂O₅–Al₂O₃–WO₃, shows that the composition $Ta_{15}Al_{\frac{1}{3}}W_{\frac{1}{3}}O_{40}$ (or 45Ta₂O₅.Al₂O₃.4WO₃) should have an 8 UO₃-type subcell structure with contents $M_{16}O_{40}$.

Experimental

X-ray data were collected from a near-spherical crystal with average radius 0.018 mm.* The crystal data are:

$Ta_{15}Al_{\frac{1}{3}}W_{\frac{1}{3}}O_{40}$, $M = 3485$;
$a = 6.182 \pm 0.001$, $b = 29.200 \pm 0.001$, $c = 3.876 \pm 0.001$; Å
$V = 699$ Å³, $Z = 1$, $D_c = 8.28$ g.cm⁻³.

Unit-cell dimensions were obtained using a Philips powder diffractometer with Cu $K\alpha$ radiation and single-crystal data were collected using a General Electric single-crystal orienter.

Intensities were measured by the 2θ-scan method with Mo $K\alpha$ radiation. The rate of scanning was 1° min⁻¹, and the scan range (SR) was calculated using the equation $SR = 1.8 + 1.0 \tan \theta$. The backgrounds were measured for 60 seconds at $2\theta \pm \frac{1}{2}SR$. The intensities of three standard reflections measured periodically with the data were found to hold constant to within 5%. A standard deviation (σ) was calculated for each intensity and if the net number of counts was less than 2σ the reflection was considered as a 'less than' and its intensity was set equal to 2σ. In the 2θ range 0 to 60°, encompassing the copper sphere of reflection, a unique set of 1282 reflections was recorded, of which 524 were labelled as 'less thans'. Lorentz,
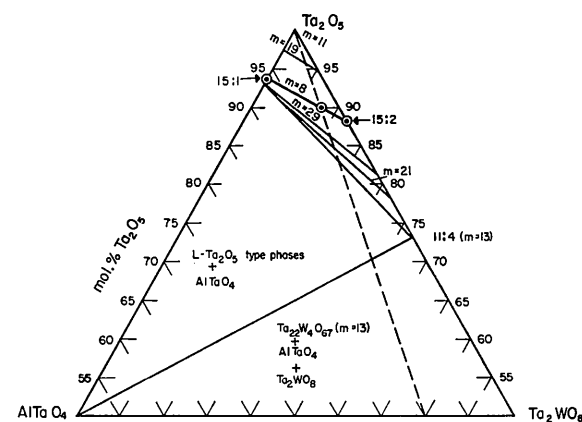
* The crystal was selected from a specimen quenched after heating for 112 hours at 1575 °C in a sealed Pt tube.

polarization and absorption corrections ($\mu R = 1\cdot 2$) were applied to these data.

The atomic scattering factors for O^{2-}, Ta^{5+} and Al^{3+} were taken from Suzuki (1960) and Cromer & Waber (1965). The real part of the anomalous dispersion corrections was applied to the scattering curve for tantalum (Dauben & Templeton, 1955). The metal ions Ta^{5+}, W^{6+} and Al^{3+} were assumed to be statistically distributed over all metal sites and a composite scattering curve $(15\cdot 67\ f_{Ta^{5+}} + 0\cdot 33\ f_{Al^{3+}})/16$ was used in structure factor calculations, assuming identical scattering curves for Ta^{5+} and W^{6+}.

