

The Crystal Structure of $\text{Nb}_{16}\text{W}_{18}\text{O}_{94}$, a Member of a $(\text{MeO})_x\text{MeO}_3$ Family of Compounds

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The structure of a compound with the ideal formula $\text{Nb}_{16}\text{W}_{18}\text{O}_{94}$ has been determined from single crystal X-ray data. The actual composition of the crystal used is believed to be $0.4\text{Nb}_{2.5} \cdot 0.6\text{WO}_3$. The space group is $P2_12_12$ with the unit-cell dimensions:

$$a = 12.251 \text{ \AA} \quad b = 36.621 \text{ \AA} \quad c = 3.94 \text{ \AA}$$

The structure is very similar to that of tetragonal potassium wolfram bronze, K_xWO_3 , and belongs to a family of the general formula $(\text{MeO})_x\text{MeO}_3$ where (MeO) has replaced the potassium in the pentagonal tunnels. Nonstoichiometry and results at other compositions in the $\text{Nb}_2\text{O}_5-\text{WO}_3$ and $\text{Ta}_2\text{O}_5-\text{WO}_3$ systems are discussed.

In a previous note¹ it was pointed out that a better understanding of the structural relationships between certain Nb—W and Ta—W oxides and the tetragonal potassium wolfram bronze (TKWB)² had been obtained. A more detailed account of these relationships, including the structure of $\text{Nb}_{16}\text{W}_{18}\text{O}_{94}$, will be given here.

Banks and Noval³ first pointed out the existence of a composition in the Ta—W—O system (30 % $\text{Ta}_2\text{O}_5 \cdot 70$ % WO_3) which gave an X-ray diffraction pattern very similar to TKWB. They were of the opinion that the phase actually existed over a range of compositions. The presence of this phase in the $\text{Ta}_2\text{O}_5-\text{WO}_3$ system has also been reported by Kovba and Trunov⁴ who referred to it as having the formula $\text{Ta}_2\text{O}_5 \cdot 3\text{WO}_3$.

The phase $\text{Nb}_2\text{O}_5 \cdot 3\text{WO}_3$ was first reported by Goldschmidt.⁵ Kovba and Trunov⁴ confirmed this, and Mohanty and Fiegel^{6,7} demonstrated that the phase was structurally similar to TKWB. It was the opinion of Goldschmidt and of Mohanty and Fiegel that this phase also exists over a range of compositions.

A study of the $\text{Nb}_2\text{O}_5-\text{WO}_3$ and $\text{Ta}_2\text{O}_5-\text{WO}_3$ systems was undertaken to elucidate the structural principles involved. Since there are no alkali (or similar) cations present and since the oxygen-to-metal ratio is considerably

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less than three, it was not apparent how these phases could be structurally related to TKWB. It was of further interest to determine if the phases were truly nonstoichiometric.

EXPERIMENTAL

Metal powders were used as starting materials. Niobium and tantalum were "Matthey Specpure" and wolfram was 99.9 %. Two methods of preparation were used. In the first, intimate mixtures of the metals in correct proportions were oxidized in air at 500°C in alumina crucibles. Complete oxidation was confirmed by weight gain and sample appearance. The resulting mixture of oxides was pelleted and then sealed in a platinum tube with air (~1 atm.) present. (Attempts to use evacuated tubes led to reduced products). The sealed platinum tubes were heated at temperatures from 1200° to 1400°C for one to three days. In general, the platinum tubes were heated in about one atmosphere of air, but in a few runs an external pressure of about 30 atm. of argon was used. The second preparative method was identical to the first except that the pure metals were oxidized and then intimately mixed in the correct proportions. No difference in the results for these two methods was detected.

The $\text{NbO}_{2.5}-\text{WO}_3$ and $\text{TaO}_{2.5}-\text{WO}_3$ systems were studied from $0.2\text{NbO}_{2.5}(\text{TaO}_{2.5}) \cdot 0.8\text{WO}_3$ up to $0.5\text{NbO}_{2.5}(\text{TaO}_{2.5}) \cdot 0.5\text{WO}_3$, since this is roughly the region of occurrence for phases structurally related to TKWB. Products were pale yellow to white, and needles were generally present. In a few cases the products were grey or black due to reduction of the sample. Such products were not considered to be true members of the $\text{Ta}_2\text{O}_5-\text{WO}_3$ or $\text{Nb}_2\text{O}_5-\text{WO}_3$ systems. X-Ray powder patterns were obtained for all products using a Guinier camera with strictly monochromatic $\text{CuK}\alpha_1$ radiation and potassium chloride ($a = 6.2919 \text{ \AA}$ at 20°) as an internal standard. True single crystals were rare at any composition. Needles between 0.3 and 0.4Nb or Ta were in fact always found to be polycrystalline, while needles between 0.4 and 0.5Nb or Ta were generally incoherently twinned.

