JOURNAL OF RESEARCH of the National Bureau of Standards—A. Physics and Chemistry
Vol. 70A, No. 4, July–August 1966

Phase Equilibria as Related to Crystal Structure in the System Niobium Pentoxide-Tungsten Trioxide

R. S. Roth and J. L. Waring

Institute for Materials Research, National Bureau of Standards, Washington, D.C.

(April 1, 1966)

The phase equilibrium diagram for the binary system niobium pentoxide-tungsten trioxide has been constructed from results of x-ray diffraction studies on both single crystals and powders and from fusion characteristics. Twelve stable compounds have been found in the system. The exact composition of eight of these compounds has been established by single crystal analyses at the $Nb_2O_5:WO_3$ ratios of 6 : 1, 13 : 4, 7 : 3, 8 : 5, 9 : 8, 1 : 1, 4 :9, and 2 : 7. The approximate compositions of the remaining four other phases are 30 : 1, 6 : 11, 1 : 11, and 1 : 15. The 6 : 1, "6 : 11", 4 : 9, and 2 : 7 phases melt congruently at 1476, 1378, 1380, and 1357 °C, respectively. The "30 : 1", 7 : 3, 8 :5, 9 : 8, "1 : 11", and "1 : 15" phases melt incongruently at 1470, 1440, 1385, 1375, 1356, and 1358 °C, respectively; and the 13 : 4 and 1 : 1 phases decompose before melting at 1435 and 1115 °C, respectively. The 8 : 5, 9 : 8, "6 : 11", 2 : 7, "1 : 11", and "1 : 15" compounds are shown on the phase diagram as having minimum temperatures of stability. One metastable phase having a narrow range of composition near the 3 : 8 ratio was also encountered. Although Nb_2O_5 apparently exhibits no solid solution, WO_3 was found to accept a maximum of three mole percent niobia in solid solution enabling all the reported polymorphs of WO_3 to be obtained at room temperature.

Key Words: Crystal structure, niobium pentoxide, phase equilibria, system, tungsten trioxide.

1. Introduction

A complete study of the phase relationships in the binary system $Nb_2O_5-WO_3$ has been conducted as part of a continuing program of fundamental phase equilibria studies of ceramic materials. This particular system was selected for study in order to further the knowledge of the crystal chemistry of niobates in view of the results obtained from previous structural studies of single crystals [1–4].[1]

Due to the complex nature of the x-ray diffraction powder patterns in this system, conflicting interpretations of the data have been reported [5–11]. In a previous study of the Nb_2O_5–WO_3 system, Goldschmidt [5] concluded that Nb_2O_5 could accept more than 50 mole percent WO_3 in solid solution and reported the existence of a compound at approximately $Nb_2O_5:3WO_3$. He also found a limited solid solution of Nb_2O_5 in WO_3. Kovba and Trunov [6] reported that the 1 : 3 compound was tetragonal with a structure related to that of a tetragonal tungsten-bronze. Fiegel et al. [7], studied the phase equilibria in the system at 1200 °C and below. They reported only about 33 mole percent solid solution of WO_3 in Nb_2O_5 with a 3 : 2 compound occurring at 1200 °C and a 1 : 1 compound at 1100 °C and below. They found very little, if any, solid solution of Nb_2O_5 in WO_3 and confirmed the existence of a compound at about 1 : 3 with a limited solid solution for both Nb_2O_5 and WO_3. Later [8] they reported that the 1 : 3 composition gave single crystal x-ray diffraction patterns which showed superstructure differing from one crystal to the next. Kovba et al. [9], also attempted to determine the phases formed in this system at about 1200 °C. They concluded that compounds existed at the $Nb_2O_5:WO_3$ ratios of 4 : 1, 2 : 1, 4 : 7, and 1 : 3. They also reported a phase with variable WO_3 content occurring at high WO_3 concentrations and observed a small amount of solid solution in both Nb_2O_5 and WO_3.

In a description of preliminary phase identification, Roth and Wadsley [1] on the basis of single crystal x-ray diffraction studies reported the existence of five compounds structurally related to Nb_2O_5 occurring at $Nb_2O_5:WO_3$ ratios of 15 : 1, 6 : 1, 7 : 3, 8 : 5, and 9 : 8. They also confirmed the 1 : 1 phase and noted the existence of at least three phases related to the tetragonal tungsten bronze-type structure. The crystal structures of 6 : 1, 7 : 3, 8 : 5, and 9 : 8, were reported [2, 3] and the "building block" principle was elaborated as the basis of the crystal-chemistry of niobate compounds [4].

Schäfer and Gruehn [10] and Felten [11] have indicated in private communications that their interpretations of x-ray diffraction powder data for the Nb_2O_5–WO_3 system differ in some respects from the previously mentioned published reports.

Because of the conflicting nature of the reported data, it was thought desirable to study completely the phase equilibria of the Nb_2O_5–WO_3 system. With the use of the unit cell dimensions derived from

---

[1] Figures in brackets indicate the literature references at the end of this paper.

single crystal data the existence of the various phases in the powder patterns can now be established more readily. The exact compositions of phases can often be determined only by a solution of the crystal structure. The approximate composition and even the existence of a phase can sometimes be found only by a rather complete phase equilibria study. The two disciplines, crystal structure analysis and phase equilibria are therefore complimentary and no system can be considered to be well characterized unless both such studies have been made. Therefore, x-ray diffraction data together with the melting points of the compounds and solidus and liquidus temperatures at various compositions across the system have been obtained in order to construct an equilibrium diagram.

2. Sample Preparation and Test Methods

The following starting materials were employed for the preparation of the majority of the specimens:

Nb_2O_5—high purity niobium pentoxide. Spectrographic analysis indicated less than about 0.01 percent Si; 0.001 percent Ca and Mg with As, Cu, and Ta only questionably present.

WO_3 —high purity tungsten anhydride. Spectrographic analysis indicated less than about 0.1 percent Si; 0.001 percent B, Ca, Cr, and Mg; 0.0001 percent Cu with Pb only questionably present.

A few specimens were prepared with less pure starting materials, in order to determine qualitatively the effect of impurities on the equilibrium products. The following is a typical example of the nature of the impurities present in two specimens of Nb_2O_5 : WO_3 ratio of 16 : 5. For the less pure specimen the first series transition elements, in general, are present in amounts of an order of magnitude greater than for the more pure specimen.

Nb_2O_5 : WO_3 (16 : 5)—higher purity end members. Spectrochemical analyses indicated less than about 0.01 percent Cr, Cu, and Si; 0.001 percent Al, B, Ca, Mg, and Ni; 0.0001 percent Mn with Pb only questionably present.

Nb_2O_5 : WO_3 (16 : 5)—less pure end members. Spectrochemical analyses indicated less than about 0.01 percent Al, Ca, Cr, Cu, Fe, Mg, Ni, and Si; 0.001 percent Mn; 0.0001 percent B with Pb only questionably present.

For the preparation of the specimens, the weight percentages were calculated to within ±0.01 percent, with no corrections made for percentage of purity of the starting materials except for loss on ignition.

For the higher purity specimens, the starting materials were weighed to the nearest ±0.1 mg, in sufficient quantities to yield 3 g batches. Each batch was mixed in a mechanical shaker for about 15 min and pressed into a disk in a $5/8$-in. diam mold at 10,000 lb/in^2. The disks were placed on Pt foil and calcined by heating in air at 700 °C for 19 hrs, with heating and cooling rates of approximately 4 °C/min.

The less pure specimens were weighed out in approximately 1 g batches and mixed with an alumina mortar and pestle. In order to minimize any possible loss of WO_3 these specimens were not calcined after mixing.

Subsolidus, as well as melting point data, were obtained by the quenching technique on samples sealed in platinum tubes. An electrically heated vertical tube furnace wound with 80 percent Pt-20 percent Rh wire was used for the quenching experiments. The furnace was controlled by an a-c Wheatstone bridge controller which was capable of holding the temperature to at least ±2 °C for an extended period of time. Temperatures were measured with a Pt versus Pt-10 percent Rh thermocouple which had been calibrated against the melting points of Au (1063 °C) and Pd (1552 °C) [12]. The thermocouple was recalibrated several times during the course of the work. Specimens were suspended in the furnace by fine Pt wire. In order to quench the wire was fused allowing the sealed tubes to drop out of the heating chamber into a beaker of water. When the tubes were opened the specimens were examined for physical appearances of melting. The first sign of glazing of the surface of the specimen was interpreted as the first experimental evidence for the solidus temperature. Acceptance of this appearance as evidence of melting was found justified in many specimens by an abrupt difference in the x-ray diffraction powder patterns of the specimens. The formation of a concave meniscus, without the formation of relatively large crystals, indicated the liquidus temperature. The overall reproducibility of the temperature measurements for the experimental data points was within ±2 °C or better and the overall accuracy of the reported temperatures was within ±5 °C or better.

Equilibrium was considered to have been obtained when the x-ray diffraction patterns of specimens successively heated for longer times and/or at higher temperatures showed no change. X-ray diffraction powder patterns were made using a high-angle recording Geiger counter diffractometer and nickel-filtered copper radiation, with the Geiger counter traversing the specimen at 1/4°2θ/min and the intensity of the radiation being recorded on the chart at 1°2θ/in. The unit cell dimensions reported can be considered accurate to about ±2 in the last decimal place listed.

3. Compounds in the Nb_2O_5-WO_3 System

3.1. Nb_2O_5

The stability relations of the various reported polymorphs of Nb_2O_5 have been summarized by several workers [13–17]. It has been concluded that the high-temperature monoclinic form of Nb_2O_5 is the only stable form at atmospheric pressure [14, 16, 17]. The crystal structure of the high-temperature modification of Nb_2O_5 has been described by Gatehouse and Wadsley [18]. They report this phase to be monoclinic, (space group P2) with 14 formula units in the unit cell and $a=21.16$ Å, $b=3.822$ Å, $c=19.35$ Å, $\beta=119°50'$. The x-ray diffraction powder pattern previously listed for Nb_2O_5 [19] can be more correctly indexed on the basis of the published single-crystal intensity data and is shown in table 1. This indexing leads to slightly revised values of the unit cell dimensions, as follows: $a=21.149$ Å, $b=3.823$ Å, $c=19.352$ Å, $\beta=119°48'$, in excellent agreement with the lattice constants given by Gatehouse and Wadsley [18]. The melting point of the pure Nb_2O_5 used for this study was previously determined to be 1485 °C [20].

TABLE 1. *X-ray diffraction powder data for* Nb_2O_5 *(*CuK_a *radiation)*

d[a]	I[b]	$\frac{1}{d^2}$ obs	$\frac{1}{d^2}$ calc	hkl[c]
16.66	6	0.0036	0.0036	001
10.517	5	.0090	.0090	$20\bar{1}$
10.063	2	.0099	.0097	101
9.615	2	.0108	.0107	$10\bar{2}$
9.148	5	.0120	.0118	200
8.354	4	.0143	.0142	002
6.942	2	.0208	.0206	$30\bar{1}$
6.486	3	.0238	.0236	102
6.285	11	.0253	.0252	$10\bar{3}$
5.590	4	.0320	.0319	003
5.273	6	.0360	.0359	$40\bar{2}$
5.116	48	.0382	.0382	$40\bar{1}$
4.734	4	.0446	.0446	103
4.616	36	.0469	.0465	$10\bar{4}$
3.852	6	.0674	.0670	$30\bar{5}$
3.821	6	.0685	.0683	$20\bar{5}$
			.0684	010
3.737	100	.0716	.0714	110
			.0717	$11\bar{1}$
3.636	100	.0756	.0755	$10\bar{5}$
3.577	4	.0782	.0782	111
3.553	4	.0792	.0791	$11\bar{2}$
3.515	4	.0809	.0807	$60\bar{3}$
3.483	100	.0824	.0824	602
			.0826	012
3.406	4	.0862	.0859	$60\bar{4}$
3.383	4	.0877	.0877	303
3.351	28	.0891	.0886	005
			.0890	$31\bar{1}$
3.316	5	.0909	.0911	$60\bar{1}$
3.264	4	.0939	.0936	$11\bar{3}$
3.247	4	.0949	.0951	310
3.153	11	.1006	.1003	013
3.078	6	.1055	.1051	$50\bar{6}$
2.994	7	.1116	.1113	$10\bar{6}$
2.832	36	.1247	.1246	$51\bar{2}$
2.826	38	.1252	.1248	014
			.1262	$51\bar{3}$
2.771	31	.1303	.1301	$51\bar{1}$
2.701	34	.1371	.1367	$21\bar{5}$
			.1377	$70\bar{6}$
2.668	3	.1405	.1401	$41\bar{5}$
			.1405	$20\bar{7}$
2.644	4	.1431	.1426	510
			.1433	$80\bar{4}$
2.628	5	.1448	.1445	$80\bar{3}$
			.1452	$60\bar{7}$
2.543	36	0.1546	0.1526	$80\bar{2}$
			.1541	$10\bar{7}$
			.1543	$61\bar{4}$
2.523	5	.1571	.1571	015
2.491	26	.1612	.1612	$70\bar{7}$
2.478	8	.1629	.1623	511
			.1625	214
2.452	5	.1664	.1662	$41\bar{6}$
			.1672	$61\bar{5}$
2.314	29	.1865	.1865	413
			.1869	$61\bar{6}$
			.1872	$20\bar{8}$
2.114	4	.2244	.2239	414
2.076	38	.2321	.2321	$10, 0, \bar{3}$
2.037	34	.2411	.2410	$20\bar{9}$
1.912	29	.2736	.2736	020
1.873	5	.2852	.2846	$3, 0, \overline{10}$
			.2847	$11, 0, \bar{7}$
			.2847	$11, 0, \bar{3}$
			.2855	220
1.856	3	.2903	.2904	208
1.819	20	.3020	.3020	$2, 0, \overline{10}$
			.3031	$11, 0, \bar{8}$
1.789	16	.3124	.3115	407
			.3118	$42\bar{1}$
			.3127	902
1.765	5	.3211	.3201	$12\bar{4}$
			.3227	$12, 0, \bar{5}$
			.3230	$12, 0, \bar{6}$
			.3231	$6, 0, \overline{11}$
1.742	23	.3295	.3292	$11\bar{9}$
			.3296	$12, 0, \bar{4}$
1.727	25	.3353	.3353	$8, 0, \overline{11}$
1.709	10	.3424	.3422	$11, 1, \bar{4}$
			.3425	$11, 1, \bar{6}$
1.692	20	.3493	.3491	$12\bar{5}$
1.683	51	.3529	.3530	$3, 1, \overline{10}$
			.3531	$11, 1, \bar{3}$
1.627	8	.3776	.3776	408
1.592	27	.3945	.3946	$7, 1, \overline{11}$
1.582	20	.3994	.3982	11, 0, 1
			.3995	318
1.579	18	.4012	.4011	10, 1, 1
1.556	22	.4130	.4133	$12, 1, \bar{8}$

[a] Interplaner spacing.

[b] Intensity relative to the strongest peak(s).

[c] **Indexed on the basis of a monoclinic unit cell (space group P_2) $a=21.149$ Å, $b=3.823$ Å, $c=19.352$ Å, $\beta=119°48'$ and the previously reported observed structure factors from the** single crystal data [18].