Determination of the structure

A comparison of unit-cell dimensions, and powder and single-crystal X-ray diffraction data leaves no doubt that the compounds $Ta_{15}Al_{\frac{1}{3}}W_{\frac{1}{3}}O_{40}$ and $Ta_{15}WO_{40\frac{1}{3}}$ are isostructural so that the positional coordinates of corresponding metal atoms in each structure are similar. The plane group of a projection of the structure of $Ta_{15}Al_{\frac{1}{3}}W_{\frac{1}{3}}O_{40}$ onto the (001) plane can also be expected to be either pm or pg. Extensive intensity checks failed to detect any significant deviations from Laue symmetry $D2h$-mmm and therefore the space group can be either $P2mm$ or $Pb2_1m$ depending on the selection of either plane group pm or pg (see Table 1). Metal atoms were given appropriate x and y values from the structure refinements of $Ta_{15}WO_{40\frac{1}{3}}$, and these positional parameters as well as isotropic thermal parameters were refined by full-matrix least-squares methods using the F_o data for the compound $Ta_{15}Al_{\frac{1}{3}}W_{\frac{1}{3}}O_{40}$. Refinements were made in both space groups using the weighting scheme described in a previous paper. Least-squares refinement cycles, in the space group $Pbmm$ (see Table 1), of the x, y and isotropic thermal parameters of the metal atoms failed to reduce the conventional R_1 value below 0·34. Oxygen atoms were located from three-dimensional difference Fourier syntheses calculated after each refinement cycle and subsequently included for isotropic refinement in later least-squares cycles.

Table 2 shows there is still extensive interdependence of atomic parameters. The use of three-dimensional data did reduce the actual number of very large correlation coefficients compared with the two-dimensional refinement of $Ta_{30}W_2O_{81}$ (Stephenson & Roth, 1971b). Nevertheless the rate of convergence was still very slow: dampening coefficients of the order of 0·10 had to be used to minimize oscillation of parameter values, and standard deviations were disappointingly high (0·01 − 0·03 Å for metal atoms) in view of the relatively low R_1 values ($\sim 0\cdot 11$).

Strong interactions in pairs of positional parameters are to be expected for structures having a substructure (Geller, 1961), and considerable overlap of crystallographically non-equivalent interatomic vectors in the three-dimensional Patterson function is particularly indicative of potentially strong interactions. The space group $P2mm$ and $Pb2_1m$ limit interatomic vectors to (001) and (002) planes thereby enhancing the probability of vector overlap. It was therefore considered worth while to attempt a structure refinement in which z parameters were allowed to vary. The z atomic parameters differing appreciably from 0 or $\frac{1}{2}$ should cause differences to appear between zero and upperlevel equiinclination Weissenberg photographs and the Laue symmetry to change from $D2h$-mmm to $C2h$-$2/m$. Since these changes were not experimentally confirmed, it must be deduced that any such deviations are small.

The structural parameters of $Ta_{15}W_{\frac{1}{3}}Al_{\frac{1}{3}}O_{40}$ were therefore refined in the space groups Pm, $P2$, Pb and $P2_1$ using the F_o data from $\frac{1}{8}$ of the reciprocal lattice. In each case the metal atom positions were initially refined separately, the commencement model involving $M(1)$ fixed with $z = 0$, $M(3)$ displaced from the (001) plane by 0·1 Å with the z parameters of the remaining metal atoms equal to zero but allowed to vary in the least-squares refinement.

The space groups $P2$ and Pb gave essentially the same z-coordinate distribution for the metal atoms of the asymmetric unit and indicated that a small degree of sheet puckering occurs; the minimum displacement

Table 1. *Possible plane and space groups for the compound* $45Ta_2O_5$.Al_2O_3.$4WO_3$

The atomic parameters were refined in each symmetry group.

Laue symmetry	Plane group of (001) projection	Space group		Coordinates of equivalent positions
mmm (D_{2h})	pgm	$Pbm2$ (No. 28)*	$4d$	$x,y,z;\ \bar{x},\bar{y},z;\ x,\frac{1}{2}-y,z;\ \bar{x},\frac{1}{2}+y,z$
	pgm	$Pbmm$ (No. 51)*	$4i$	$x,y,0;\ \bar{x},\bar{y},0;\ x,\frac{1}{2}-y,0;\ \bar{x},\frac{1}{2}+y,0$
			$4j$	$x,y,\frac{1}{2};\ \bar{x},\bar{y},\frac{1}{2};\ x,\frac{1}{2}-y,0;\ \bar{x},\frac{1}{2}+y,0$
	pm	$P2mm$ (No. 25)*	$2e$	$x,y,0;\ x,\bar{y},0$
			$2f$	$x,y,\frac{1}{2};\ x,\bar{y},\frac{1}{2}$
	pg	$Pb2_1m$ (No. 26)*	$2a$	$x,y,0;\ \bar{x},\frac{1}{2}+y,0$
			$2b$	$x,y,\frac{1}{2};\ \bar{x},\frac{1}{2}+y,\frac{1}{2}$
$2/m$ (C_{2h})	pm	Pm (No. 6)	$2c$	$x,y,z;\ x,\bar{y},z$
	pm	$P2$ (No. 3)	$2e$	$x,y,z;\ x,\bar{y},\bar{z}$
	pg	Pb (No. 7)	$2a$	$x,y,z;\ \bar{x},\frac{1}{2}+y,z$
	pg	$P2_1$ (No. 4)	$2a$	$x,y,z;\ \bar{x},\frac{1}{2}+y,\bar{z}$