The crystal used for single crystal analysis was picked from a sample of the composition 0.4Nb which had been heated at 1400°C for one day. The crystal was a parallelepiped with a length of 0.078 mm and sides of 0.015 and 0.021 mm. Weissenberg photographs were taken around the needle axis (c axis) using $\text{CuK}\alpha$ radiation. All the layer lines thus obtainable were registered using multiple film techniques. Precession photographs were taken for $0kl$ and $h0l$ data using $\text{MoK}\alpha$ radiation. The relative intensities of the reflections were visually estimated by comparison with an intensity scale prepared by registering accurately defined exposures with a suitable reflection from the crystal. The crystal was twinned but most of the reflections were resolved. The intensity ratio for equivalent reflections from the two individuals of the twin ranged from five to ten. The data were corrected for absorption using a program by Werner.⁸ Due to the twinning of the crystal these corrections were not very accurate; however, the shape of the crystals provides an absorption correction which is nearly constant for the reflections used.

The W^{3+} and Nb^{3+} scattering curves used were taken from Thomas and Umeda.⁹ The O^- scattering curve was taken from Hartree.¹⁰ Corrections for dispersion were made. Most of the calculations involved in the crystal structure determination were facilitated by the use of the electronic computers BESK and FACIT.

DERIVATION OF THE STRUCTURE

The single crystal photographs showed orthorhombic symmetry. The cell constants are given in Table 1. The only systematic absences were h odd for $h00$ reflections and k odd for $0k0$ reflections; thus, the space group was uniquely determined as $P2_12_12$. Since upper level photographs were very similar to the zero level, it is likely that all atoms lie very close to the (001) and (002) planes. However, the increasing differences between the various layer lines most likely indicates a puckering of the network. In view of this and the size

Table 1. Cell dimensions with reaction temperatures.*

	a , Å	b , Å	c , Å	T°C
0.20Ta	11.97		3.84	1400
0.30Ta	12.217		3.875	1200—1400
0.40Ta	12.223		3.880	1200 (or 1400 ² with ~60 atm. O ₂)
0.40Ta	12.266	36.274	3.886	1370
0.50Ta	12.257	36.298	3.886	1200—1400
0.35Nb	12.163		3.920	1200—1400
0.40Nb	12.172		3.928	1200 (or 1400 ² with ~60 atm. O ₂)
0.40Nb	12.251	36.621	3.943	1370
0.50Nb	12.248	36.610	3.950	1200—1400

* Oxygen pressure was about one atmosphere except where otherwise indicated.

of the cell, the structure was solved in projection using $hk0$ data only. The close agreement of the intensity data with those given by crystals in the TaO_{2.5}—WO₃ system indicated that there was no appreciable ordering among the niobium and wolfram atoms. Therefore, Nb and W were assumed to be randomly distributed at the metal sites. It was further obvious from the data that this structure could be viewed as a superstructure of TKWB.

The structure of TKWB (Fig. 1b) can be regarded as a complex network of WO₃ octahedra sharing corners. The resulting pentagonal tunnels and perovskite-like cages are partially filled with K atoms. Although the potassium content may vary, the ratio of oxygen to wolfram in the network remains at three. In the Nb₂O₅—WO₃ and Ta₂O₅—WO₃ systems the ratio of oxygen-to-metal is less than three. The high density of the 0.4Nb composition, 5.95, indicated that, rather than oxygen deficiency, the tunnels were being filled in some manner.