3.2. Compounds Structurally Related to Nb_2O_5

a. Compounds Belonging to the Homologous Series $B_{nm+1}O_{3nm-(n+m)+4}$

Roth and Wadsley [4] have shown that most of the phases formed by the addition to Nb_2O_5 of oxides with cations similar in size to Nb^{+5}, regardless of valence, can be described by the homologous series notation $B_{nmp+1}O_{3nmp-(n+m)p+4}$. Structurally, these phases are made up of blocks of octahedra in a given plane n long and m wide with a variable number (p) of blocks connected by edge sharing of octahedra at the corners of the blocks. Similar block units occur at two levels in the unit cell, zero and one-half, in a

TABLE 2. *X-ray diffraction powder data for the compound* $WNb_{12}O_{33}$ *(*CuK_a *radiation)*

d[a] obs	I[b] obs	$\frac{1}{d^2}$ obs	$\frac{1}{d^2}$ calc	hkl[c]
14.77	19	0.0046	0.0046	001
11.08	23	.0081	.0081	$20\bar{1}$
7.42	16	.0182	.0183	002
6.43	8	.0242	.0241	201
5.54	18	.0326	.0325	$40\bar{2}$
5.35	6	.0349	.0348	$40\bar{1}$
5.04	48	.0394	.0394	$40\bar{3}$
4.937	12	.0410	.0411	003
4.674	58	.0458	.0458	202
3.743	76	.0714	.0713	110
3.729	96	.0719	.0718	$11\bar{1}$
3.702	40	.0730	.0730	004
3.697	40	.0732	.0732	$60\bar{3}$
3.670	20	.0742	.0742	$60\bar{2}$
3.616	284	.0765	.0766	203
3.535	43	.0800	.0798	111
3.510	300	.0812	.0811	$60\bar{4}$
3.437	13	.0847	.0846	$60\bar{1}$
3.415	15	.0857	.0857	$20\bar{5}$
3.358	29	.0887	.0887	$31\bar{2}$
3.203	27	.0974	.0975	112
2.930	16	.1165	.1165	204
2.901	5	.1189	.1189	$51\bar{2}$
2.866	58	.1217	.1218	$51\bar{3}$
2.836	37	.1243	.1243	113
2.799	7	.1277	.1279	$20\bar{6}$
2.735	41	.1337	.1337	$51\bar{4}$
2.706	31	.1365	.1366	312
2.682	17	.1390	.1392	$80\bar{2}$
			.1392	$80\bar{5}$
2.542	8	.1548	.1548	$51\bar{5}$
2.520	116	.1575	.1574	$80\bar{1}$
			.1580	$40\bar{7}$
2.499	10	.1602	.1599	$60\bar{7}$
			.1603	114
2.462	16	.1650	.1651	511
2.410	4	.1722	.1722	$71\bar{2}$
2.339	6	.1828	.1831	404
2.328	15	.1845	.1842	$71\bar{5}$
			.1848	800
2.316	29	.1864	.1865	$71\bar{1}$
			.1868	$31\bar{6}$
2.215	11	.2038	.2043	$60\bar{8}$
2.183	7	.2098	.2099	710
2.167	6	0.2130	0.2135	$10. 0, \bar{6}$
2.128	5	.2209	.2213	801
			.2213	$80\bar{8}$
2.116	6	.2233	.2236	007
			.2237	206
2.112	6	.2242	.2244	$51\bar{7}$
2.072	67	.2325	.2328	$10, 0, \bar{7}$
2.042	52	.2398	.2401	405
2.006	6	.2484	.2487	$91\bar{2}$
1.9375	9	.2664	.2669	802
			.2669	$80\bar{9}$
1.9324	8	.2678	.2683	315
1.9121	60	.2735	.2735	020
1.8729	4	.2851	.2851	220
1.8664	5	.2871	.2873	$22\bar{2}$
1.8560	15	.2899	.2903	$12, 0, \bar{5}$
1.8524	29	.2914	.2910	207
			.2918	022
			.2920	008
1.8342	8	.2969	.2972	$12, 0, \bar{4}$
1.8144	8	.3038	.3040	$12, 0, \bar{7}$
1.8090	20	.3056	.3063	406
1.8007	8	.3084	.3093	$20\bar{9}$
1.7895	13	.3126	.3123	$11, 1, \bar{5}$
1.7720	8	.3185	.3185	$11, 1, \bar{6}$
1.7697	9	.3193	.3193	222
1.7640	22	.3214	.3217	$8, 0, \overline{10}$
1.7567	19	.3240	.3245	$12, 0, \bar{8}$
1.7403	21	.3302	.3305	316
1.7329	19	.3330	.3332	10, 0, 1
1.7311	18	.3337	.3339	$11, 1, \bar{7}$
1.6903	20	.3500	.3501	223
1.6805	42	.3541	.3545	515
			3547	$62\bar{4}$
1.6709	26	.3582	.3585	$11, 1, \bar{8}$
1.6088	21	.3864	.3869	10, 0, 2
1.6070	23	.3872	.3880	$2, 0, \overline{10}$
1.5975	16	.3918	.3924	912
1.5838	21	.3987	.3992	$9, 1, \overline{10}$
1.5801	20	.4005	.4006	$14, 0, \bar{5}$
			.4017	$10, 0, \overline{11}$
1.5734	21	.4039	.4049	119
1.5608	19	.4105	.4109	$13, 1, \bar{5}$
1.5527	9	.4148	.4154	$14, 0, \bar{4}$
1.5405	5	.4214	.4227	$4, 0, \overline{11}$

[a] Interplanar spacing.

[b] Observed intensity.

[c] Indexed on the basis of a monoclinic unit cell (space group C_2) $a=22.282$ Å, $b=3.824$ Å, $c=17.724$ Å, $\beta=123°22'$ and the previously reported structure factors from the single crystal data [2].

plane perpendicular to one axis which always has a value of approximately 3.8 Å. This axis is the *b*-axis of a monoclinic cell or the *c*-axis of a tetragonal cell. The octahedra occurring at the two different levels are connected to each other by edge sharing except at the junction of four such blocks, two at each level, where they are bonded by a tetrahedrally coordinated cation. Those compounds in the Nb_2O_5–WO_3 system whose structures have been described all have $p=1$ and the formula simplifies to $B_{nm+1}O_{3nm-(n+m)+4}$, where the tetrahedral position is always occupied by W^{+6} ions. In this arrangement when $n=m$, the unit cell is body-centered tetragonal as in PNb_9O_{25} [21]. When $n \neq m$ the cell is C-centered monoclinic.

b. $6Nb_2O_5 \cdot WO_3$,$WNb_{12}O_{33}$)

The unit cell of this compound is C-centered monoclinic (probable space group C_2) having $n=3$, $m=4$ [2]. The indexed x-ray diffraction powder pattern obtained in the present study is listed in table 2. The unit cell dimensions derived from this pattern are $a=22.282$ Å, $b=3.824$ Å, $c=17.724$ Å, $\beta=123°22'$. $WNb_{12}O_{33}$ is apparently stable from room temperature to the congruent melting point at 1476 °C.

c. $7Nb_2O_5 \cdot 3WO_3$ ($W_3Nb_{14}O_{44}$)

The unit cell of this compound is body-centered tetragonal, space group I4/m or $I\bar{4}$($n=4$, $m=4$ [3]). The indexed x-ray diffraction powder pattern is listed in table 3 and the unit cell dimensions derived from this pattern are $a=21.002$ Å, $c=3.820$ Å.

d. $8Nb_2O_5 \cdot 5WO_3$ ($W_5Nb_{16}O_{55}$)

The unit cell of this phase is C-centered monoclinic space group C_2 ($n=4$, $m=5$, [2]). The indexed x-ray diffraction powder pattern is listed in table 4 and the unit cell dimensions derived from this pattern are $a=29.638$ Å, $b=3.820$ Å, $c=23.126$ Å, $\beta=126°27'$.

TABLE 4. *X-ray diffraction powder data for the compound* $W_5Nb_{16}O_{55}$ *(CuKa radiation)*

d^a	I^b	$\frac{1}{d^2}$ obs	$\frac{1}{d^2}$ calc	hkl^c
18.58	7	0.0029	0.0029	001
14.84	12	.0045	.0046	$20\bar{1}$
9.31	13	.0115	.0116	002
7.40	17	.0183	.0183	$40\bar{2}$
6.75	4	.0220	.0220	$40\bar{3}$
6.21	12	.0260	.0260	003
5.85	6	.0293	.0293	202
4.935	12	.0411	.0411	$60\bar{3}$
4.701	45	.0453	.0453	$60\bar{4}$
4.652	10	.0462	.0462	004
4.512	35	.0491	.0491	203
3.771	130	.0703	.0703	110
3.767	142	.0705	.0705	$11\bar{1}$
3.717	26	.0724	.0722	005
3.705	22	.0729	.0731	$80\bar{4}$
3.660	250	.0747	.0743 .0747	$80\bar{3}$ 204
3.630	40	.0759	.0759	111
3.587	222	.0777	.0777	$80\bar{5}$
3.539	25	.0798	.0799	$31\bar{2}$
3.506	8	.0813	.0813	$80\bar{2}$
3.406	8	.0862	.0863	403
3.386	10	.0872	.0872	112
3.252	6	.0946	.0947	$40\bar{7}$
3.188	16	.0984	.0984	$51\bar{3}$
3.095	12	.1044	.1044	113
3.072	10	.1060	.1061	205
2.980	7	.1126	.1126	800
2.897	8	.1192	.1192	$10,0,\bar{6}$
2.832	16	.1246	.1245	$71\bar{3}$
2.817	47	.1260	.1260	$71\bar{4}$
2.804	40	.1272	.1273 .1274	114 $40\bar{8}$
2.775	5	.1299	.1300	$10,0,\bar{7}$
2.740	54	.1332	.1332	$71\bar{5}$
2.732	65	.1340	.1339	$10,0,\bar{2}$
2.727	71	.1345	.1345	313
2.615	8	.1462	.1463	$71\bar{6}$
2.574	16	.1509	.1509	512
2.562	84	.1524	.1520 .1528	$10,0,\bar{1}$ $60\bar{9}$
2.549	22	.1539	.1538 .1540	$80\bar{9}$ 405
2.533	8	.1558	.1559	115
2.479	6	.1627	.1627 .1628	$91\bar{5}$ 314
2.425	11	.1701	.1699 .1704	$12,0,\bar{7}$ $91\bar{6}$
2.397	4	0.1741	0.1744	$91\bar{2}$
2.382	8	.1763	.1764	711
2.350	4	.1811	.1811	$12,0,\bar{8}$
2.316	7	.1864	.1862 .1873	207 $8,0,\overline{10}$
2.294	37	.1900	.1898 .1903	$91\bar{1}$ $51\bar{8}$
2.254	6	.1969	.1968 .1970	315 $10,0,\overline{10}$
2.177	6	.2111	.2111	910
2.104	8	.2260	.2260	$51\bar{9}$
2.067	8	.2340	.2340	$11,1,\bar{2}$
2.036	52	.2413	.2413	$14,0,\bar{9}$
2.021	36	.2448	.2448	407
1.9453	4	.2642	.2638	606
1.9099	37	.2742	.2742	020
1.8827	6	.2821	.2823	10,0,3
1.8783	6	.2835	.2837	$12,0,\overline{12}$
1.8602	17	.2890	.2890	0,0,10
1.8503	7	.2921	.2919	$16,0,\bar{7}$
1.8329	18	.2977	.2972 .2978	$16,0,\bar{6}$ $2,0,\overline{11}$
1.8294	26	.2988	.2988	408
1.8007	12	.3084	.3083	$16,0,\bar{5}$
1.7944	18	.3106	.3107	$16,0,\overline{10}$
1.7800	4	.3156	.3153 .3157	$62\bar{3}$ $4,0,\overline{12}$
1.7691	7	.3195	.3195	$62\bar{4}$
1.7580	25	.3236	.3233 .3238	$22\bar{3}$ $12,0,\overline{13}$
1.7452	8	.3283	.3285	119
1.7421	14	.3295	.3292	12,0,2
1.7311	24	.3337	.3336	318
1.7229	12	.3369	.3368	$15,1,\bar{9}$
1.6943	28	.3484	.3479 .3489	517 224
1.6862	57	.3517	.3515 .3518	$15,1,\overline{10}$ 825
1.6303	12	.3763	.3762	12,0,3
1.6284	13	.3771	.3772	$4,0,\overline{13}$
1.6101	10	.3857	.3861	$14,0,\overline{14}$
1.5888	12	.3962	.3958	11,1,3
1.5783	14	.4014	.4015 .4015	$13,1,\bar{3}$ $42\bar{8}$
1.5732	26	.4041	.4041	3,1,12
1.5654	30	.4081	.4078 .4081	$17,1,\bar{6}$ $10,2,\bar{2}$

[a] Interplaner spacing.

[b] Observed intensity.

[c] Indexed on the basis of a monoclinic unit cell (space group C_2) $a=29.638$ Å, $b=3.820$ Å, $c=23.126$ Å, $\beta=126°27'$ and the previously reported observed structure factors from the single crystal data [2].

TABLE 3. *X-ray diffraction powder data for the compound* $W_3Nb_{14}O_{44}$ *(*CuK_α *radiation)*

d^a obs	I^b obs	$\frac{1}{d^2}$ obs	$\frac{1}{d^2}$ calc	hkl^c	d^a obs	I^b obs	$\frac{1}{d^2}$ obs	$\frac{1}{d^2}$ calc	hkl^c	d^a obs	I^b obs	$\frac{1}{d^2}$ obs	$\frac{1}{d^2}$ calc	hkl^c
14.87	25	0.0045	0.0045	110	2.560	22	0.1526	0.1524	611	1.8620	6	0.2884	0.2884	941
10.52	5	.0090	.0091	200	2.546	122	.1543	.1542	820	1.8564	15	.2902	.2902	880
7.42	33	.0181	.0181	220	2.488	10	.1616	.1615	541	1.8419	28	.2948	.2947	11,3,0/970
6.65	8	.0226	.0227	310	2.441	7	.1679	.1678	750	1.8367	15	.2964	.2967	312
4.951	23	.0408	.0408	330	2.421	16	.1706	.1705	631	1.8007	54	.3084	.3083	10,6,0
4.694	82	.0454	.0453	420	2.358	9	.1799	.1796	701	1.7694	16	.3194	.3194	422
4.118	5	.0590	.0589	510	2.347	8	.1814	.1815	840	1.7546	10	.3248	.3247	871
3.757	142	.0708	.0708	101	2.319	13	.1860	.1859	910	1.7499	40	.3266	.3265	12,0,0
3.712	37	.0726	.0725	440	2.302	41	.1887	.1887	721	1.7305	43	.3339	.3338	961
3.598	480	.0772	.0771	530	2.215	2	.2037	.2040	930	1.6874	65	.3512	.3511	532
3.539	52	.0798	.0799	211	2.152	9	.2159	.2159	811/741	1.6857	85	.3519	.3519	11,2,1/10,5,1
3.321	20	.0907	.0907	620	2.121	3	.2222	.2222	770	1.6612	4	.3624	.3627	12,4,0
3.195	42	.0980	.0980	321	2.100	11	.2268	.2267	10,0,0/860	1.6559	5	.3647	.3647	622
2.968	8	.1135	.1134	710/550	2.067	18	.2341	.2340	831	1.6396	5	.3720	.3718	10,8,0
2.912	22	.1179	.1179	640	2.039	130	.2405	.2403	950	1.6239	4	.3792	.3791	11,4,1
2.826	80	.1252	.1252	501/431	1.9497	3	.2631	.2630	10,4,0	1.6103	35	.3856	.3854	13,1,0/11,7,0
2.756	21	.1317	.1315	730	1.9102	40	.2741	.2743	002	1.5861	40	.3975	.3973	12,1,1/981
2.649	105	.1344	.1343	521	1.9004	10	.2769	.2766	11,1,0	1.5686	62	.4064	.4063	10,7,1
2.623	4	.1453	.1451	800	1.8797	5	.2830	.2831	202					

[a] Interplaner spacings.