* Non-standard setting.

from (001) occurs for metal atoms with $y=0$ and $\frac{1}{2}$ and maximum displacement ($\sim 0\cdot15$ Å) occurs at $y=0\cdot25$ and $0\cdot75$. The space groups Pm and $P2_1$ gave completely random distributions of z parameters and no systematic puckering could be ascribed to the model defined by these space groups. They were therefore considered unlikely.

Correlation coefficients for x–x and y–y type parameter interactions for the space groups $P2$ and Pb,

where z atomic parameters are not restricted to 0 or $\frac{1}{2}$ values, are lower than the corresponding coefficients for the space groups $P2mm$ and $Pb2_1m$, where metal atoms are coplanar. However, these values remain relatively large, resulting in high standard deviations for atomic parameters and a very slow rate of convergence for the least-squares refinement cycles.

The data used in the above refinement cycles were limited to those encompassed by the copper sphere of

Table 2. *Correlation coefficients*, ϱ_{ij}, *for metal–metal positional parameter interactions*

Values calculated were for the space groups indicated in parts (a) to (e) of the Table. In parts (a) to (d) data encompassed by the copper sphere of reflection were used and in part (e) $hk0$ data, collected with Mo $K\alpha$ radiation out to $2\theta=100°$, were used. x_i–x_j type interactions are shown below the ϱ_{ii} diagonal while y_i–y_j type interactions are found above this diagonal.

The values omitted were not calculated.

(a) $P2mm$	1	2	3	4	5	6	7	8	9
1	1·0	—	—	—	—	—	—	—	—
2	—	1·0	—	—	—	—	—	—	—
3	—	0·60	1·0	−0·02	0·40	−0·01	−0·12	−0·16	−0·11
4	—	0·61	0·43	1·0	0·05	0·21	−0·05	0·00	0·10
5	—	0·73	0·81	0·45	1·0	−0·23	−0·29	0·18	−0·02
6	—	0·66	0·54	0·45	0·68	1·0	0·12	0·07	0·46
7	—	0·72	0·57	0·51	0·63	0·59	1·0	0·33	0·29
8	—	0·69	0·70	0·59	0·74	0·67	0·80	1·0	0·13
9	—	0·68	0·76	0·62	0·73	0·77	0·61	0·77	1·0

(b) $Pb2_1m$	1	2	3	4	5	6	7	8	9
1	1·0	—	—	—	—	—	—	—	—
2	—	1·0	—	—	—	—	—	—	—
3	0·52	—	1·0	0·51	0·87	0·44	0·50	0·24	0·51
4	0·33	—	0·34	1·0	0·48	0·46	0·41	0·24	0·61
5	0·18	—	0·56	0·19	1·0	0·48	0·31	0·29	0·58
6	−0·26	—	−0·27	0·10	0·16	1·0	0·38	0·46	0·84
7	0·34	—	0·60	0·32	0·02	−0·34	1·0	0·56	0·41
8	0·78	—	0·36	0·28	0·15	−0·22	0·28	1·0	0·34
9	−0·19	—	0·32	0·05	−0·09	0·64	−0·26	−0·22	1·0