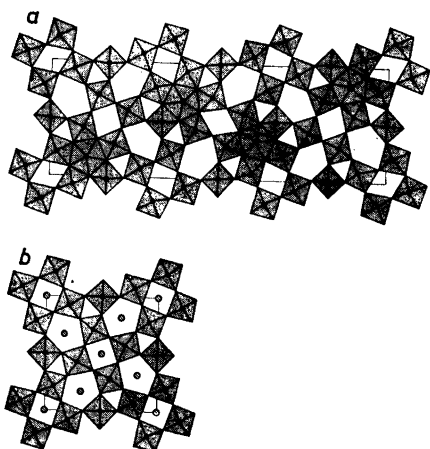


Fig. 1. The crystal structure of (a) Nb₁₆W₁₈O₉₄ and (b) tetragonal potassium wolfram bronze according to Magnéli.²

Table 2. Observed and calculated F -values. $l = 0$.

h	k	F_{obs}	F_{calc}	h	k	F_{obs}	F_{calc}
0	4	181	158	2	19	180	166
0	6	121	142	2	20	174	147
0	8	114	98	2	22	291	261
0	10	362	397	2	23	122	103
0	12	354	299	2	24	402	366
0	14	133	133	2	25	143	147
0	16	185	194	2	27	153	166
0	20	177	169	2	28	204	192
0	24	548	505	2	30	332	292
0	26	107	90	2	33	477	450
0	30	462	507	2	34	332	310
0	32	298	291	2	35	139	131
0	36	128	116	2	36	372	356
0	40	152	154	2	39	300	308
0	42	389	447	2	40	322	328
0	44	147	146	2	43	221	241
0	46	166	197	3	1	167	170
1	2	130	132	3	2	80	79
1	4	84	108	3	3	605	684
1	6	239	238	3	4	140	161
1	8	102	111	3	5	186	205
1	9	596	701*	3	6	631	721*
1	10	66	75	3	7	89	94
1	11	146	137	3	9	496	553
1	12	669	800*	3	12	114	82
1	13	129	123	3	14	118	90
1	17	184	189	3	15	303	274
1	18	95	101	3	18	561	708*
1	19	131	110	3	19	353	348
1	20	198	217	3	21	104	104
1	21	639	845*	3	23	294	286
1	22	258	224	3	24	532	524
1	24	238	206	3	25	125	97
1	25	134	127	3	28	149	151
1	29	123	138	3	29	166	155
1	30	291	284	3	33	151	151
1	31	364	364	3	34	194	197
1	36	221	214	3	37	154	154
1	39	146	149	3	38	174	169
1	40	123	148	3	39	211	237
1	42	97	106	3	41	96	100
1	43	227	229	3	42	103	88
1	44	143	152	3	43	179	184
1	45	219	259	3	45	120	134
1	46	71	85	4	0	352	366
2	0	145	132	4	1	183	163
2	1	95	109	4	3	663	826*
2	3	248	262	4	4	70	67
2	4	82	89	4	5	85	86
2	6	261	253	4	6	527	571
2	7	181	175	4	7	89	101
2	8	180	220	4	8	95	86
2	9	575	634	4	9	107	103
2	11	167	192	4	10	60	62
2	12	464	543*	4	11	112	98
2	18	549	683*	4	12	111	117

<i>h</i>	<i>k</i>	F_{obs}	F_{calc}	<i>h</i>	<i>k</i>	F_{obs}	F_{calc}
4	13	247	256	6	11	134	139
4	15	250	264	6	13	116	117
4	16	169	178	6	14	210	219
4	19	130	137	6	15	348	329
4	20	80	83	6	16	154	167
4	21	149	141	6	17	139	148
4	22	164	174	6	18	306	293
4	24	140	147	6	24	330	338
4	25	120	127	6	27	129	129
4	26	196	186	6	28	264	277
4	27	667	673	6	30	234	238
4	28	107	81	6	32	172	150
4	29	128	131	6	33	300	303
4	31	94	101	6	34	141	151
4	36	227	215	6	35	126	137
4	37	133	118	6	36	477	462
4	38	104	99	6	37	116	118
4	39	204	227	6	39	154	140
4	40	194	175	6	41	103	119
4	41	159	144	6	42	149	162
4	42	103	111	7	3	693	915*
4	43	96	90	7	4	177	182
5	2	176	187	7	7	102	111
5	3	73	60	7	8	184	196
5	6	69	54	7	9	125	134
5	7	63	65	7	10	234	256
5	9	274	267	7	12	109	104
5	11	113	117	7	13	206	211
5	12	301	300	7	15	439	360
5	15	781	1026*	7	21	460	452
5	16	211	213	7	22	214	192
5	17	177	173	7	23	118	107
5	18	373	349	7	24	280	254
5	20	120	138	7	25	109	117
5	21	374	337	7	27	138	148
5	22	154	152	7	28	138	128
5	24	172	181	7	29	108	88
5	25	230	223	7	33	269	242
5	26	116	111	7	35	204	197
5	27	392	375	7	36	148	120
5	30	326	309	7	37	106	116
5	31	295	263	7	39	178	171
5	34	196	194	8	0	489	493
5	36	155	138	8	3	202	211
5	37	322	318	8	4	176	168
5	39	249	263	8	6	477	431
5	40	103	97	8	7	189	176
5	42	133	132	8	8	104	103
5	43	79	90	8	9	562	536
5	45	36	27	8	11	187	169
6	1	186	176	8	12	126	139
6	3	75	77	8	15	200	204
6	4	117	135	8	16	123	116
6	5	59	55	8	18	316	296
6	7	131	112	8	19	204	192
6	8	128	138	8	21	335	317
6	9	621	721*	8	23	120	135
6	10	127	104	8	24	521	475