[b] Observed intensities.

[c] Indexed on the basis of a tetragonal unit cell (space group I4/m or $I\bar{4}$) $a=21.002$ Å, $c=3.820$ Å.

TABLE 5. *X-ray diffraction powder data for the compound* $W_8Nb_{18}O_{69}$ *(CuK_α radiation)*

d^a	I^b	$\frac{1}{d^2}$ obs	$\frac{1}{d^2}$ calc	hkl^c	d^a	I^b	$\frac{1}{d^2}$ obs	$\frac{1}{d^2}$ calc	hkl^c	d^a	I^b	$\frac{1}{d^2}$ obs	$\frac{1}{d^2}$ calc	hkl^c
18.43	4	0.0029	0.0029	110	2.731	119	0.1341	0.1340	631	1.9340	4	0.2674	0.2673	11,4,1
9.33	8	.0115	.0116	220	2.626	12	.1450	.1449	10,0,0/860	1.9068	40	.2750	.2750	002
6.20	10	.0260	.0261	330	2.622	18	.1455	.1456	721	1.8578	10	.2898	.2893	14,2,0/10,10,0
5.88	10	.0290	.0290	420	2.575	96	.1508	.1507	10,2,0	1.8482	12	.2928	.2927	11,9,0
4.640	8	.0464	.0464	440	2.522	11	.1573	.1572	651	1.8216	48	.3014	.3014	12,8,0
4.503	80	.0493	.0493	530	2.477	15	.1630	.1629	811/741	1.7791	12	.3160	.3159	13,7,0
4.375	5	.0522	.0522	600	2.458	7	.1744	.1745	831	1.7561	15	.3243	.3243	532
3.771	146	.0703	.0702	101	2.378	9	.1769	.1768	11,1,0	1.7474	26	.3275	.3275	15,1,0
3.712	25	.0726	.0725	710/550	2.304	6	.1885	.1884	11,3,0/970	1.7384	7	.3309	.3310	10,9,1
3.642	372	.0753	.0754	640	2.283	38	.1918	.1919	921/761	1.7235	28	.3366	.3362 .3368	14,6,0 13,4,1/11,8,1
3.450	15	.0840	.0840	730	2.253	11	.1970	.1971	10,6,0	1.6943	57	.3484	.3484	12,7,1
3.378	17	.0876	.0876	321	2.248	7	.1978	.1977	851	1.6897	65	.3503	.3504	642
3.185	12	.0986	.0985	820	2.242	6	.2086	.2087	12,0,0	1.6614	5	.3623	.3624	15,5,0/13,9,0
3.088	25	.1049	.1043 .1050	660 501/431	2.156	9	.2151	.2145 .2151	12,2,0 10,1,1	1.6532	6	.3659	.3658	14,3,1/13,6,1
3.054	15	.1072	.1072	750	2.100	12	.2267	.2267	10,3,1	1.6292	22	.3768	.3768	16,2,0/14,8,0
2.901	5	.1189	.1188	910	2.077	5	.2319	.2319	12,4,0	1.5801	28	.4005	.4006	15,2,1
2.793	82	.1282	.1282	541	2.015	85	.2463	.2463	13,1,0/11,7,0	1.5688	48	.4063	.4064	13,8,1
2.769	26	.1304	.1304	930	1.9584	5	.2607	.2608	12,6,0					

[a] Interplaner spacing.
[b] Observed intensity.
[c] Indexed on the basis of a tetragonal unit cell (space group I$\bar{4}$) $a = 26.270$ Å, $c = 3.814$ Å.

Due to the very large monoclinic cell this powder pattern can only be indexed unambiguously with the aid of single crystal data. By utilizing the published F_{obs} values for $W_5Nb_{16}O_{55}$ [2] it was possible to assign indices to the observed peaks in the powder pattern with reasonable certainty up to about 60°2θ (Cu radiation). $W_5Nb_{16}O_{55}$ is probably not stable below about 1090 °C and melts incongruently at about 1385 °C.

e. $9Nb_2O_5 \cdot 8WO_3$ ($W_8Nb_{18}O_{69}$)

The unit cell of the last compound observed in this structural series has $n=5$, $m=5$ [3] and is body-centered tetragonal with the most probable space group I$\bar{4}$. The indexed x-ray diffraction powder pattern is given in table 5 and the unit cell dimensions derived from this pattern are $a = 26.270$ Å, $c = 3.814$ Å. This compound is not stable below about 1265 °C and melts incongruently at about 1375 °C.

It should be noted that the binary equilibrium stability regions of this structural group of compounds tend to decrease with increasing W^{+6} content. This phenomenon is probably due to the increasing size of the basic "building block" unit, and therefore to the greater energy needed to maintain long range ordering.

f. Other Compounds Structurally Related to Nb_2O_5

In addition to the compounds with structures described by the homologous series formula $B_{mnp+1}O_{3nmp-(n+m)p+4}$, the existence of several other phases has been reported, but their structures are, as yet, unknown. Notable among these is the $NbO_{2.482}$ (and $(Ti,Nb)O_{2.482}$) reported by Gruehn and Schäfer [22] which is apparently similar to the 'X' phase reported by Waring and Roth in the system vanadium-oxide-niobium oxide [23]. There are several stable phases in the Nb_2O_5–WO_3 system which fall in this category.

g. $13Nb_2O_5 \cdot 4WO_3$ ($W_4Nb_{26}O_{77}$)

Another phase, previously unreported, was found to occur between the known 6:1 and 7:3 compounds. The composition of this phase was deduced by Schäfer (private communication) to be 13:4 based on oxygen analyses. It was postulated that this compound might have an Nb_2O_5:WO_3 ratio of 16:5 and the structure would then be related to that of Nb_2O_5 by increasing the size of the basic "building blocks" from 3 × 4 and 3 × 5 (reported for Nb_2O_5 [18]) to 4 × 4 and 4 × 5. However, single crystals obtained from a 16:5 composition were found by A. D. Wadsley (private communication) to have a unit cell which is C-centered monoclinic $a = 29.74$ Å, $b = 3.823$ Å, $c = 26.02$ Å, $\beta = 92°18'$. These values are *not* in agreement with the primitive space group and approximate unit cell dimensions which can be derived for the postulated 16:5 structure. The partially indexed powder pattern is given in table 6. It cannot be fully indexed without the aid of single crystal intensity data due to the very large size of the unit cell. The structure of this phase, is actually a mixture of blocks of 3 × 4 and 4 × 4 occurring in alternate sequence to make an "ordered intergrowth" structure [24]. The composition can be arrived at by adding the homologous series twice (as for Nb_2O_5 [4]) $n=3$, $m=4$, $p=1$ ($B_{13}O_{33}$) plus $n=4$, $m=4$, $p=1$ ($B_{17}O_{44}$) $= B_{30}O_{77}$ ($13Nb_2O_5 \cdot 4WO_3$). Although this compound does not form in short-time experiments (about 1 hr) it can be prepared readily by heating for several days at about 1400 °C. This phase was observed to decompose at about 1435 °C into $6Nb_2O_5 \cdot WO_3$ and $7Nb_2O_5 \cdot 3WO_3$.

h. "$30Nb_2O_5$:WO_3"[2]

Another phase was found to occur in the Nb_2O_5-WO_3 system at a ratio of approximately 3.5 mole

---

[2] Quotation marks are used around a composition whenever the phase referred to has not been completely characterized.

TABLE 6. *X-ray diffraction powder data for the compound* $W_4Nb_{26}O_{77}$ *(CuK_α radiation)*

d^a	I^b	hkl^c	d^a	I^b	hkl^c
14.82	10	200	2.418	10	
12.93	8	002	2.346	7	
7.43	12	400	2.309	22	
6.55	5		2.277	5	
5.19	7		2.113	7	
4.951	14	600	2.067	13	
4.833	15	205	2.055	42	
4.686	60	$60\bar{2}$	2.042	88	
3.786	18	110	1.912	68	020
3.748	200	$11\bar{1}$ 111	1.857	12	
3.711	40	007 800	1.854	15	
3.657	15	112 $20\bar{7}$	1.848	25	
3.610	250	$80\bar{2}$	1.835	5	
3.564	190	207	1.816	5	
3.542	50	802 $31\bar{1}$	1.805	33	
3.463	10	113	1.781	16	
3.367	10		1.763	15	
3.264	10	114	1.756	19	
3.199	16		1.744	13	
2.966	5		1.736	16	
2.919	15		1.731	15	
2.845	32		1.706	5	
2.832	48		1.689	25	
2.777	10		1.684	68	
2.731	52		1.675	12	
2.724	55		1.610	25	
2.529	90		1.597	8	
			1.592	20	
			1.585	18	
			1.571	25	
			1.565	38	

[a] Interplaner spacing.
[b] Observed intensity.
[c] Partially indexed on the basis of a C-centered monoclinic unit cell with $a=29.74$ Å, $b=3.823$ Å, $c=26.02$ Å, $\beta=92°18'$ by comparison with the single crystal intensities observed from a film taken with a Weisingberg camera [A. D. Wadsley, private communication].

percent WO_3. This phase is apparently the same as that previously reported to occur at about 15:1, the structure of which could not be verified [1]. The 30:1 ratio is that deduced by Schäfer (private communication). It is apparently composed of some complex packing of the "building blocks" previously described. One possible structure might be $n=3$, $m=4$, $p=2$ ($B_{25}O_{62}$) plus two blocks of $n=3$, $m=4$, $p=1$ ($\mathbf{B_{25}O_{66}}$)$=B_{51}O_{128}$ ($25Nb_2O_5 \cdot WO_3$). Another possibility might be $n=3$, $m=4$, $p=2$ ($B_{25}O_{62}$)$+n=3$, $m=5$, $p=1$ ($B_{16}O_{41}$)$=B_{41}O_{105}$ ($20Nb_2O_5 \cdot WO_3$). The exact structure and composition remain to be proven because no good single crystal data is yet available. The "30:1" phase was found to melt incongruently at about 1470 °C. Its unindexed x-ray diffraction powder pattern is listed in table 7.

3.3. Compounds Containing Pentagonal Bipyramid (Sevenfold) Coordinated Cations

a. $Nb_2O_5 \cdot WO_3$ (WNb_2O_8)

A phase isostructural with Nb_3O_7F [25] might be thought likely to occur in this system, but no such structure has ever been reported in pure oxide systems.

TABLE 7. *X-ray diffraction powder data for the composition* $30Nb_2O_5:WO_3$ *(CuK_α radiation)*

d^a	I^b	d^a	I^b
16.20	10	2.435	9
13.93	4	2.376	40
10.73	16	2.212	6
8.96	7	2.100	8
8.10	5	2.076	74
6.37	14	2.041	90
5.36	8	1.999	5
5.10	50	1.936	8
4.797	7	1.913	48
4.645	60	1.871	10
3.742	132	1.866	10
3.638	312	1.857	12
3.579	10	1.825	18
3.556	10	1.819	42
3.493	228	1.796	8
3.354	37	1.791	8
3.173	16	1.782	23
3.093	7	1.769	7
2.984	14	1.746	14
2.845	55	1.743	25
2.836	47	1.731	30
2.763	38	1.716	10
2.707	46	1.693	22
2.693	18	1.684	30
2.647	8	1.680	60
2.614	7	1.623	15
2.597	6	1.603	8
2.538	65	1.595	30
2.503	45	1.581	44
2.476	10	1.558	28
2.458	10	1.548	8

[a] Interplaner spacing.
[b] Observed intensity.

Instead a new phase was found with unit cell dimensions related to the tetragonal tungsten bronze-type structures. Single crystals of the 1:1 compound were prepared by decomposing the 9:8 phase (made with the less pure end members) at about 1100 °C. Single crystal precession patterns of this phase made by A. Perloff of the National Bureau of Standards staff showed these crystals to be orthorhombic, probable space groups Pmab or $P2_1ab$. From these data the x-ray diffraction powder pattern given in table 8 was indexed with $a=16.615$ Å, $b=17.616$ Å, $c=3.955$ Å. The compound $Nb_2O_5 \cdot WO_3$ could not be made as a single phase in the quenching experiments. X-ray diffraction powder patterns of these specimens always showed a trace of a metastable bronze-type phase plus some $7Nb_2O_5 \cdot 3WO_3$. However, high temperature x-ray powder patterns showed that the extra phases disappeared quickly above about 900 °C. The 1:1 compound was found to dissociate at about 1115 °C to $8Nb_2O_5 \cdot 5WO_3$ plus a bronze-like phase, probably $4Nb_2O_5 \cdot 9WO_3$.