(c) Pb	1	2	3	4	5	6	7	8	9
1	1·0	—	—	—	—	—	—	—	—
2	—	1·0	—	—	—	—	—	—	—
3	0·42	—	1·0	0·40	0·90	0·50	0·49	0·43	0·46
4	0·26	—	0·42	1·0	0·36	0·44	0·42	0·37	0·37
5	0·09	—	0·14	0·14	1·0	0·54	0·41	0·46	0·55
6	−0·24	—	0·07	0·43	0·43	1·0	0·22	0·31	0·85
7	0·39	—	0·75	0·40	−0·07	−0·05	1·0	0·75	0·21
8	0·76	—	−0·30	−0·11	0·05	−0·22	0·27	1·0	0·26
9	−0·38	—	0·14	0·07	−0·49	0·03	−0·10	−0·30	1·0

(d) $P2$	1	2	3	4	5	6	7	8	9
1	1·0	—	—	—	—	—	—	—	—
2	—	1·0	—	—	—	—	—	—	—
3	—	0·46	1·0	−0·17	0·16	0·13	−0·13	−0·26	0·04
4	—	0·43	0·55	1·0	−0·06	0·05	−0·03	0·08	−0·11
5	—	0·49	0·74	0·55	1·0	−0·16	−0·30	0·05	0·30
6	—	0·54	0·59	0·39	0·57	1·0	0·09	0·06	0·22
7	—	0·50	0·64	0·41	0·48	0·64	1·0	0·36	0·09
8	—	0·26	0·59	0·44	0·44	0·59	0·73	1·0	0·15
9	—	0·46	0·66	0·45	0·56	0·87	0·60	0·62	1·0

(e) $P2$		2	3	4	5	6	7	8	9
2		1·0	—	—	—	—	—	—	—
3		0·41	1·0	−0·07	0·39	0·01	0·05	−0·01	−0·07
4		0·54	0·42	1·0	−0·06	0·23	−0·06	−0·15	0·11
5		0·58	0·72	0·46	1·0	−0·30	−0·13	0·14	0·02
6		0·60	0·38	0·45	0·49	1·0	0·22	0·15	0·32
7		0·55	0·51	0·48	0·48	0·59	1·0	0·56	0·20
8		0·42	0·52	0·43	0·44	0·61	0·72	1·0	0·17
9		0·49	0·50	0·52	0·48	0·81	0·49	0·62	1·0

Table 3. *Positional and thermal parameters for the compound* 45Ta$_2$O$_5$.Al$_2$O$_3$.4WO$_3$
refined in the space group P2

Standard deviations are given in brackets and the form of the anisotropic thermal ellipsoid is
$$\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\right].$$