STRUCTURE OF Nb₁₆W₁₈O₉₄

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<i>h</i>	<i>k</i>	<i>F</i> _{obs}	<i>F</i> _{calc}	<i>h</i>	<i>k</i>	<i>F</i> _{obs}	<i>F</i> _{calc}
8	25	240	237	11	21	233	210
8	27	166	151	11	22	124	117
8	28	116	126	11	24	490	464
8	29	123	118	11	28	208	225
8	30	152	166	11	30	337	324
8	33	444	430	11	31	83	103
8	34	218	225	11	33	76	86
8	36	167	152	12	0	174	177
8	40	99	116	12	3	261	236
9	2	99	89	12	5	136	138
9	6	110	103	12	6	363	349
9	8	121	122	12	7	214	192
9	10	154	149	12	12	271	270
9	12	623	662	12	15	156	137
9	15	480	448	12	18	557	538
9	18	162	157	12	19	187	172
9	19	120	108	12	21	195	160
9	20	84	114	12	24	113	110
9	21	163	152	12	25	118	115
9	23	161	143	12	26	189	176
9	24	193	179	12	28	203	192
9	25	248	227	13	3	149	139
9	27	392	369	13	4	215	193
9	30	195	177	13	5	133	129
9	32	161	158	13	6	377	341
9	33	123	119	13	9	336	323
9	39	134	162	13	10	192	166
10	0	477	503	13	12	305	301
10	1	196	207	13	14	207	197
10	3	422	382	13	15	251	245
10	4	143	159	13	18	104	119
10	6	388	344	13	21	290	285
10	15	368	330	14	0	496	630*
10	16	146	127	14	5	143	137
10	17	138	129	14	7	230	245
10	18	195	188	14	9	63	80
10	19	175	182	14	10	125	125
10	20	118	103	14	11	123	116
10	22	142	134	14	12	139	139
10	24	145	125	14	13	67	76
10	25	110	100	14	14	98	93
10	27	263	269	14	15	105	92
10	31	91	100	14	16	42	51
10	32	126	123	14	17	92	96
10	33	342	327	14	18	130	152
11	2	235	219	14	19	85	99
11	3	184	193	14	21	114	131
11	5	110	100	15	1	105	112
11	6	521	515	15	2	96	106
11	9	202	208	15	3	200	226
11	11	97	98	15	4	89	110
11	12	84	96	15	5	102	103
11	13	223	197	15	9	192	232
11	16	288	269	15	10	68	78
11	18	379	343				

The metals present seemed too small to occupy the K positions. (The coordination of K is 15 in the pentagonal tunnels and 12 in the perovskite-like cages). However, by placing oxygens in K positions, more suitable sites for the metal atoms could be provided. Placing oxygen in the perovskite cages produces octahedra, but these are electrostatically unfavorable since they would share edges with four others. Placing oxygen in the pentagonal tunnels produces pentagonal bipyramids. These also share edges, but are more favorable because the metal-to-metal distances are greater.

The unit cell contains 12 pentagonal tunnels which are divided into 3 four-fold sites by symmetry. From the composition it was thought that only one of these sites was being used. (At 0.47Nb one fourfold site would be exactly filled). The site thought most probable is shown in Fig. 1a. Refinement of this model by the least squares and Fourier methods proved it to be correct.

As previously stated the Nb and W atoms were assumed to be statistically distributed at the metal sites. A difference map, after refinement of the parameters to an R value of 8.0 %, indicated that the distribution was not strictly statistical. Refinement of the Nb to W ratio at each site led to an R -factor of 6.9 %. A difference map then showed mainly satellite peaks of the metal atoms. The largest of these was less than 25 % of an oxygen. These peaks were thought to arise from at least three sources: disorder, anisotropic temperature factors for the metal atoms, and super-position errors due to the assumption that an oxygen in projection with a metal atom has the same x and y coordinates. Cruickshank's weighting scheme¹¹ was used in the final least squares refinement.