WNb_2O_8 is related to WTa_2O_8 ($a=16.701$ Å, $b=8.864$ Å, $c=3.877$ Å) by a doubled b-axis. The crystal structure of $LiNb_6O_{15}F$ which is apparently isostructural with WTa_2O_8 was found by S. Andersson and M. Lundberg [26] to be made up of octahedrally coordinated cations. These octahedra are corner shared to form a ring of five octahedra. Within this ring is a cation in sevenfold coordination, in a penta-

TABLE 8. *X-ray diffraction powder data for the compound* WNb_2O_8 (*CuK_α radiation*)

d[a]	I[b]	$\frac{1}{d^2}$ obs	$\frac{1}{d^2}$ calc	hkl[c]
8.83	6	0.0128	0.0129	020
8.30	25	.0145	.0145	200
4.689	6	.0455	.0455	320
4.403	5	.0516	.0516	040
4.259	12	.0551	.0552	140
3.952	272	.0640	.0639	001
3.894	46	.0660	.0660	240
3.759	112	.0708	.0708	420
3.608	4	.0768	.0768	021
3.570	9	.0785	.0785	201
3.449	202	.0841	.0841	340
3.279	20	.0930	.0929	031
3.215	8	.0967	.0966	131
3.165	22	.0998	.0997	311
3.110	98	.1034	.1034	520
3.051	16	.1075	.1074	231
2.937	4	.1159	.1160	060
2.893	80	.1195	.1196	160
2.825	11	.1253	.1251 .1255	411 331
2.771	78	.1303	.1303 .1305	600 260
2.725	50	.1347	.1348	421
2.654	16	.1420	.1421	540
2.644	18	.1430	.1432	620
2.633	12	.1443	.1445	051
2.599	86	.1481	.1481 .1481	341 151
2.573	8	.1511	.1509	431
2.518	8	.1577	.1577	511
2.510	8	.1587	.1590	251
2.445	44	.1673	.1673	521
2.398	7	.1739	.1739	460
2.375	8	.1773	.1771	351
2.334	40	.1835	.1834 .1836	531 161
2.293	5	.1901	.1903	720
2.268	23	.1943	.1943 .1944	601 261
2.250	8	.1976	.1975	611
2.223	8	.2023	.2024	451
2.203	19	.2061	.2060 .2062	541 080
2.198	19	.2070	.2072	621
2.117	4	.2232	.2233	631
2.091	8	.2288	.2290	740
2.078	14	.2316	.2317	800
2.050	6	.2381	.2379	461
2.023	18	.2443	.2445 .2446	711 820
1.9774	50	.2558	.2557	002
1.9652	7	.2589	.2590	012
1.9473	18	.2637	.2642	480
1.9247	13	.2699	.2702 .2702 .2703	081 202 731
1.8797	16	.2830	.2831 .2833	222 840
1.8743	15	.2847	.2846 .2847	281 032
1.8521	18	.2915	.2915	312
1.8475	24	.2930	.2929 .2934	741 760
1.8373	30	.2962	.2956 .2968	801 580
1.8284	15	.2991	.2988 .2992	811 232
1.8178	6	.3026	.3027	381
1.8081	6	.3059	.3061	920
1.8017	8	.3081	.3073 .3085	042 821
1.7908	7	.3118	.3109 .3123	142 571
1.7852	6	.3138	.3137	402
1.7762	9	.3170	.3169	412
1.7637	14	.3215	.3218 .3219 .3223	242 751 0,10,0
1.7546	16	.3248	.3246 .3249	831 091
1.7496	20	.3267	.3266	422
1.7464	23	.3279	.3281	481
1.7247	15	.3362	.3363 .3366	052 680
1.7154	16	.3398	.3394 .3399 .3399	291 342 152
1.6969	40	.3473	.3472 .3477	841 860
1.6885	9	.3507	.3508	252
1.6740	7	.3569	.3573	761
1.6684	22	.3593	.3591	522
1.6662	28	.3602	.3604	911
1.6651	27	.3607	.3607	581
1.6625	26	.3618	.3620	10,0,0
1.6548	5	.3652	.3652	442
1.6434	4	.3703	.3701	921
1.6396	4	.3720	.3717	062
1.6326	12	.3752	.3749 .3752 .3754	10,2,0 532 162
1.6234	14	.3795	.3802	4,10,0
1.6096	13	.3860	.3861 .3861 .3862 .3862	602 0.10,1 931 262
1.6029	9	.3892	.3893 .3898	612 1,10,1
1.5928	6	.3942	.3942	452
1.5853	8	.3979	.3978	542
1.5826	8	.3993	.3990 .3992	622 771
1.5808	10	.4002	.4005 .4006	681 2,10,1
1.5640	14	.4088	.4087 .4093	941 960
1.5592	26	.4114	.4116	861
1.5326	12	.4257	.4260	10,0,1

[a] Interplaner spacing.
[b] Observed intensity.
[c] Indexed on the basis of an orthorhombic unit cell (space group Pmab or $P2_1ab$) $a = 16.615$ Å, $b = 17.616$ Å, $c = 3.955$ Å.

gonal bipyramid configuration. These rings are connected by further corner sharing to form double chains. The doubled cell in WNb_2O_8 is probably due to an alternate puckering of the positions occupied by the sevenfold coordinated ions, but the proof of this must await a complete single crystal structure analysis.

b. $4Nb_2O_5 \cdot 9WO_3(Nb_8W_9O_{47})$

A compound having a general diffraction pattern similar to tetragonal potassium tungsten bronze (K_xWO_3) was reported by Roth and Wadsley [1] to occur at the composition $4Nb_2O_5 \cdot 9WO_3$. Sleight and Magneli [27] described the structure of this phase from a crystal obtained from a 1:3 composition which had been heated to a temperature of 1200–1400 °C. The structure of this crystal was found to be made up of three tetragonal-bronze-like unit cells with four out of the twelve possible five-fold rings being occupied by cations, with oxygens above and below forming pentagonal bipyramid coordination polyhedra. This structure represents the composition $Nb_{16}W_{18}O_{94}$ and has orthorhombic symmetry. The unit cell dimensions found in the present work are $a = 36.692$ Å, $b = 12.191$ Å, $c = 3.945$ Å, and were obtained from the indexed x-ray diffraction powder pattern given in table 9. This compound was found to be stable from at least 1150 °C to the congruent melting point of about 1380 °C.

The presence of cations in the pentagonal holes of the tetragonal tungsten bronze structure suggests a possible homologous series which can be expressed as:

$$nB_{10}O_{30} + mBO \text{ or } B_{10n+m}O_{30n+m}$$

where n is the number of subcells of the tetragonal bronze type in the true unit cell and m is the number of pentagonal bipyramid polyhedra occupied by a cation. Each bronze-type subcell has only four pentagonal holes, therefore the maximum value of m must be equal to or less than $4n$.

c. $2Nb_2O_5 \cdot 7WO_3$ ($Nb_4W_7O_{31}$)

One method of reducing the general formula $B_{10n+m}O_{30n+m}$ to include the 4 : 9 compound and to predict a *minimum* number of other phases is to assume $m=4$. This results in the formula $B_{10n+4}O_{30n+4}$.

TABLE 9. *X-ray diffraction powder data for the compound* $W_9Nb_8O_{47}$ *(*CuK_α *radiation)*

d[a]	I[b]	$\frac{1}{d^2}$ obs	$\frac{1}{d^2}$ calc	hkl[c]
11.59	4	0.0074	0.0075	110
10.14	12	.0097	.0097	210
9.16	8	.0119	.0119	400
8.64	9	.0134	.0134	310
7.34	6	.0186	.0186 .0186	500 410
6.12	6	.0267	.0267	600
6.09	11	.0269	.0269	020
5.46	57	.0335	.0335	610
5.08	5	.0388	.0388	420
4.314	22	.0537	.0537	620
4.081	6	.0601	.0602	900
4.064	10	.0605	.0606	030
4.044	10	.0612	.0613	130
3.945	212	.0643	.0643	001
3.867	176	.0669	.0669	910
3.858	195	.0672	.0672	330
3.754	6	.0710	.0709 .0710	301 011
3.732	7	.0718	.0717	111
3.678	10	.0739	.0740	211
3.660	28	.0746	0.0743 0.0746	10,0,0 820
3.587	4	.0777	.0777	311
3.559	14	.0790	.0791	530
3.474	6	.0829	.0828 .0829	501 411
3.388	164	.0871	.0871	920
3.384	166	.0873	.0873	630
3.316	5	.0909	.0910	601
3.260	13	.0941	.0942	221
3.197	60	.0978	.0977 .0979	611 321
3.145	7	.1011	.1012	10,2,0
3.115	4	.1030	.1031	421
3.058	20	.1070	.1070	12,0,0
3.048	25	.1076	.1077	040
3.019	6	.1097	.1098	521
2.964	146	.1138	.1137	12,1,0
2.958	158	.1143	.1143	340
2.912	17	.1180	.1179	621
2.878	50	.1208	.1207	930
2.835	5	.1244	0.1244	901
2.827	9	.1251	.1248 .1256	031 131
2.799	7	.1277	.1276 .1278	721 231
2.783	76	.1315	.1311 .1315	911 331
2.732	80	.1340	.1339	12,2,0
2.727	78	.1344	.1344	640
2.684	12	.1388	.1387	821
2.643	7	.1432	.1434	531
2.569	77	.1515	.1514 .1516	921 631
2.490	6	.1613	.1612	731
2.442	5	.1677	.1675 .1678	12,3,0 940
2.416	9	.1713	.1712	12,0,1
2.411	10	.1720	.1719	041
2.405	6	.1729	.1727	141
2.370	52	.1780	.1779	12,1,1
2.366	64	.1787	.1786	341
2.325	22	.1850	.1850	931
2.245	33	.1984	.1982 .1987	12,2,1 641
2.158	4	.2147	.2146	12,4,0
2.095	10	.2278	.2277	15,3,0
2.091	14	.2286	.2284	950
2.078	10	.2316	.2314 .2318 .2321	15,0,1 12,3,1 941
2.072	10	.2330	.2325 .2332	051 151
1.9725	54	.2570	.2570	002
1.9681	35	.2582	.2583	15,2,1
1.9644	12	.2591	.2592	651
1.9473	4	.2637	.2637 .2637	012 302
1.9332	45	.2676	.2676	18,2,0
1.9278	48	.2691	.2690	660
1.9072	12	.2749	.2748 .2752	15,4,0 12,5,0
1.8671	15	.2869	.2869	222
1.8553	34	.2905	.2905 .2906	612 322
1.8503	20	.2921	.2919 .2926	15,3,1 951
1.8219	34	.3013	.3012	18,3,0
1.8178	53	.3026	.3024	960
1.8040	6	.3073	.3072	161
1.7924	10	.3113	.3107 .3116	622 18,1,1
1.7872	5	.3131	.3132	361
1.7749	8	.3174	.3172 .3176	902 032
1.7568	22	.3240	.3239 .3243	912 332
1.7397	12	.3303	.3304	170
1.7360	30	.3318	.3319	18,2,1
1.7305	60	.3339	.3332 .3343	661 21,1,0
1.7269	80	.3353	.3353	15,5,0
1.7238	55	.3365	.3364	370
1.7172	20	.3391	.3390 .3394	15,4,1 12,5,1
1.7045	20	.3442	.3441 .3443	922 632
1.6808	6	.3540	.3545	21,2,0
1.6703	7	.3583	.3584	16,5,0
1.6540	32	.3655	.3655	18,3,1
1.6513	40	.3667	.3666	961
1.6417	24	.3710	.3707 .3714	12,1,2 342
1.6273	7	.3776	.3777	932
1.5991	12	.3911	.3909 .3914	12,2,2 642
1.5921	9	.3946	.3947	171
1.5841	40	.3985	.3985	21,1,1
1.5818	46	.3997	.3996	15,5,1
1.5798	42	.4007	.4006	371
1.5635	10	.4091	.4089 .4094	18,5,0 15,6,0

[a] Interplaner spacing.
[b] Observed intensity.
[c] Indexed on the basis of an orthorhombic unit cell with $a=36.692$ Å, $b=12.191$ Å, $c=3.945$ Å.

For the 4:9 compound $n=3$. The composition of $n=2$ is $Nb_2O_5 \cdot WO_3$ and the composition of $n=4$ would be $2Nb_2O_5:7WO_3$. The 1:1 compound does not belong to the general homologous series but has a unique structure only vaguely related to the tetragonal tungsten bronze type, as previously described. The structure predicted for $2Nb_2O_5 \cdot 7WO_3$ would be either orthorhombic with one a-axis multiplied by four or tetragonal with both a-axes doubled. The latter structure, which exhibits a higher symmetry than the former, was found to occur for the 2:7 composition between a minimum temperature of about 1245 °C and the probable congruent melting point of 1357 °C. A crystal structure analysis of this compound is currently being conducted by N. Stephensen [28]. The unit cell dimensions of $Nb_4W_7O_{31}$ are $a=24.264$ Å, $c=3.924$ Å, and were obtained from the indexed x-ray diffraction powder pattern listed in table 10.

d. "$6Nb_2O_5 \cdot 11WO_3$" ($Nb_{12}W_{11}O_{63}$)

Roth and Wadsley [1] reported another compound in this system occurring at a ratio of about $13Nb_2O_5:24WO_3$. Kovba and Trunov [9] described a phase to which they assigned the composition $4Nb_2O_5:7WO_3$. The only logical ratio, near this composition, which could belong to the general formula $B_{10n+m}O_{30n+m}$ is $6Nb_2O_5:11WO_3$. In order to include this composition with the 4:9 and 2:7 compounds in one simplified formula, it is sufficient to postulate a series limited to the case $m=n+1$. The new homologous series formula then becomes $B_{11n+1}O_{31n+1}$. In this case for the 2:7 compound, $n=\infty$ and for $4Nb_2O_5 \cdot 9WO_3$, $n=3$. When $n=2$ the composition is $B_{23}O_{63}$ and the predicted structure has two bronze-like subcells in the unit cell, with three filled pentagonal holes. Such a structure would have a very low symmetry and is apparently not formed

Table 10. *X-ray diffraction powder data for the compound* $W_7Nb_4O_{31}$ *(CuK_α radiation)*

d [a]	I [b]	$\frac{1}{d^2}$ obs	$\frac{1}{d^2}$ calc	hkl [c]
10.84	10	0.0085	0.0085	210
8.56	8	.0136	.0136	220
6.06	8	.0272	.0272	400
5.43	35	.0340	.0340	420
4.508	8	.0493	.0493	520
4.289	18	.0544	.0544	440
4.046	5	.0611	.0612	600
3.996	5	.0626	.0628	610
3.924	194	.0649	.0649	001
3.839	256	.0679	.0679	620
3.792	25	.0696	.0696	540
3.735	10	.0717	.0717	201
3.617	16	.0764	.0764	630
3.429	25	.0850	.0849	710/550
3.366	136	.0883	.0883	640
3.333	8	.0900	.0900	720
3.265	10	.0938	.0938	411
3.181	52	.0989	.0989	421
3.052	7	.1074	.1074	501/431
3.034	18	.1086	.1087	800
2.942	146	.1155	.1155	820
2.898	5	.1191	.1193	441
2.860	31	0.1223	0.1223	660
2.838	8	.1242	.1240	830
2.822	8	.1256	.1257	750
2.816	10	.1261	.1261	601
2.743	98	.1329	.1329	621
2.713	102	.1359	.1359	840
2.660	10	.1414	.1414	631
2.851	18	.1500	.1499	711/551
2.555	50	.1532	.1533	641
2.473	8	.1635	.1635	731
2.399	5	.1737	.1737	801
2.349	50	.1804	.1804	821
2.311	10	.1872	.1872	661
2.290	5	.1907	.1906	751
2.232	40	.2008	.2008	841
2.177	5	.2209	.2208	11,3,0/970
2.128	12	.2308	.2310	10,6,0
2.064	14	.2347	.2348	10,0,1/861
1.9620	42	.2598	.2598	002
1.9182	60	.2718	.2718	12,4,0
1.8967	7	.2780	.2773 .2786	11,2,1/10,5,1 10,8,0
1.8664	9	0.2871	0.2869	402
1.8606	11	.2887	.2886	412
1.8447	24	.2939	.2937	422
1.8384	11	.2959	.2960	10,6,1
1.8189	12	.3023	.3022	502/432
1.8087	36	.3057	.3058	12,6,0
1.7878	7	.3129	.3129	11,5,1
1.7839	8	.3142	.3141 .3142	442 13,4,0/11,8,0
1.7468	20	.3277	.3277	622
1.7232	50	.3368	.3367	12,4,1
1.7160	104	.3396	.3397	14,2,0/10,10,0
1.6949	15	.3481	.3481	642
1.6825	6	.3533	.3533	12,8,0
1.6480	7	.3682	.3685	802
1.6426	30	.3706	.3707	12,6,1
1.6326	15	.3752	.3753	822
1.6177	4	.3822	.3821	662
1.5896	12	.3958	.3957	842
1.5720	63	.4047	.4047	14,2,1/10,10,1
1.5535	7	.4144	.4145	12,10,0

[a] Interplanar spacing

[b] Observed intensity.