	x/a	y/b	z/c	$\beta_{11}\times10^4$ or B	$\beta_{22}\times10^5$	$\beta_{33}\times10^3$	$\beta_{12}\times10^4$	$\beta_{13}\times10^4$	$\beta_{23}\times10^4$
M(1)	0·0784 (17)	0·0000	0·0000	−87 (24)	114 (34)	21 (19)	0	0	−39 (28)
M(2)	0·9247 (24)	0·5000	0·0000	−63 (25)	−51 (16)	12 (20)	0	0	1 (20)
M(3)	0·9828 (26)	0·11533 (36)	0·0147 (47)	−21 (19)	−36 (11)	1 (10)	1 (3)	2 (39)	20 (11)
M(4)	0·9962 (34)	0·24710 (42)	0·0147 (77)	56 (18)	−37 (13)	47 (15)	−9 (4)	40 (48)	−1 (16)
M(5)	0·9858 (33)	0·37723 (41)	0·0139 (52)	32 (33)	−42 (12)	−1 (11)	3 (4)	9 (53)	6 (12)
M(6)	0·5141 (30)	0·06895 (58)	−0·0000 (59)	−54 (21)	59 (19)	29 (16)	−1 (5)	5 (45)	−3 (18)
M(7)	0·5616 (43)	0·18729 (50)	0·0183 (52)	40 (71)	−30 (12)	−7 (11)	7 (7)	−38 (73)	6 (14)
M(8)	0·4477 (27)	0·30757 (44)	0·0099 (45)	−11 (24)	−37 (12)	14 (13)	4 (3)	15 (38)	−4 (14)
M(9)	0·4601 (32)	0·43506 (46)	0·0100 (55)	34 (27)	−41 (12)	31 (17)	−5 (4)	23 (51)	−5 (16)
O(1)	0·420 (29)	0·0000	0·0000	0·32 (3·16)					
O(2)	0·194 (26)	0·0649 (79)	0·032 (60)	0·15 (2·42)					
O(3)	0·288 (34)	0·2434 (102)	0·013 (80)	2·16 (3·91)					
O(4)	0·081 (21)	0·3198 (58)	−0·022 (47)	0·36 (2·06)					
O(5)	0·272 (24)	0·1571 (72)	0·010 (62)	0·15 (2·42)					
O(6)	0·162 (23)	0·4592 (72)	−0·010 (61)	0·61 (2·59)					
O(7)	0·806 (22)	0·0460 (67)	0·0000	0·78 (2·47)					
O(8)	0·667 (20)	0·1247 (65)	0·013 (51)	−0·18 (2·31)					
O(9)	0·906 (20)	0·1939 (57)	−0·025 (46)	−0·02 (2·23)					
O(10)	0·676 (30)	0·2564 (94)	0·013 (78)	−0·03 (2·98)					
O(11)	0·704 (27)	0·3552 (71)	−0·004 (64)	1·52 (3·65)					
O(12)	0·797 (34)	0·4229 (88)	0·019 (83)	1·27 (3·53)					
O(13)	0·085 (26)	0·00000	0·500	0·20 (2·14)					
O(14)	0·981 (21)	0·1188 (62)	0·513 (54)	1·10 (2·67)					
O(15)	0·994 (23)	0·2480 (71)	0·513 (61)	0·07 (2·05)					
O(16)	0·004 (28)	0·3830 (76)	0·513 (58)	1·24 (2·84)					
O(17)	0·506 (19)	0·0710 (63)	0·500	0·91 (3·01)					
O(18)	0·550 (27)	0·1930 (69)	0·519 (68)	0·64 (2·67)					
O(19)	0·439 (31)	0·3084 (62)	0·510 (61)	1·20 (2·18)					
O(20)	0·483 (22)	0·4339 (74)	0·510 (71)	0·46 (2·41)					
O(21)	Absent								
O(22)	0·583 (24)	0·5000	0·000	0·31 (3·10)					
O(23)	0·916 (21)	0·5000	0·500	0·80 (2·73)					

reflection. The $hk0$ data were re-collected out to $2\theta=$ 100° with Mo $K\alpha$ radiation. The appropriate structural parameters in the plane groups pm and pg were then refined, allowing comparisons to be made between the correlation matrices for the various space (or plane) groups and data used.

Table 2 indicates that atomic parameter interactions can be minimized by using extensive three-dimensional data. However, the interdependence of parameters is determined mainly by the model that is being refined, and the use of the maximum amount of data serves only to minimize rather than remove the intractability associated with the structure refinement.

Table 4. *Bond distances* (Å) *and angles* (°) *for the coor-dination polyhedra*

Space group $P2$. Prime (′) indicates atoms related by x, $\bar{y}$, $\bar{z}$. Second number in parentheses denotes frequency of occurrence.

M(1) Pentagonal bipyramid

M(1) –O(1)	2·11 (18) (1)
–O(2)	2·03 (22) (2)
–O(7)	2·15 (16) (2)
–O(13)	1·94 (20) (2)
O(1)—O(2)	2·36 (23) (2)
O(2)—O(7)	2·46 (22) (2)
O(7)—O(7′)	2·69 (28) (1)
O(13)–O(1)	2·84 (18) (2)

Table 4 (*cont.*)

O(13)–O(2)	2·88 (23) (4)
–O(7)	2·92 (15) (4)
O(1)—O(2)—O(7)	113 (11) (2)
O(2)—O(7)—O(7′)	103 (8) (2)
O(2)—O(1)—O(2′)	107 (10) (1)