The observed and calculated structure factors are given in Table 2. The observed structure factors with asterisks were not used in the final least squares refinement. The R -factor including these reflections is 8.0 %. The final parameters are given in Table 3. The standard deviations for the metal positions amount to about 0.004 Å while those for oxygens 1–15 amount to about 0.05 Å. Oxygens 16–23 were assumed to have the same x and y coordinates as metal atoms 1–8. The standard deviations of a , the atom fraction of W on a site, are about 0.05. Correlations of about 0.60 were found between the temperature factor at a metal site and the atom fraction of W at that site. It should be noted that it was assumed that the Me_1 site was completely filled with a mixture of Nb and W. (Also 0.6 moles of O_2 per unit cell was left unaccounted for). However, if this pentagonal tunnel is not completely filled, as discussed in the next section, the value of a for Me_1 given in Table 3 would be low.

Some interatomic distances and angles are given in Table 4. The standard deviations average at 0.05 Å for the metal-oxygen distances and 0.07 Å for the oxygen-oxygen distances. The standard deviations for the angles average at 0.2°. It should be noted that the filled tunnel is much more regular and *smaller* than the empty tunnels.

NONSTOICHIOMETRY AND RESULTS AT OTHER COMPOSITIONS

Crystals examined from the compositions 0.4Ta (1400°C and ~ 1 atm. O_2), 0.5Nb and 0.5Ta showed the same superstructure as that of 0.4Nb (1400°C

Table 3. Final atomic parameters. Space group *P*2₁2₁2.

Atom	Position	<i>x</i>	$\sigma(x)$	<i>y</i>	$\sigma(y)$	<i>z</i>	β	$\sigma(\beta)$	<i>u</i>
<i>Me</i> ₁	4(<i>c</i>)	0.3321	0.0004	0.3898	0.0001	~1/2	0.37	0.11	0.16
<i>Me</i> ₂	»	0.0744	0.0003	0.0700	0.0001	~1/2	0.46	0.09	0.68
<i>Me</i> ₃	»	0.0713	0.0003	0.4028	0.0001	~1/2	0.01	0.09	0.65
<i>Me</i> ₄	»	0.4205	0.0004	0.2324	0.0001	~1/2	0.22	0.10	0.59
<i>Me</i> ₅	»	0.2935	0.0004	0.4785	0.0001	~1/2	0.22	0.08	0.60
<i>Me</i> ₆	»	0.2097	0.0003	0.3070	0.0001	~1/2	0.14	0.09	0.53
<i>Me</i> ₇	»	0.2943	0.0004	0.1386	0.0001	~1/2	0.37	0.09	0.54
<i>Me</i> ₈	»	0.0153	0.0003	0.1731	0.0001	~1/2	0.06	0.07	1.00
<i>Me</i> ₉	2(<i>b</i>)	1/2		0		~1/2	0.48	0.12	0.75
O ₁	4(<i>c</i>)	0.342	0.005	0.001	0.002	~1/2			
O ₂	»	0.120	0.005	0.023	0.002	~1/2			
O ₃	»	0.206	0.005	0.099	0.002	~1/2			
O ₄	»	0.442	0.005	0.121	0.002	~1/2			
O ₅	»	0.006	0.005	0.449	0.002	~1/2			
O ₆	»	0.165	0.005	0.165	0.002	~1/2			
O ₇	»	0.004	0.005	0.222	0.002	~1/2			
O ₈	»	0.070	0.005	0.291	0.002	~1/2			
O ₉	»	0.290	0.005	0.262	0.002	~1/2			
O ₁₀	»	0.350	0.005	0.189	0.002	~1/2			
O ₁₁	»	0.355	0.005	0.335	0.002	~1/2			
O ₁₂	»	0.176	0.005	0.362	0.002	~1/2			
O ₁₃	»	0.217	0.005	0.072	0.002	~1/2			
O ₁₄	»	0.412	0.005	0.442	0.002	~1/2			
O ₁₅	»	0.497	0.005	0.381	0.002	~1/2			
O ₁₆	»	0.332		0.390		~0			
O ₁₇	»	0.074		0.070		~0			
O ₁₈	»	0.071		0.403		~0			
O ₁₉	»	0.420		0.232		~0			
O ₂₀	»	0.294		0.478		~0			
O ₂₁	»	0.210		0.307		~0			
O ₂₂	»	0.294		0.139		~0			
O ₂₃	»	0.015		0.173		~0			
O ₂₄	2(<i>b</i>)	1/2		0		~0			

and ~1 atm. O₂). All crystals exhibited a strong tendency to twin, but the tendency was definitely greater in the Ta system. The individuals of the twin had their *c* axes in common and were joined in such a way as to create the fourfold axis of the derivative structure (TKWB). The unit cell thus had the superficial appearance of being tetragonal with *a* = 36 Å.