[c] Indexed on the basis of a tetragonal unit cell with $a=24.264$ Å, $c=3.924$ Å.

in this system. Experimentally the compound "$6Nb_2O_5 \cdot 11WO_3$" was found to be orthorhombic, probably with the a-axis of the tetragonal bronze subcell tripled. It is stable from about 1210 °C to the apparently congruent melting point of 1378 °C. The x-ray diffraction powder pattern listed in table 11 is indexed with $a=36.740$ Å, $b=12.195$ Å, $c=3.951$ Å. It may be concluded from the size and symmetry of the unit cell, that the homologous series formula $B_{11n+1}O_{31n+1}$ is not correct for this compound. Therefore, "$6Nb_2O_5 \cdot 11WO_3$" either has a defect structure or belongs to some other structural homologous series, as yet unknown. A single crystal structure analysis is currently under study by N. Stephenson [28].

e. Metastable Tetragonal Bronze-Type Solid Solution ("3:8")

In addition to the ordered bronze-like phases which have been found in the Nb_2O_5–WO_3 system, another, apparently disordered, phase has also been reported at about the Nb_2O_5:$3WO_3$ composition [5, 6, 7]. In the present study a tetragonal bronze-type phase without any indication of superstructure in the powder pattern was found to occur from about 72 to 74 mole percent WO_3 in a temperature range from about 1100 to 1250 °C. The unit cell dimensions of this phase were found to vary from about $a=12.190$ Å, $c=3.968$ Å for the composition containing 72 mole percent WO_3 to $a=12.178$ Å, $c=3.930$ Å for the composition containing 75 mole percent WO_3. It must be concluded that the lower temperature phase is only metastable, because it decomposes at high temperatures into the two ordered compounds, $4Nb_2O_5 \cdot 9WO_3$ and $2Nb_2O_5 \cdot 7WO_3$.

3.4. Compounds Related to the ReO_3 Structure-Type. The Magneli "Shear Phases"

In the temperature interval from about 1270 to 1358 °C, at least two phases have been found to occur with x-ray diffraction powder patterns suggestive of the Magneli "shear phases" [29], which are structurally related to WO_3. These phases have been found to occur between about 91 and 94 mole percent WO_3. Due to the difficulty of obtaining equilibrium and the complex nature of the diffraction patterns, it is very difficult to decipher the exact composition of the phases by powder data alone. Although no single crystals have been examined, the best interpretation of the data suggests that there are two equilibrium phases having the Nb_2O_5:WO_3 ratios of 1:11 and 1:15. These compositions would correspond to the members $n=13$ and $n=17$ of the homologous series B_nO_{3n-1}. It is possible that other structurally related phases are formed in this compositional region which have very little or no thermal stability. Unindexed x-ray diffraction powder patterns for the "1:11" and "1:15" phases are given in tables 12 and 13, respectively.

3.5. Polymorphs of WO_3 and WO_3 Solid Solutions

WO_3 has been reported to occur in many different polymorphs [30–32]. None of the various high- or low-temperature polymorphs have been previously reported to be quenchable to room temperature. However, many of these reported phases have been found at room temperature in the Nb_2O_5–WO_3 system.

TABLE 11. *X-ray diffraction powder data for the phase "$6Nb_2O_5 \cdot 11WO_3$" (CuK_α radiation)*

d[a]	I[b]	$\frac{1}{d^2}$ obs	$\frac{1}{d^2}$ calc	hkl[c]
11.62	5	0.0074	0.0075	110
10.18	14	.0097	.0097	210
9.16	8	.0119	.0119	400
8.62	8	.0135	.0134	310
5.47	36	.0334	.0334	610
4.320	16	.0536	.0536	620
4.070	8	.0604	.0600 .0605	900 030
3.952	236	.0640	.0641	001
3.865	140	.0669	.0667 .0672	910 330
3.742	7	.0714	.0707 .0708 .0715	301 011 111
3.682	8	.0738	.0738	211
3.663	19	.0745	.0741 .0743	10,0,0 820
3.596	6	.0774	.0775	311
3.562	10	.0788	.0790	530
3.388	156	.0871	.0869 .0872	920 630
3.223	12	.0962	.0964	11,1,0
3.201	24	.0976	.0975 .0976	611 321
3.061	14	.1067	.1067	12,0,0
3.049	22	.1076	.1076	040
2.968	100	.1135	.1134	12,1 0
2.959	106	0.1142	0.1143	340
2.917	10	.1175	.1176	621
2.880	33	.1205	.1205	930
2.803	5	.1273	.1273	721
2.763	76	.1310	.1308 .1313	911 331
2.735	45	.1337	.1336	12,2,0
2.730	49	.1342	.1343	640
2.687	12	.1385	.1384	821
2.644	5	.1431	.1431	531
2.573	62	.1511	.1510 .1513	921 631
2.492	5	.1610	.1609	731
2.421	6	.1706	.1708	12,0,1
2.414	7	.1716	.1717	041
2.373	49	.1776	.1775	12,1,1
2.368	59	.1783	.1783	341
2.328	15	.1846	.1846	931
2.248	25	.1978	.1977	12,2,1
2.246	22	.1983	.1983	641
2.097	7	.2273	.2272	15,3,0
2.095	8	.2282	.2281	950
2.072	6	.2330	.2329	151
1.9754	85	.2563	.2563	002
1.9355	22	.2669	.2669	18,2,0
1.9290	26	.2688	.2688	660
1.9087	8	.2745	.2743 .2748	15,4,0 12,5,0
1.8696	7	.2861	.2861	222
1.8585	13	.2895	.2897 .2898	612 322
1.8528	15	.2913	.2913	15,3,1
1.8496	11	.2923	.2922	951
1.8239	25	.3006	.3006	18,3,0
1.8195	32	.3021	.3021	960
1.7593	23	.3231	.3230 .3235	912 332
1.7384	22	.3309	.3302 .3310	170 18,2,1
1.7332	33	.3329	.3328	661
1.7317	35	.3335	.3334	21,1,0
1.7284	52	.3348	.3348	15,5,0
1.7244	51	.3363	.3362	370
1.7184	8	.3386	.3384 .3389	15,4,1 12,5,1
1.7072	22	.3431	.3432 .3435	922 631
1.6559	15	.3647	.3646	18,3,1
1.6524	25	.3663	.3662	961
1.6442	22	.3699	.3697 .3705	12,1,2 342
1.6294	8	.3766	.3768	932
1.6012	12	.3901	.3899 .3905	12,2,2 642
1.5926	5	.3943	.3943	171
1.5858	25	.3977	.3975	21,1,1
1.5833	32	.3989	.3989	15,5,1
1.5801	24	.4005	.4002	371
1.5654	5	.4081	.4081	18,5,0
1.5640	7	.4089	.4088	15,6,0

[a] Interplanar spacing.
[b] Observed intensity.
[c] Indexed on the basis of an orthorhombic unit cell with $a=36.740$ Å, $b=12.195$ Å, $c=3.951$ Å.

a. Room Temperature Monoclinic Polymorph

A monoclinic polymorph of WO_3 was reported by Tanisaki [32] to have a monoclinic unit cell with $a=7.30$ Å, $b=7.53$ Å, $c=7.68$ Å, $\beta=90°54'$ at room temperature. However, the x-ray diffraction powder pattern can be completely indexed with the c-axis equal to one-half that of the true unit cell. The presence of superstructure requiring the doubled cell can apparently only be found with single crystal data. For this reason, the x-ray diffraction powder pattern listed in table 14 has been indexed on the basis of one-half the real c-axis value. The unit cell dimensions obtained from this pattern were found to be $a=7.299$ Å, $b=7.535$ Å, $c=7.688$ (3.844) Å, $\beta=90°54'$. With 1 mole percent solid solution of Nb_2O_5 in WO_3, the parameters are changed to $a=7.317$ Å, $b=7.532$ Å, $c=7.684$ (3.842) Å, $\beta=90°55'$. For pure WO_3 this monoclinic polymorph is apparently stable from about 17 °C [32] to about 310 °C.

TABLE 12. *X-ray diffraction powder data for the composition Nb_2O_5:$11WO_3$ (CuK_α radiation)*

d[a]	I[b]
4.638	5
4.308	7
3.966	25
3.850	350
3.726	230
3.690	350
3.116B	15
2.764B	10
2.677	178
2.670	190
2.579	28
2.202	25
2.190	25
2.139	12
1.998B	10
1.927	90
1.910	30
1.865	58
1.845	90
1.812B	18
1.712	32
1.700	14
1.677	100
1.664	50
1.569	8
1.541	18
1.530	25
1.493B	10

B = broad.
[a] Interplaner spacing.
[b] Observed intensity.

TABLE 13. *X-ray diffraction powder data for the composition Nb_2O_5:$15WO_3$ (CuK_α radiation)*

d[a]	I[b]
3.931	25
3.839	284
3.760	116
3.682	336
3.134	10
3.089	23
2.763	7
2.676	140
2.647	96
2.584	18
2.214	14
2.181	30
2.152	12
2.006B	10
1.922	58
1.898	27
1.869	65
1.855	20
1.841	40
1.812B	15
1.799	25
1.711	23
1.695	20
1.671B	65
1.652	15
1.573	8
1.555	10
1.546	15
1.529	34
1.525	30

B = broad.
[a] Interplaner spacing.
[b] Observed intensity.

b. Low-Temperature Triclinic Polymorph

According to Tanisaki [32] the room temperature polymorph of WO_3 transforms to a triclinic form at about 17 °C, on cooling. However, on reheating there is still some of the triclinic form remaining at room temperature, indicating some hysteresis in the phase transition. It was found in the present study, that the room temperature monoclinic polymorph could be partially transformed to the triclinic modification by grinding the specimen in a mortar and pestle, without lowering the temperature. The unit cell dimensions of the triclinic form were reported [32] as $a=7.30$ Å, $b=7.52$ Å, $c=7.69$ Å, $\alpha=88°50'$, $\beta=90°55'$, $\gamma=90°56'$. The indexed x-ray diffraction

TABLE 14. *X-ray diffraction powder data for the room temperature (monoclinic) form of* WO_3 *(*CuK_α *radiation)*

d [a]	I [b]	$\frac{1}{d^2}$ obs	$\frac{1}{d^2}$ calc	hkl [c]
3.840	154	0.0678	0.0677	001
3.761	160	.0707	.0705	020
3.646	268	.0752	.0751	200
3.419	5	.0856	.0853	011
3.344	65	.0894	.0892	120
3.114	70	.1031	.1030	$11\bar{1}$
3.083	50	.1052	.1052	111
2.689	132	.1383	.1382	021
2.667	72	.1407	.1406	210
2.629	54	.1447	.1450	$20\bar{1}$
2.620	152	.1457	.1455	220
2.533	22	.1559	.1558	$12\bar{1}$
2.514	27	.1582	.1580	121
2.176	38	.2112	.2110	$22\bar{1}$
2.154	36	.2156	.2155	221
2.103	6	.2262	.2262	031
2.043	17	.2395	.2394	320
2.025	12	.2438	.2439	$13\bar{1}$
2.016	14	.2461	.2461	131
1.9955	20	.2511	.2509	$31\bar{1}$
1.9709	12	.2574	.2576	311
1.9216	44	.2708	.2708	002
1.8838	60	.2818	.2818	040
1.8246	133	.3004	.3004 .3006	400 140
1.8111	45	0.3049	0.3050	$11\bar{2}$
1.7977	42	.3094	.3094	112
1.7116	48	.3414	.3413 .3414	022 $20\bar{2}$
1.6914	40	.3495	.3495	041
1.6894	32	.3504	.3504	202
1.6740	35	.3569	.3569	240
1.6581	34	.3637	.3636	$40\bar{1}$
1.6504	24	.3671	.3672	$14\bar{1}$
1.6455	42	.3693	.3694	141
1.6423	80	.3708	.3708	420
1.6385	50	.3725	.3725	401
1.6231	5	.3919	.3918	$33\bar{1}$
1.5843	5	.3984	.3985	331
1.5584	30	.4117	.4119	$22\bar{2}$
1.5419	32	.4206	.4208	222
1.5384	27	.4225	.4224	$24\bar{1}$
1.5312	10	.4265	-4268	241
1.5179	15	.4341	.4341	$42\bar{1}$
1.5029	20	.4427	.4430	421
1.4981	22	.4456	.4459	$13\bar{2}$
1.4899	42	.4505	.4503 .4507 .4508	132 $31\bar{2}$ 340
1.4679	14	.4641	.4641	312

[a] Interplaner spacing.
[b] Observed intensity.
[c] Indexed on the basis of a monoclinic unit cell with $a = 7.299$ Å, $b = 7.535$ Å, $c = 3.844$ Å ($\frac{1}{2} \times 7.688$ Å), $\beta = 90°54'$.

powder pattern of the triclinic polymorph obtained at room temperature from a specimen which had been removed from liquid nitrogen, is listed in table 15. The value of the *c*-axis was again halved, as the larger value is not necessary to index the powder pattern. According to Tanisaki, this phase is stable from about -40 °C to about 17 °C. The triclinic polymorph was never observed in any of the Nb_2O_5–WO_3 solid solutions.

c. Lowest Temperature Polymorph (Monoclinic)

From about -40 °C to below liquid nitrogen temperature, another monoclinic polymorph occurs in pure WO_3 which was reported by Tanisaki [32] to have $a = 5.27$ Å, $b = 5.16$ Å, $c = 7.67$ Å, $\beta = 91°43'$. This polymorph can be obtained essentially single phase at room temperature by *quenching* a solid solution of $2Nb_2O_5 : 98WO_3$ from the temperature interval 1230 °C to about 1385 °C, the solidus temperature. This polymorph also occurs as a mixture with other polymorphs in specimens containing 1 and 3 mole percent Nb_2O_5. The unit cell dimensions obtained from the powder pattern for the 2 mole percent Nb_2O_5 specimen are $a = 5.305$ Å, $b = 5.192$ Å, $c = 7.671$ Å, $\beta = 91°33'$. The indexed x-ray diffraction powder pattern is given in table 16, utilizing the 7.671 Å value for *c* as several peaks necessitating this doubled value are observed in the powder pattern. High-temperature x-ray patterns show this phase to be apparently stable in the 2 mole percent Nb_2O_5 composition up to a temperature of about 735 °C, at which temperature it transforms to a tetragonal polymorph. If the temperature is not raised above about 750 °C, this transition is reversible. However, if the temperature is raised to 900 °C the low-temperature monoclinic polymorph is not recovered and the tetragonal phase transforms to the orthorhombic polymorph.

Tungsten trioxide has been reported to be ferroelectric below about -40 °C [33]. Specimens of sintered WO_3 containing 2 to 4 mole percent Ta_2O_5 were reported to exhibit ferroelectric behavior at room temperature [34]. The low-temperature monoclinic polymorph formed by quenching a specimen containing 2 mole percent Nb_2O_5 was examined for evidence of ferroelectricity [35]. However, no conclusive ferroelectric properties could be found.