M(2) Pentagonal bipyramid

M(2) –O(6)	1·89 (17) (2)
–O(12)	2·38 (25) (2)
–O(22)	2·11 (15) (1)
–O(23)	1·94 (20) (2)
O(6)—O(12)	2·50 (27) (2)
O(12)–O(22)	2·61 (26) (2)
O(6)—O(6′)	2·38 (30) (1)
O(23)–O(6)	2·76 (22) (4)
–O(12)	3·01 (28) (4)
–O(22)	2·83 (14) (2)
O(6)—O(6′) –O(12)	115 (9) (2)
O(6)—O(12)–O(22)	95 (10) (2)
O(12)–O(22)–O(12′)	119 (9) (1)

M(3) Pentagonal bipyramid

M(3) –O(2)	1·97 (20) (1)
–O(5)	2·16 (17) (1)
–O(7)	2·30 (18) (1)
–O(8)	1·97 (13) (1)
–O(9)	2·35 (17) (1)
–O(14)	1·93 (21) (2)
O(2)—O(7)	2·46 (22) (1)

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Table 4 (cont.)

O(7)—O(8)	2·45 (26) (1)	
O(8)—O(9)	2·51 (23) (1)	
O(9)—O(5)	2·51 (21) (1)	
O(5)—O(2)	2·74 (31) (1)	
O(14)-O(2)	2·77 (29) (2)	
—O(5)	2·88 (27) (2)	
O(14)-O(7)	3·04 (24) (2)	
—O(8)	2·75 (24) (2)	
—O(9)	2·87 (26) (2)	
O(2)—O(7)—O(8)	97 (9)	
O(7)—O(8)—O(9)	123 (7)	
O(8)—O(9)—O(5)	101 (8)	
O(9)—O(5)—O(2)	105 (8)	
O(5)—O(2)—O(7)	113 (9)	

M(4) Octahedron

M(4) –O(3)	1·81 (21) (1)
–O(4)	2·19 (17) (1)
–O(9)	1·66 (16) (1)
–O(10)	2·00 (19) (1)
–O(15)	1·93 (24) (2)
O(3)—O(4)	2·58 (32) (1)
O(4)—O(10)	3·12 (26) (1)
O(10)-O(9)	2·32 (29) (1)
O(9)—O(3)	2·77 (27) (1)
O(15)-O(3)	2·66 (33) (2)
–O(4)	2·82 (28) (2)
–O(9)	2·45 (28) (2)
–O(10)	2·77 (32) (2)
O(3)—O(4)—O(10)	83 (8)
O(4)—O(10)-O(9)	88 (7)
O(10)-O(9)—O(3)	96 (10)
O(9)—O(3)—O(4)	91 (8)

M(5) Octahedron

M(5) –O(4)	1·78 (17) (1)
–O(11)	1·86 (17) (1)
–O(12)	1·77 (24) (1)
–O(6)	2·63 (20) (1)
–O(16)	1·95 (23) (2)
O(4)—O(6)	4·10 (27) (1)
O(6)—O(12)	2·50 (27) (1)
O(12)-O(11)	2·06 (33) (1)
O(11)-O(4)	2·55 (22) (1)
O(16)-O(4)	2·62 (28) (2)
–O(6)	3·05 (31) (2)
–O(11)	2·76 (29) (2)
–O(12)	2·58 (35) (2)
O(6)—O(4)—O(11)	64 (12)
O(4)—O(11)-O(12)	98 (10)
O(11)-O(12)-O(6)	131 (13)
O(12)-O(6)—O(4)	67 (13)

M(6) Octahedron

M(6) –O(1)	2·10 (05) (1)
–O(2)	1·99 (16) (1)
–O(7)	1·93 (14) (1)
–O(8)	1·88 (18) (1)
–O(17)	1·94 (08) (2)
O(1)—O(2)	2·36 (23) (1)
O(2)—O(8)	3·40 (23) (1)
O(8)—O(7)	2·45 (26) (1)
O(7)—O(1)	2·74 (22) (1)
O(17)-O(1)	2·89 (14) (2)
–O(2)	2·65 (22) (2)
–O(7)	2·78 (14) (2)
–O(8)	2·72 (22) (2)
O(1)—O(2)—O(8)	84 (6)
O(2)—O(8)—O(7)	80 (7)
O(8)—O(7)—O(1)	98 (6)
O(7)—O(1)—O(2)	97 (6)

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Table 4 (cont.)