Compositions somewhat richer in W gave powder diffraction patterns also very similar to TKWB but with no superstructure as indicated in Table 1. It should be pointed out that the compositions 0.4Nb and 0.4Ta can exist with or without the superstructure depending on the conditions. The upper limit of WO₃ in these phases was about 0.65W in the niobium system but at least 0.8W in the tantalum system. The diffraction lines for 0.2Ta were, however, very broad.

The formula for all these TKWB-like phases could be written as W_{30-3x}Nb_{4x}O_{90+x} (or W_{30-3x}Ta_{4x}O_{90+x}) assuming that the metal to oxygen ratio in the tunnels is always one. When *x* is four (or very close to four) an ordering of the filled tunnels occurs. For values of *x* less than four the

Therefore, it is suggested that when the compositions 0.4Nb or 0.4Ta were heated to 1400°C under low oxygen pressure (~ 1 atm.) some oxygen left the sample, and the formula $Me_{34}O_{94}$ was obtained. The color of the products indicated, however, that the W was fully oxidized. The necessary oxygen may have entered some of the empty tunnels. The accuracy of the data for the crystal of composition 0.4Nb is not sufficient to prove this suggestion. However, an observation which further indicates this mechanism is that a superstructure was not found at 0.4Nb or 0.4Ta at 1400°C under higher oxygen pressure (~ 60 atm.) or in any case at 1300°C.

The contents of the unit cell at 0.4Nb according to this latter model would be $Me_{34}O_{95.2}$ leading to a density of 6.14. If instead some "filled tunnels" were vacant, *i.e.*, $Me_{33.3}O_{93.3}$, a density of 6.01 would be obtained. Unfortunately, the experimentally determined density of 5.95 is not sufficiently accurate to distinguish between these two models.

DISCUSSION

There are actually a large number of compounds which have structures that can be viewed as two-dimensional networks of corner-sharing octahedra. In the third dimension these networks are stacked one directly upon the other and fused again by corner-sharing octahedra. These networks form 3, 4, 5, or 6 membered rings which become tunnels in three dimensions.¹⁴⁻¹⁷ The tunnels may be empty as in ReO_3 , $MoW_{11}O_{36}$, and $MoW_{14}O_{45}$.¹⁸ They may also be (partially) filled with alkali or similar cations as in the various wolfram bronzes of the type A_xWO_3 .¹⁶

The pentagonal tunnels may also be filled with metal and oxygen forming a string of pentagonal bipyramids which share apices. This is the case for $Nb_{16}W_{18}O_{94}$ and $Ta_{16}W_{18}O_{94}$ and suggests a family of structures with the general formula $(MeO)_xMeO_3$. A previously known structure which would fall into this family is $Mo_{10}O_{28}$ or $(MoO)Mo_9O_{27}$.¹⁹ The structures of $W_{18}O_{49}$ ²⁰ and $Mo_{17}O_{47}$ ²¹ are very closely related to those of this family, but they involve some edge-sharing octahedra as well.

The next step would be a family of the type $A_x(MeO)_yMeO_3$. Recent structure determinations for $NaNb_6O_{15}F$ ²² and $LiNb_6O_{15}F$ ²³ performed at this Institute have established that indeed such a family does exist. Furthermore, in many other systems: $BaO-Nb_2O_5$,²⁴ $PbO-Nb_2O_5$,²⁵ $Na_2O-Nb_2O_5$,²⁶ $K_2O-Nb_2O_5$,²⁷ $Na_2O-Ta_2O_5$,²⁷ and $K_2O-Ta_2O_5$,²⁷ phases have been reported to give diffraction patterns very similar to that of TKWB. Most of these phases will fit the general formula $A_x(MeO)_yMeO_3$. For example, $BaO \cdot 2Nb_2O_5$ could be rewritten as $Ba_2(NbO)Nb_7O_{21}$ or $x = 2/7$ and $y = 1/7$.

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