TABLE 15. *X-ray diffraction powder data for the triclinic form of* WO_3 *(*CuK_α *radiation)*

d [a]	I [b]	$\frac{1}{d^2}$ obs	$\frac{1}{d^2}$ calc	hkl [c]
3.840	284	0.0678	0.0677	001
3.760	224	.0707	.0707	020
3.652	350	.0750	.0749	200
3.362	20	.0885	.0885	$\bar{1}20$
3.322	25	.0906	.0906	120
3.143	42	.1012	.1013	$\overline{111}$
3.099	20	.1041	.1042	$\bar{1}11$
3.085	65	.1051	.1051	$1\bar{1}1$
3.070	42	.1061	.1059	$11\bar{1}$
2.714	55	.1359	.1358	$02\bar{1}$
2.667	108	.1407	.1407	$20\bar{1}$
2.660	102	.1413	.1413	021
2.640	80	.1435	.1435	$\bar{2}20$
2.632	93	.1443	.1443	201
2.600	58	.1480	.1477	220
2.562	13	.1524	.1524	$\overline{121}$
2.527	11	.1567	.1564	$\bar{1}21$
2.501	15	.1598	.1598	$12\bar{1}$
2.500	17	.1600	.1600	$1\bar{2}1$
2.202	20	.2063	.2066	$22\bar{1}$
2.159	20	0.2145	0.2145	$\bar{2}21$
2.154	53	.2155	.2158	$22\bar{1}$
2.150	51	.2163	.2163	$2\bar{2}1$
2.120	3	.2224	.2227	$03\bar{1}$
2.082	5	.2306	.2310	031
2.059	4	.2358	.2360	$\bar{3}20$
2.046	8	.2388	.2389	$13\bar{1}$
2.032	5	.2422	.2423	320
2.025	10	.2439	.2439	$\bar{1}31$
2.011	9	.2474	.2481	$31\bar{1}$
2.005	12	.2487	.2490	$13\bar{1}$
1.9985	10	.2504	.2503	$1\bar{3}1$
1.9844	9	.2540	.2540	$3\bar{1}1$
1.9746	12	.2565	.2564	$31\bar{1}$
1.9713	14	.2573	.2568	$\bar{3}11$
1.9216	48	.2708	.2708	002
1.8801	52	.2829	.2829	040
1.8273	148	.2995	.2995 .2995	400 $\bar{1}40$
1.8198	44	.3020	.3021	$\overline{112}$
1.8040	26	0.3073	0.3068	$\bar{1}12$
1.8007	43	.3084	.3086	$1\bar{1}2$
1.7931	26	.3110	.3113	$11\bar{2}$
1.7244	17	.3363	.3360	$02\bar{2}$
1.7113	24	.3415	.3420	$20\bar{2}$
1.7013	23	.3455	.3451 .3457	$04\bar{1}$ 202
1.6975	22	.3470	.3470	022
1.6897	17	.3503	.3506	041
1.6825	13	.3533	.3536	$\bar{2}40$
1.6653	16	.3606	.3608	$\bar{1}41$
1.6612	52	.3624	.3620	240
1.6570	31	.3642	.3635	$40\bar{1}$
1.6537	28	.3657	.3660	$\bar{4}20$
1.6502	33	.3672	.3669 .3672	$\bar{1}41$ 401
1.6358	30	.3738	.3736	$14\bar{1}$
1.6337	35	.3747	.3744	420
1.6303	18	.3763	.3760	$1\bar{4}1$

[a] Interplaner spacing.
[b] Observed intensity.
[c] Indexed on the basis of a triclinic unit cell with $a = 7.30$ Å, $b = 7.52$ Å, $c = 3.845$ Å ($\frac{1}{2} \times 7.69$ Å), $\alpha = 88°50'$, $\beta = 90°55'$, $\gamma = 90°56'$.

TABLE 16. *X-ray diffraction powder data for the low-temperature monoclinic form of* WO_3 *taken from* $2Nb_2O_5 : 98WO_3$ *solid solution* (*CuK_a radiation*)

d [a]	I [b]	$\frac{1}{d^2}$ obs	$\frac{1}{d^2}$ calc	hkl [c]	d [a]	I [b]	$\frac{1}{d^2}$ obs	$\frac{1}{d^2}$ calc	hkl [c]
3.834	400	0.0680	0.0680	002	1.7990	54	0.3090	0.3090	014
3.703	380	.0729	.0729	110	1.7875	28	.3130	.3130	104
3.145	25	.1011	.1011	$10\bar{2}$	1.7163	37	.3395	.3394	$11\bar{4}$
3.083	50	.1052	.1051	012	1.6900	25	.3501	.3501	114
3.067	32	.1063	.1064	102	1.6805	37	.3541	.3542	$22\bar{2}$
2.691	138	.1381	.1382	112	1.6692	41	.3589	.3592	310
2.641	144	.1433	.1432 .1435	200 112	1.6557 1.6448	28 26	.3648 .3697	.3648 .3696	222 130
2.594	40	.1486	.1484	020	1.6179	4	.3820	.3821	$30\bar{2}$
2.458	6	.1655	.1654	021	1.5851	4	.3980	.3981	302
2.294	10	.1900	.1900	013					
					1.5776	5	.4018	.4018	032
2.236	5	.2000	.1998 .1999	121 211	1.5729 1.5464	10 18	.4042 .4195	.4044 .4192	$20\bar{4}$ $31\bar{2}$
2.206	22	.2056	.2058	$20\bar{2}$	1.5422	21	.4205	.4202	024
2.148	70	.2167	.2163 .2165	022 202	1.5326	6	.4257	.4257	204
2.120	12	.2429	.2429	$21\bar{2}$					
2.002	14	.2496	.2495	$12\bar{2}$	1.5161	28	.4351	.4349 .4352	$13\bar{2}$ 312
1.9860	17	.2535	.2536	212	1.5056	26	.4412	.4402 .4415	132 $21\bar{4}$
1.9815	18	.2547	.2548	122	1.4895	13	.4508	.4507	$12\bar{4}$
1.9178	68	.2719	.2719	004					
1.8521	100	.2915	.2915	220	1.4700	24	.4621	.4614 .4628	124 214
1.8192	27	.3022	.3023	$10\bar{4}$					

[a] Interplaner spacing.

[b] Observed intensity.

[c] Indexed on the basis of a monoclinic unit cell with $a=5.305$ Å, $b=5.192$ Å, $c=7.671$ Å, $\beta=91°33'$.

d. High-Temperature Orthorhombic Polymorph

Although no thermal effect was indicated with DTA, the room-temperature monoclinic polymorph of pure WO_3 is observed in the high temperature x-ray furnace to transform reversibly at 310 °C to an orthorhombic phase in agreement with Wyart and Foex [31]. This orthorhombic form is observed at room temperature in the solid solutions whenever the low-temperature monoclinic polymorph is heated to about 900 °C and cooled by removing from the furnace. The indexed x-ray diffraction powder pattern of a specimen of this polymorph containing 2 mole percent Nb_2O_5 is listed in table 17. It shows no indication of a doubled *c*-axis and is indexed on the basis of the smaller orthorhombic cell. The unit cell dimensions obtained for this composition, at room temperature, are $a=7.384$ Å, $b=7.512$ Å, $c=7.692$ (3.846) Å. The orthorhombic phase is observed in this composition to transform to tetragonal in the high temperature x-ray furnace at 510 °C and the reverse transition was observed to take place at 440 °C.

e. Tetragonal High-Temperature Polymorph(s)

In pure WO_3 the orthorhombic polymorph was found to undergo a transition to the tetragonal form at about 750 °C in the high-temperature x-ray furnace. The DTA data indicated that the phase transition occurred at a temperature of 740 °C on heating and 730 °C on cooling. These results are in reasonable agreement with those of previous workers [7, 31]. The tetragonal polymorph is found as a single phase as low as 440 °C in the specimen containing 2 mole percent Nb_2O_5. However, in the 3 mole percent Nb_2O_5 specimen, the low-temperature monoclinic polymorph transforms after heating at about 900 °C into a mixture consisting predominantly of a tetragonal modification with only a trace of the orthorhombic form. The unit cell dimensions obtained at room temperature from this composition are $a=5.265$ Å, $c=3.846$ Å, and the x-ray diffraction powder pattern from which the data were obtained, indexed on the basis of the smaller cell, is listed in table 18.

In addition to the transformation at 730–740 °C, another transition is observed at about 900 °C in pure WO_3, as indicated by a very small peak in the DTA pattern. High-temperature x-ray diffraction powder patterns indicate that WO_3 is tetragonal both above and below this minor thermal discontinuity. It is possible that the unit cell has a doubled *c*-axes below 900 °C and only above this temperature does the powder pattern yield the correct unit cell. However, this hypothesis cannot be verified without single crystal data.

Although WO_3 might be expected to have a cubic polymorph of the ReO_3-type, there is no evidence in either the present work or previously reported studies that such a polymorph exists.

TABLE 17. *X-ray diffraction powder data for the orthorhombic form of* WO_3 *taken from* $2Nb_2O_5:98WO_3$ *solid solution* (*CuK_a radiation*)

d [a]	I [b]	$\frac{1}{d^2}$ obs	$\frac{1}{d^2}$ calc	hkl [c]
3.845	248	0.0676	0.0676	001
3.754	156	.0710	.0709	020
3.691	232	.0734	.0734	200
3.427	5	.0852	.0853	011
3.346	18	.0893	.0892	120
3.104	60	.1038	.1037	111
2.686	85	.1386	.1385	021
2.662	80	.1411	.1409	201
2.633	126	.1443	.1442	220
2.525	10	.1568	.1568	121
2.173	42	.2119	.2118	221
2.099	5	.2270	.2271	031
2.056	5	.2365	.2359	320
2.018	20	.2455	.2454	131
1.9976	14	.2506	.2504	311
1.9232	48	.2704	.2704	002
1.8779	33	.2836	.2836	040
1.8461	46	.2934	.2934	400
1.8198	21	.3020	.3019	140
1.8064	37	.3065	.3064	112
1.7119	24	.3412	.3413	022
1.7057	25	.3437	.3437	202
1.6879	35	.3510	.3512	041
1.6740	26	.3569	.3569	240
1.6645	32	.3609	.3610	401
1.6568	34	.3643	.3643	420
1.6453	14	.3694	.3695	141
1.5968	5	.3922	.3922	331
1.5530	10	.4147	.4146	222
1.5349	17	.4244	.4245	241
1.5217	20	.4319	.4319	421
1.4933	16	.4484	.4482 .4486	132 340
1.4858	13	.4530	.4531	312

[a] Interplaner spacing.

[b] Observed intensity.

[c] Indexed on the basis of an orthorhombic unit cell with $a=7.384$ Å, $b=7.512$ Å, $c=3.846$ Å ($\frac{1}{2}\times 7.692$ Å).

TABLE 18. *X-ray diffraction powder data for the tetragonal form of* WO_3 *taken from* $3Nb_2O_5 : 97WO_3$ *solid solution* (CuK_α *radiation*)

d [a]	I [b]	$\frac{1}{d^2}$ obs	$\frac{1}{d^2}$ calc	hkl [c]
3.847	280	0.0676	0.0676	001
3.725	252	.0721	.0722	110
3.106	58	.1037	.1037	101
2.674	116	.1398	.1398	111
2.638	96	.1438	.1443	200
2.173	40	.2118	.2119	201
2.008	25	.2481	.2480	211
1.923	45	.2705	.2705	002
1.861	48	.2886	.2886	220
1.806	42	.3067	.3066	102
1.707	26	.3430	.3426	112
1.675	40	.3566	.3563	201
1.665	48	.3606	.3608	310
1.597	5	.3922	.3923	301
1.552	8	.4150	.4148	202
1.528	28	.4284	.4284	311
1.489	15	.4510	.4509	212

[a] Interplanar spacing.
[b] Observed intensity.
[c] Indexed on the basis of a tetragonal unit cell with $a = 5.265$ Å, $c = 3.846$ Å.

4. Discussion of Phase Equilibria

The postulated phase equilibrium diagram of the binary system $Nb_2O_5-WO_3$ is shown in figure 1. The experimental data from which this diagram was constructed are given in table 19. The system contains four compounds which are shown as melting congruently, $6Nb_2O_5 \cdot WO_3$, "$6Nb_2O_5 \cdot 11WO_3$," $4Nb_2O_5 \cdot 9WO_3$, and $2Nb_2O_5 \cdot 7WO_3$. Six compounds melt incongruently "$30Nb_2O_5 \cdot WO_3$," $7Nb_2O_5 \cdot 3WO_3$, $8Nb_2O_5 \cdot 5WO_3$, $9Nb_2O_5 \cdot 8WO_3$, and the two Magneli phases estimated to be "$Nb_2O_5 \cdot 11WO_3$" and "$Nb_2O_5 \cdot 15WO_3$." In addition, two stable phases, $13Nb_2O_5 \cdot 4WO_3$ and $Nb_2O_5 \cdot WO_3$ dissociate before melting as does the apparently metastable disordered bronze type solid solution labeled "3 : 8" in the phase diagram. Six of the compounds (8 : 5, 9 : 8, "6 : 11", 2 : 7, "1 : 11," and "1 : 15") are shown on the phase diagram as having minimum stability temperatures. In many of these cases, it is impossible to determine whether or not the minimum temperature represents a stable transition. The existence of solid solution could neither be definitely established in any of the compounds nor in Nb_2O_5. However, WO_3 accepts a maximum of about 3 mole percent Nb_2O_5 in solid solution.

The solidus temperature between the "30 : 1" phase and $6Nb_2O_5 \cdot WO_3$ has been found to be about 1464 °C. The exact eutectic composition has not been determined but probably exists between about 7 and 10 mole percent WO_3. The peritectic corresponding to the incongruent melting point of $7Nb_2O_5 \cdot 3WO_3$ occurs at 1440 °C and about 40 mole percent WO_3. However, the composition of the two peritectics at 1385 and 1375 °C and of the eutectic at 1364 °C, were not determined exactly. They probably occur between about 60 and 63 mole percent WO_3.

Both the 8:5 and 9:8 compounds apparently have minimum temperatures of stability. However, all efforts to locate accurately the temperature of these minimums proved inconclusive (table 19). For both compounds, the experimental temperature at which the phase begins to form on heating and the temperature at which it begins to dissociate on cooling had a wide range of overlap. Furthermore, the actual temperature of the minimum stability seemed to be strongly dependent on the purity content (table 19, parts I and II). For these reasons the minimum stability temperatures of the 8:5 and 9:8 are indicated on the phase diagram by dashed lines and the temperatures assigned to each, ~ 1090 and ~ 1265 °C, respectively, represent the best compromise between the inconsistencies in the experimental data.

None of the ordered bronze-type phases can be prepared in reasonable laboratory time at 1100 °C. The "6:11" phase was not found to be well crystallized below about 1210 °C. The minimum line at this temperature is dashed to indicate uncertainty in both the temperature value and the stability relation. The same discussion also is relative for the minimum value of the 2:7. In this case, however, the superstructure lines characteristic of this phase do not begin to appear below about 1245 °C. The three ordered bronze-type phases, "6:11", 4:9, and 2:7, all appear to melt congruently at 1378, 1380 and 1357 °C, respectively. The solidus temperatures between these phases at 1365 and 1335°C appear to be measurably lower than the observed melting temperature of the compounds. However, no eutectic compositions could be experimentally determined, possibly due to reduction and, therefore, the liquidus curves are necessarily dashed (see discussion on reduction in sec. 5).