M(7) Pentagonal bipyramid

M(7) –O(3)	2·36 (26) (1)
–O(5)	2·00 (16) (1)
–O(8)	1·94 (18) (1)
–O(9)	2·14 (13) (1)
–O(10)	2·14 (27) (1)
–O(18)	1·95 (26) (2)
O(3)—O(5)	2·52 (36) (1)
O(5)—O(8)	2·62 (21) (1)
O(8)—O(9)	2·51 (23) (1)
O(9)—O(10)	2·32 (29) (1)
O(10)-O(3)	2·43 (28) (1)
O(18)-O(3)	2·94 (36) (2)
–O(5)	2·82 (30) (2)
–O(8)	2·89 (30) (2)
–O(9)	3·05 (27) (2)
–O(10)	2·81 (37) (2)
O(3)—O(5)—O(8)	109 (9)
O(5)—O(8)—O(9)	105 (9)
O(8)—O(9)—O(10)	106 (8)
O(9)—O(10)-O(3)	119 (13)
O(10)-O(3)—O(5)	101 (12)

M(8) Octahedron

M(8) –O(3)	2·12 (28) (1)
–O(4)	2·30 (13) (1)
–O(10)	2·06 (24) (1)
–O(11)	2·11 (19) (1)
–O(19)	1·94 (24) (2)
O(3)—O(4)	2·58 (32) (1)
O(4)—O(11)	2·55 (22) (1)
O(11)-O(10)	2·89 (34) (1)
O(10)-O(4)	3·12 (27) (1)
O(19)-O(3)	2·86 (36) (2)
–O(4)	2·88 (26) (2)
–O(10)	2·86 (34) (2)
–O(11)	2·92 (30) (2)
O(4)—O(3)—O(10)	110 (13)
O(3)—O(10)-O(11)	102 (11)
O(10)-O(11)-O(4)	72 (7)
O(11)-O(4)—O(3)	75 (7)

M(9) Octahedron

M(9) –O(6)	1·97 (15) (1)
–O(11)	2·78 (20) (1)
-O(12)	2·11 (21) (1)
-O(22)	2·04 (06) (1)
–O(20)	1·94 (28) (2)
O(6)—O(22)	2·86 (21) (1)
O(22)-O(12)	2·61 (26) (1)
O(12)-O(11)	2·06 (33) (1)
O(11)-O(6)	4·52 (26) (1)
O(20)-O(6)	2·82 (29) (2)
–O(22)	2·83 (25) (2)
–O(12)	2·79 (35) (2)
–O(11)	3·33 (32) (2)
O(6)—O(22)-O(12)	96 (7)
O(22)-O(12)-O(11)	133 (11)
O(12)-O(11)-O(6)	64 (8)
O(11)-O(6)—O(22)	67 (4)

Description of the structure

The space group of the compound $Ta_{15}Al_4W_4O_{40}$ is most likely $P2$, based on the most satisfactory structure refinement, a plausible model for the puckering of the metal atom sheets and a resulting structure involving the association of distortion sheets into doublets. This latter point was discussed when describing the structure of $Ta_{30}W_2O_{81}$ and subsequent crystal structure

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Table 5. *Observed and calculated structure factors*

Unobserved data are marked with L.

work on other members of the Ta_2O_5–WO_3 system has confirmed this feature. The following description of the structure of $Ta_{15}Al_{\frac{1}{4}}W_{\frac{3}{4}}O_{40}$ is therefore based on the space group $P2$ and the atomic coordinates, listed in Table 3.