The ability to distinguish a two-phase region between the two bronze-type phases $4Nb_2O_5 \cdot 9WO_3$ and $2Nb_2O_5 \cdot 7WO_3$ was greatly increased by a separation of those phases in the experiments of long-time duration. The top of the specimens within the two-phase region showed only 4:9 in the x-ray diffraction pattern while the bottom of the specimen showed mostly 2:7. This apparent gravity separation is probably enhanced by an appreciable vapor phase in the sealed Pt tube and is considered to be due mainly to vapor transport. A similar gravity separation takes place throughout most of the system and adds more evidence to the probability of a two-phase region between "$6Nb_2O_5 \cdot 11WO_3$" and $4Nb_2O_5 \cdot 9WO_3$. This two-phase region is based mostly on the different morphology and color of these phases, as well as the slight differences in the superstructure exhibited by single crystal patterns. Almost all of the high-temperature phases in the Nb_2O_5-WO_3 system are needle formers. Most of those which contain appreciable WO_3 are yellow-green or blue-green in color. However, the "6:11" phase is white and forms tabular crystals rather than needles.

A eutectic exists between the 2:7 compound and the Magneli "shear" phases at about 1340 °C and 83 mole percent WO_3. However, the exact compositions of the peritectics at 1356 and 1358 °C, corresponding to the decomposition temperatures have not been determined.

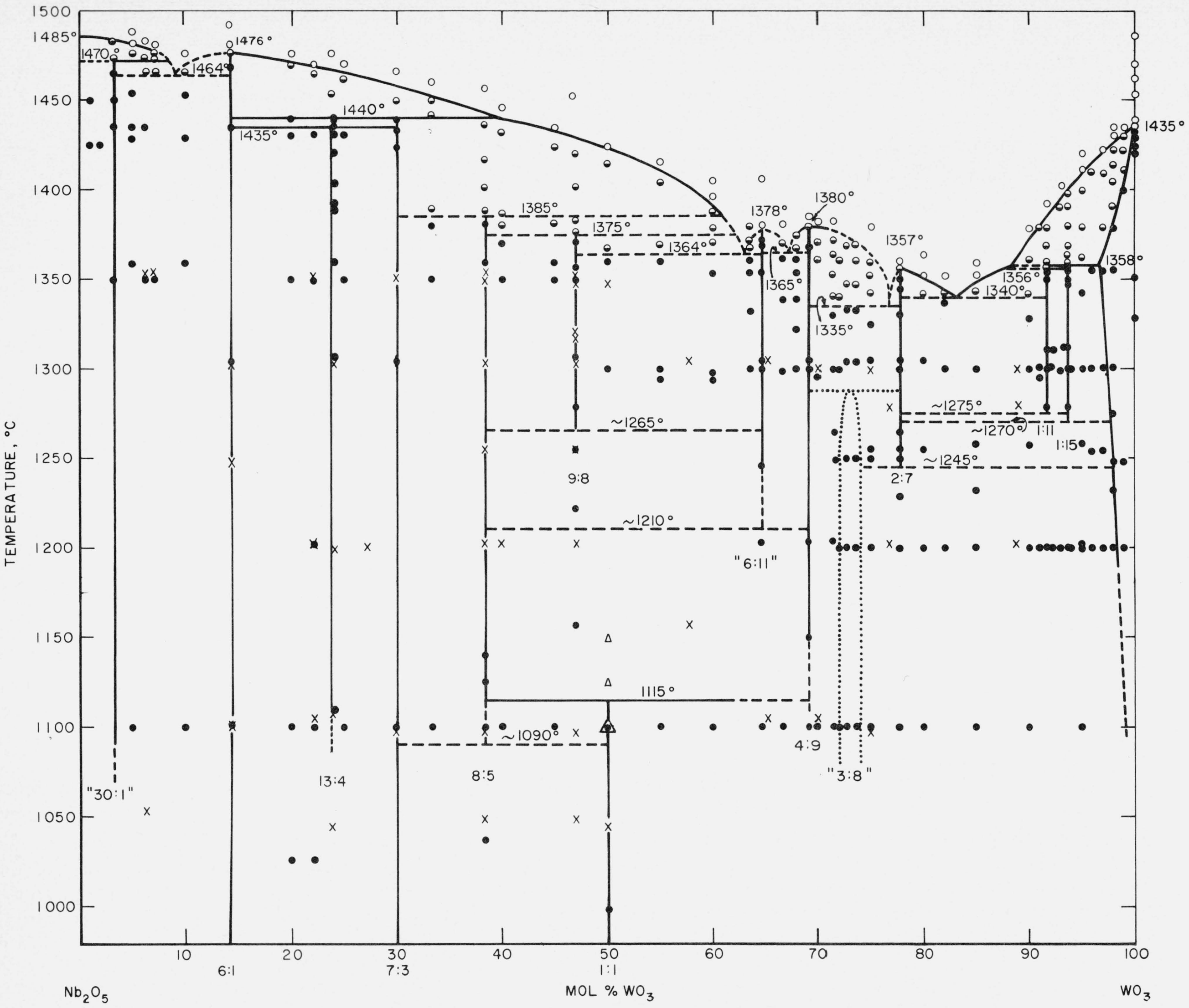

FIGURE 1. *Postulated phase equilibrium diagram of the binary system* Nb_2O_5-WO_3.

Heavy lines represent well-established portions of the system and dashed lines represent not as well-established portions. Dotted lines represent persistent metastable equilibrium.

● — not melted.

◒ — partially melted.

○ — completely melted.

× — experimental data obtained from "less-pure" materials.

△ — high-temperature x-ray data.

Tungsten trioxide has been found to accept a maximum of about 3 mole percent Nb_2O_5 in solid solution at the solidus temperature of 1358 °C. The amount of solid solution decreases with decreasing temperature to about 2 mole percent at 1230 °C and less than 1 mole percent at 1100 °C. The melting point of WO_3 was found, in the present study, to be 1435 °C. This value was independently confirmed by E. M. Levin [36] and is in disagreement with the previously published value of 1472 °C (Jaeger and Germs) [37]. In a discussion of the 1472 °C value for the melting point of WO_3, Phillips and Chang [38] concluded that this temperature was probably too low and might actually represent the eutectic between WO_3 and $W_{20}O_{58}$. However, they did not attempt to experimentally determine the melting points of the compounds WO_3 and $W_{20}O_{58}$ or the solidus temperature between them. The 1435 °C value for the melting point of WO_3 is internally consistent with the experimental phase diagram of both the Nb_2O_5-WO_3 and WO_3-B_2O_3 systems [36]. This value apparently represents the practical melting point for the experimental conditions utilized: sealed Pt tube, heated for very short intervals of time (≦5 min). This method is preferable to that of Jaeger and Germs [37] who utilized an open Pt crucible and much longer heating time. However, the true melting point of WO_3 can probably only be established by utilizing an oxygen pressure furnace and extrapolating to one atmosphere pressure.

TABLE 19. *Experimental data for compositions in the binary system* Nb_2O_5–WO_3. *Part I*

Composition		Heat treatments				Results	
		Initial[a]		Final[b]		Physical observation	X-ray diffraction analyses[c]
Nb_2O_5	WO_3	Temp.	Time	Temp.	Time		
Mole %	*Mole %*	*°C*	*Hour*	*°C*	*Hour*		
99	1			1425	65	No melting	Nb_2O_5.
				1450	66	do	Nb_2O_5.
98	2			1425	65	No melting	Nb_2O_5 + "30:1".
96.77	3.23	1350	2			No melting	
(30:1)				1435	46	do	"30:1".
				1450	66	do	"30:1".
				1465	1	No melting (?)	"30:1".
				1474	0.5	Partially melted	"30:1".
				1483	.5	do	
95	5			1100[d]	60	No melting	"30:1"+Nb_2O_5 (?)+6:1 (?)[e].
		1359	2			do	"30:1"+6:1 (?).
				1429	88	do	"30:1"+6:1 (?).
				1435	46	do	"30:1"+6:1 (?)
				1454	1	do	"30:1"+6:1 (?)
				1476	1	Partially melted	"30:1"+6:1.
				1481	1	Completely melted	
				1488	0.833	do	Low Nb_2O_5.
93.75	6.25	1350	2				
(15:1)				1435	46	No melting	"30:1" +6:1.
				1468	0.5	Partially melted	"30:1"+6:1.
				1474	.5	do	"30:1"+6:1.
				1483	.5	Completely melted	
92.86	7.14	1350	2				
(13:1)				1466	0.5	Partially melted	6:1+"30:1" (?)
				1473	.117	do	
				1476	.5	do	6:1 (+unknown).
				1478	16.5	do	6:1.
				1481	0.5	Completely melted	
90	10			1100[d]	60	No melting	6:1+"30:1".
		1359	2			do	6:1+"30:1" (?).
				1429	88	do	6:1+"30:1" (?).
				1453	1	do	6:1+"30:1" (?).
				1466	1	Partially melted	
				1476	1	Completely melted	6:1+low Nb_2O_5.
85.71	14.29			1100[d]	60	No melting	6:1.
(6:1)		1304	2			do	6:1.
				1435	0.25	do	
				1467	.25	do	6:1.
				1476	.5	Partially melted	
				1481	.5	Completely melted	6:1+low Nb_2O_5.
				1492	.25	do	Low Nb_2O_5.
80	20			1026	136	No melting	6:1+7:3 (+unknown tr)[e].
				1100[d]	60	do	6:1+7:3.
				1102	65	do	6:1+7:3+13:4 (+unknown)[e].
		1350	2			do	6:1+7:3+13:4 (tr)[e].
				1430	1	do	6:1+13:4+7:3 (tr)[e].
				1431	17	do	6:1+13:4+7:3 (tr)[e].
				1440	1	do	6:1+7:3.
				1470	0.5	Partially melted	
				1476	.5	Completely melted	
77.78	22.22			1026	136	No melting	6:1+7:3 (+unknown tr)[e].
(7:2)				1100[d]	60	do	6:1+7:3+13:4 (+unknown tr)[e].
				1102	65	do	6:1+7:3+unknown+13:4 (tr)[e].
				1202	20	do	6:1+7:3 (+unknown tr)[e].
		1350	2			do	
7:2 (con)				1431	0.5	do	13:4+6:1+7:3[e].
				1465	.5	Partially melted	
				1470	.5	Completely melted	
76.19	23.81			1109	2	No melting	6:1+7:3+unknown[e].
(16:5)				1110	18	do	7:3+unknown+6:1 (?)[e].
				1307	1	do	6:1+7:3[e].
		1360	2			do	
				1389	119	do	
				1393	88	do	13:4.
				1404	0.25	do	
				1421	.25	do	
				1431	17	do	13:4+6:1+7:3 (?)[e].
				1452	0.5	Partially melted	
				1476	.25	Completely melted	
		1360	2				
		1389	119				
		900	0.33			No melting	13:4.
				1435	1.25	do	13:4.
				1439	17	do	13:4+7:3+6:1 (?)[e].
				1440	1	do	13:4+7:3+6:1 (?)[e].
				1454	1	Partially melted	13:4+6:1+7:3 (?)[e].
75	25			1100[d]	60	No melting	7:3+6:1+13:4[e].
				1102	65	do	7:3+6:1+13:4+unknown[e].
		1350	2			do	
				1431	17	do	13:4+7:3 (?).
				1462	0.5	Partially melted	
				1470	.5	Completely melted	
70	30			1100[d]	60	No melting	7:3+"bronze" (tr)[e].
(7:3)		1304	2			do	7:3.
				1423	1	do	

TABLE 19. *Experimental data for compositions in the binary system* Nb_2O_5–WO_3. *Part I*—Continued.

Composition		Heat treatments				Results	
		Initial [a]		Final[b]		Physical observation	X-ray diffraction analyses[c]
Nb_2O_5	WO_3	Temp.	Time	Temp.	Time		
Mole %	*Mole %*	*°C*	*Hour*	*°C*	*Hour*		
				1434	1	do	7:3.
				1439	17	do	7:3.
				1449	0.583	Partially melted	
				1466	.33	Completely melted	
66.67	33.33			1100 [d]	60	No melting	7:3 + 1:1 + “bronze” (tr) [e].
		1350	2			do	
				1381	1	do	7:3 + 8:5.
				1389	1	Partially melted (?)	
				1442	0.5	Partially melted	
				1450	.5	do	
				1461	.5	Completely melted	
61.54	38.46			1037	236	No melting	7:3 + 1:1.
(8:5)				1100 [d]	60	do	7:3 + 1:1 + “bronze” (tr) [e].
				1100	167	do	7:3 + 1:1 + 8:5 [e].
				1125	160	do	8:5 + 1:1 + 7:3 [e].
				1140	65	do	8:5 + 1:1 + 7:3 [e].
		1357	3.5			do	
				1037	236	do	8:5 + 1:1 (tr) [e].
				1100	167	do	8:5 + 1:1 (tr) [e].
				1125	160	do	
				1140	65	do	
		1359	2			do	8:5.
				1381	2	do	8:5 + 7:3 [f].
				1388	2	Partially melted (?)	7:3 + 8:5 (tr).
				1402	2	do	7:3.
				1417	1	do	
				1437	1	do	
				1457	0.5	Completely melted	
60	40			1100 [d]	60	No melting	7:3 + 1:1 + “bronze” (tr) [e].
		1350	2			do	
				1371	1	do	8:5 + 9:8 (tr).
				1381	1	Partially melted (?)	8:5.
				1387	1	Partially melted	
				1433	1	do	
				1446	0.5	Completely melted	
55	45			1100 [d]	60	No melting	1:1 + 7:3 + “bronze” (tr) [e].
		1350	2			do	
				1360	0.67	do	9:8 + 8:5.
				1381	.5	Partially melted (?)	
				1424	.5	Partially melted	
				1435	.5	Completely melted	
52.94	47.06			1157	89	No melting	8:5 + 1:1 + “bronze” [e].
(9:8)				1222	168	do	9:8 + 8:5 + “6:11” [e].
				1255	89	do	9:8 + 8:5 + “6:11” [e].
				1279	64	do	9:8 + 8:5 + “6:11” [e].
				1307	1	do	9:8 + 8:5 + “6:11” [e].
				1350	1	do	9:8 + 8:5 (tr).
				1351	2	do	9:8 + 8:5 (tr).
				1351	18	do	9:8 + 8:5 (tr).
		1357	2			No melting	
				1222	168	do	9:8 + 8:5 + “6:11”.
				1255	89	do	9:8 + 8:5 + “6:11”.
				1279	64	do	9:8 + 8:5 [f].
				1371	1	do	9:8 + 8:5 (tr).
				1377	1	Partially melted (?)	9:8 + 8:5.
				1383	1	Partially melted	9:8 + 8:5.
				1402	0.25	do	8:5 + Q − liq [f].
				1422	.25	do	
				1452	.25	Completely melted	Poorly crystalline 8:5 [f].
50	50			998	144	No melting	1:1 + 7:3 + “bronze” [e].
				1100 [d]	60	do	1:1 + 7:3 + “bronze” [e].
		1300	2			do	
				1361	0.5	do	9:8 + “6:11”.
				1368	.67	Partially melted (?)	
				1414	.5	Partially melted	
				1424	.5	Completely melted	
45	55			1100 [d]	60	No melting	1:1 + “bronze”.
				1294	65	do	9:8 + “6:11”.
				1404	0.5	Partially melted	
				1415	.583	Completely melted	9:8 + Q − liq [f].
		1300	2			No melting	
				1360	0.5	do	9:8 + “6:11”.
				1370	.5	Partially melted (?)	
40	60			1100 [d]	60	No melting	1:1 + “bronze”.
				1294	65	do	“6:11” + 9:8.
				1405	0.5	Completely melted	Q − liq + “bronze”.
		1298	2			No melting	“6:11” + 9:8 (?) + 8:5 (tr) [e].
				1353	1	do	“6:11” + 9:8.
				1371	1	Partially melted	“6:11 + 9:8.
				1379	1	do	9:8 + “6:11” + 8:5 tr + Q − liq [e].
				1388	1	do	Q − liq + 9:8 (?) [f].
				1396	0.833	Completely melted	“bronze” + Q − liq.
36.36	63.64	1300	2			No melting	
(4:7)				1332	17	do	“6:11” + 9:8 (?).
				1354	64	do	“6:11” + 9:8 (?).
				1361	0.5	do	“6:11” + 9.8 (?).
				1368	.5	Partially melted	“6:11” + 9:8 (?).