Tantalum, tungsten and aluminum atoms are statistically distributed in a close-packed hexagonal arrangement within sheets separated by 3·88 Å. The sheets are slightly puckered, the maximum displacement of a metal atom from the (001) plane being 0·08 Å. The oxygen atoms form coordination polyhedra about each metal atom in the form of either a distorted pentagonal bipyramid or octahedron and within the (001) planes these polyhedra share edges and corners. Extension of the structure along the [001] direction occurs by corner-sharing. Bond distances and angles for each polyhedron are listed in Table 4 together with e.s.d.'s. Observed and
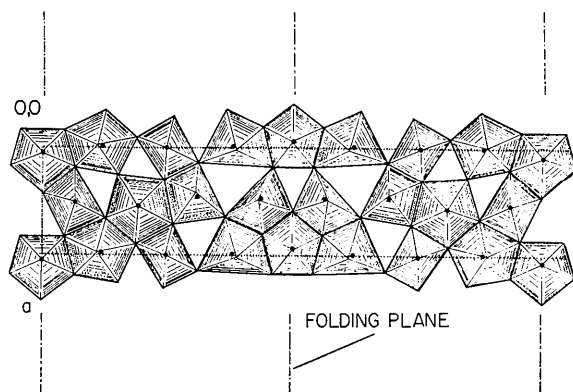
calculated structure factors are given in Table 5. A (001) projection of the structure is shown in Fig. 2.

The structure of $Ta_{15}Al_{\frac{1}{4}}W_{\frac{3}{4}}O_{40}$ differs from that of $Ta_{15}WO_{40\frac{1}{4}}$ only in that the partially occupied oxygen site O(21) of the latter structure is now completely empty in this present structure. There are thus two distortion planes per unit cell. These are related by a (020) mirror plane to form a doublet with an intraseparation distance of 7 Å. These doublets are repeated along the [010] direction at intervals of 29·2 Å ($= b$).

The most regular polyhedra are found midway between the (010) and (020) folding planes. The octahedron surrounding M(4) has metal–oxygen bond distances varying between 1·66 and 2·19 Å, oxygen–oxygen contact distances between 2·32 and 3·12 Å and a square planar arrangement of atoms within the (001) plane. The pentagonal bipyramid associated with M(7) is the most regular of this type of polyhedron, with metal–oxygen distances [2·07 (9) Å] averaging slightly greater than those in the M(4) octahedron [1·92 (6) Å]. Average oxygen–oxygen approach distances are the same for each type of polyhedron [2·72 (9) Å] and agree well with similar distances found in other studies (Stephenson & Roth, 1971a, b).

Fig. 2. A projection of the real structure of $Ta_{15}Al_{\frac{1}{4}}W_{\frac{3}{4}}O_{40}$ onto the (001) plane. Black dots represent metal atoms and shaded areas oxygen coordination polyhedra.

References

CROMER, D. T. & WABER, J. T. (1965). Acta Cryst. 18, 104.
DAUBEN, C. H. & TEMPLETON, D. H. (1955). Acta Cryst. 8, 841.
GELLER, S. (1961). Acta Cryst. 14, 1026.
STEPHENSON, N. C. & ROTH, R. S. (1971a). Acta Cryst. B27, 1010.
STEPHENSON, N. C. & ROTH, R. S. (1971b). Acta Cryst. B27, 1018.
SUZUKI, T. (1960). Acta Cryst. 13, 279.

Structural Systematics in the Binary System Ta2O5–WO3. IV. The Structure of Ta38WO98

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The structure of the composition $Ta_{38}WO_{98}$ is described in terms of a 19 UO_3-type subcell unit containing 38 metal atoms and 95·5 oxygen atoms. The orthogonal unit cell has dimensions $a = 6·188$, $b = 69·57$, $c = 3·880$ Å and the structure was solved in projection from the Patterson function utilizing photographically recorded data. Atomic positional and thermal parameters were refined by least-squares methods to a conventional R value of 0·118. The composition requires that the unit cell of the equilibrated compound be 429 UO_3-type subcells. As a result, the description of the structure in terms of an average 19 UO_3-type subcell unit introduces a splitting of certain atomic peaks. These effects are discussed.

Introduction

The composition $19Ta_2O_5.WO_3$ cannot be held in solid–liquid equilibrium like the previously described

compounds. Crystals are therefore difficult to prepare and thermal equilibration of the structure is very slow since both processes involve solid-state reactions. The crystal whose structure is described below was thermally equilibrated at 1605°C for 100 hours and can be considered to be close to the final equilibrium structure.

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