TABLE 19. *Experimental data for compositions in the binary system* Nb$_2$O$_5$–WO$_3$. *Part I*—Continued.

Composition		Heat treatments				Results	
		Initial[a]		Final[b]		Physical observation	X-ray diffraction analyses[c]
Nb$_2$O$_5$	WO$_3$	Temp.	Time	Temp.	Time		
Mole %	*Mole %*	*°C*	*Hour*	*°C*	*Hour*		
				1372	.5	do	“6:11” + 9:8 (?).
				1380	.5	do[f]	“6:11” + 9:8 (?).
35.29	64.71	...	...	1100[d]	60	No melting	“bronze” + 1:1.
(6:11)		...	...	1100	64	do	“bronze” + 1:1.
				1203	19	do	4:9 + 8:5 tr.
				1246	165	do	“6:11”.
				1305	48	do	“6:11”.
		1298	2	...	...	No melting	...
				1246	165	do	“6:11”.
				1353	1	do	“6:11”.
				1369	93	do	“6:11”.
				1371	1	do	“6:11”.
				1380	1	Completely melted	“bronze” + Q − liq.
				1406	0.5	do	“bronze” + Q − liq.
33.33	66.67	...	...	1100[d]	60	No melting	“bronze” + 1:1.
		1296	2	...	...	do	“6:11” + 4:9 (?).
				1339	166	do	“6:11” + 4:9 (?).
				1362	1	do	...
				1371	1.5	Partially melted	“6:11” + Q − liq.
				1381	1	Completely melted	“bronze” + Q − liq (tr).
32	68	1300	2	...	...	No melting	...
				1322	17	do	4:9 + “6:11” (?).
				1339	166	do	4:9 + “6:11” (?).
				1354	64	do	...
				1361	0.5	do	...
				1368	.5	Partially melted	...
				1375	.5	do	...
30.77	69.23	...	...	1100[d]	60	No melting	“bronze” + 1:1 (tr).
(4:9)		...	...	1100	64	do	“bronze” + 1:1 (tr).
				1150	160	do	Poorly crystalline 4:9.
				1203	19	do	4:9 + “bronze” + 8:5 (?)[e].
				1300[d]	48	do	4:9.
				1305	48	do	4:9.
		1299	2	...	...	do	...
				1150	160	...	4:9.
				1368	1	do	...
				1379	0.75	Partially melted	4:9.
				1405	1	Completely melted	“bronze” + Q − liq (tr).
30	70	...	...	1100[d]	60	No melting	“bronze” + 1:1 (tr).
		1296	2	...	...	do	...
				1361	1	Partially melted	...
				1371	1	do	4:9 + Q − liq.
				1382	1	Completely melted	“bronze + Q − liq.
28.57	71.43	...	...	1100[d]	60	No melting	“bronze” + 1:1 (tr).
(2:5)		...	...	1203	19	do	“bronze” + 4:9 (?).
				1300[d]	48	do	4:9 + 2:7 (?).
				1305	48	do	4:9 + 2:7 (?).
		1249	70	...	...	do	...
				1331	64	do	4:9 + 2:7 (?).
		1265	1	...	...	do	“bronze” + 4:9 (?).
				1330	0.5	do	4:9 + 2:7 (?).
		1296	2	...	...	do	...
				1329	16.5	do	4:9 + 2:7 (?).
				1341	1	Partially melted	4:9 + Q − liq.
				1353	1	do	4:9 + Q − liq.
				1364	1	do	...
				1372	1.5	do	...
				1382	1	Completely melted	“bronze” + Q − liq.
28	72	...	...	1100[d]	60	No melting	“bronze” + 1:1 (tr) + WO$_3$ (tr)[e].
		1200	70	...	...	do	...
		1300	2	...	...	do	...
				1340	0.5	Partially melted	4:9 + Q − liq.
				1361	.5	do	...
27:27	72.73	...	...	1100[d]	60	No melting	“bronze” + WO$_3$ + 1:1 (tr)[e].
(3:8)		...	...	1200	70	do	“bronze”.
				1347	64	Partially melted	4:9 + “bronze”.
		1200	2	...	...	No melting	...
		1250	65	...	...	do	...
				1333	67	do	4:9 + 2:7.
		1200	2	...	...	...	...
		1304	16	...	...	No melting	...
				1369	0.5	Partially melted	...
26.42	73.58	...	...	1100[d]	60	No melting	“bronze” + WO$_3$ + 1:1 (tr)[e].
(14:39)		...	...	1200	70	do	“bronze”.
		1200	2	...	...	do	...
		1250	65	...	...	do	...
				1333	67	do	4:9 + 2:7.
				1347	64	Partially melted	...
				1361	0.5	do	...
		1200	2	...	...	...	...
		1304	16	...	...	...	...
				1370	0.5	Partially melted	...
25	75	...	...	1100[d]	60	No melting	“bronze” + WO$_3$ + 1:1 (tr)[e].
(1:3)		...	...	1250	2	do	“bronze + L-MonWO$_{3ss}$ + “1:11” + WO$_{3ss}$[e].
				1250	260	Partially melted[g]	...

TABLE 19. *Experimental data for compositions in the binary system* Nb_2O_5–WO_3. *Part I*—Continued.

Composition		Heat treatments				Results	
		Initial ^{a}		Final ^{b}		Physical observation	X-ray diffraction analyses^c
Nb_2O_5	WO_3	Temp.	Time	Temp.	Time		
Mole %	*Mole %*	*°C*	*Hour*	*°C*	*Hour*		
		1200	2			No melting	
				1255	65	do	"bronze" + 2:7.
				1305	16	do	4:9 + 2:7 (?).
				1343	0.75	Partially melted	4:9 + Q − liq.
				1353	.5	do	4:9 + Q − liq.
				1360	.5	do	
				1379	.5	Completely melted	
		1200	68			No melting	"bronze" + L-MonWO_{3ss} (tr).
				1325	97	do	4:9 + 2:7 (?).
22.22	77.78			1100^d	60	No melting	"bronze" + WO_3 + 1:1 (tr)^e.
(2:7)				1100	64	do	"bronze" + WO_3.
				1202	20	do	"bronze" + L-MonWO_{3ss} + WO_3 (?).
				1250	260	Partially melted^g	
				1265	1	do	"bronze" + L-MonWO_{3ss}^{e}.
				1300^d	48	do	
				1343	0.5	do	
				1360	1	Completely melted	
		1200	2			No melting	
				1229	67	do	"bronze" + Tet WO_{3ss}.
				1255	65	do	2:7.
				1305	16	do	"bronze" + "1:11"^{e}.
				1342	0.5	Partially melted^g	
				1351	.583	Completely melted^g	
		1200	2				
		1249	70			No melting	2:7.
				1229	67	do	2:7.
				1331	64	do	2:7.
				1344	0.75	do	2:7.
				1350	.5	do	
				1357	.5	Partially melted	
20	80			1100^d	60	No melting	"bronze" + WO_3 + 1:1 (tr)^e.
				1200	2	do	
				1343	0.5	Partially melted	
		1200	2			No melting	
				1255	65	do	"bronze" + 2:7 + L-MonWO_{3ss}^{e}.
				1305	16	do	"bronze" + 2:7 + "1:11" + "1:15" (?)^e.
				1342	0.5	Partially melted	
				1352	.5	Completely melted (?)	
				1363	.5	Completely melted	
18	82	1200	2			No melting	
		1300	2			do	2:7 + "1:11".
				1337	0.5	do	2:7 + "1:11".
				1343	.5	Partially melted	2:7 + Q − liq.
				1352	.5	Completely melted	
15	85			1100^d	60	No melting	WO_3 + "bronze".
		1200	2			do	
				1232	17	do	"bronze" + L-MonWO_{3ss} + WO_{3ss} (tr).
				1258	16	do	"bronze" + L-MonWO_{3ss} + 2:7 (?)^e.
				1300	16	do	2:7 + "1:11".
				1343	0.5	Partially melted	
				1352	.5	Completely melted	
				1359	.5	do	
10	90			1100^d	60	No melting	WO_3 + "bronze".
				1100	20	do	WO_3 + "bronze".
				1200	90	do	L-MonWO_{3ss} + "bronze" + WO_{3ss} (?).
				1250	17	Partially melted^g	
				1275	144	do	L-MonWO_{3ss} + "bronze".
		1200	2			No melting	
				1258	16	do	L-MonWO_{3ss} + "bronze" + 2:7 (?)^e.
				1300	16	do	"1:11" + "1:15" + 2:7^e.
				1301	69	do	"1:11" + 2:7.
				1328	0.5	do	
				1342	.5	Partially melted (?)	"1:11" + Q − liq.
				1343	17	Partially melted	"1:11" + Q − liq.
				1361	0.67	do	
				1378	.5	Completely melted	
9	91	1200	2			No melting	
				1295	67	do	"1:11" + 2:7 (tr).
				1301	69	do	"1:11" + 2:7 (tr).
		1200	2				
		1300	2			No melting	
				1379	0.083	Partially melted	
8.33	91.67	1200	2			No melting	
(1:11)				1279	65	do	"1:11" + 2:7 + "1:15" (?)^e.
				1311	70	do	"1:11" + 2:7 (tr)^e.
				1350	17	do	"1:11".
		1200	2				
		1300	2			No melting	"1:11".
				1354	0.33	do	"1:11".
				1355	.5	do	"1:11".
				1357	.5	Partially melted	"1:15" + L-MonWO_{3ss} + Q − liq.
				1359	.5	do	L-MonWO_{3ss} + Q − liq.
				1369	.5	do	L-MonWO_{3ss} + Q − liq.
				1379	.083	do	
				1392	.083	Completely melted	Q − liq.

TABLE 19. *Experimental data for compositions in the binary system* Nb_2O_5–WO_3. *Part I*—Continued.

Composition		Heat treatments				Results	
		Initial [a]		Final [b]		Physical observation	X-ray diffraction analyses[c]
Nb_2O_5	WO_3	Temp.	Time	Temp.	Time		
Mole %	*Mole %*	*°C*	*Hour*	*°C*	*Hour*		
8	92	1200	2			No melting	
				1301	69	do	“1:11” + “1:15” (?).
7.69	92.31	1200	2			No melting	
(1:12)				1311	70	do	
7.14	92.86	1200	2			No melting	
(1:13)				1311	70	do	
7	93	1200	2			No melting	
				1299	67	do	“1:15” + “1:11”.
		1200	2				
		1300	2			No melting	
				1391	0.083	Partially melted	
				1402	.083	Completely melted	
6.66	93.33	1200	2			No melting	
(1:14)				1312	68	do	“1:15” + “1:11”.
6.25	92.75	1200	16			No melting	Tet WO_{3ss} + “bronze” + tr WO_{3ss}.
(1:15)				1279	65	do	“1:15” + L-MonWO_{3ss} + “1:11” + 2:7 (tr) [e].
				1312	68	do	“1:15” + L-MonWO_{3ss} (?).
				1350	17	do	“1:15” + L-MonWO_{3ss} (?).
		1200	2				
		1300	2			No melting	“1:15” + L-MonWO_{3ss} (?) + “1:11” (?) [e].
				1355	0.5	do	“1:15” + L-MonWO_{3ss} (?) + “1:11” (?) [e].
				1369	.5	Partially melted	L-MonWO_{3ss} + Q − liq.
				1380	.083	do	
				1391	.083	do	
				1398	.083	do	
		1200	2				
		1300	2				
		1347	4.5			No melting	“1:15” + L-MonWO_{3ss} (tr).
				1357	0.5	do	“1:15”.
				1359	.5	Partially melted	L-MonWO_{3ss} + Q − liq.
				1364	.5	do	L-MonWO_{3ss} + Q − liq.
6	94	1200	2			No melting	
				1299	67	do	“1:15” + L-MonWO_{3ss}.
5	95			1100 [d]	60	No melting	WO_3 + “bronze”.
				1100	20	do	WO_3 + “bronze”.
				1200	90	do	L-MonWO_{3ss} + “bronze” + WO_3 (tr).
				1202	20	do	L-MonWO_{3ss} + “bronze” + WO_3(tr).
				1250	16	Partially melted (?) [g]	L-MonWO_{3ss} + Q − liq.
				1275	144	Partially melted [g]	L-MonWO_{3ss} + “1:15” + WO_3 (tr).
		1200	2			No melting	L-MonWO_{3ss} + WO_{3ss} + “bronze”.
				1200	70	do	L-MonWO_{3ss} + WO_{3ss} + “bronze”.
				1258	16	do	L-MonWO_{3ss} + “bronze”.
				1299	67	do	“1:15” + L-MonWO_{3ss}.
				1300	16	do	L-MonWO_{3ss} + “1:15” + WO_{3ss} + “1:11” (?)[e].
				1343	0.5	do	
				1343	17	do	“1:15” + L-MonWO_{3ss} + “1:11” (?) [e].
				1362	0.75	Partially melted	L-MonWO_{3ss}.
				1379	.75	do	L-MonWO_{3ss} + Q − liq (?).
				1400	.5	do	
				1411	.083	Completely melted	
				1420	.25	do	L-MonWO_{3ss} (?).
4	96	1200	2			No melting	
				1254	66	do	
				1355	19	do	L-MonWO_{3ss} + “1:15”.
				1410	0.083	Partially melted	
		1200	2				
		1301	68			No melting	L-MonWO_{3ss} + “1:15”.
				900 [h]	0.25	do	Tet WO_{3ss} + “1:15”.
3	97	1200	2			No melting	
				1254	66	do	L-MonWO_{3ss} + 2:7.
				1355	19		L-MonWO_{3ss} + Orth WO_{3ss} (?).
				1379	0.083	Partially melted	
				1409	.083	do	
				1422	.083	Completely melted	
		1200	2				
		1301	68			No melting	L-MonWO_{3ss} + “1:15”.
				900 [h]	.025	do	Tet WO_{3ss} + “1:15”.
2	98	1200	2			No melting	
				1200	90	do	L-MonWO_{3ss} + WO_{3ss} + “bronze”.
				1232	17	do	L-MonWO_{3ss}.
				1275	19	do	L-MonWO_{3ss} + WO_{3ss} + “bronze”.
				1355	19	do	
				1379	0.083	do	
				1391	.083	Partially melted	
				1405	.083	do	
				1414	.083	do	
				1422	.083	do	
				1430	.083	Completely melted	
				1435	.083	do	L-MonWO_{3ss}.
		1200	2				
		1248	67			No melting	L-MonWO_{3ss}.
				900 [h]	0.25	do	Orth WO_{3ss} + Tet WO_{3ss} (tr).
				900	.25	do	Orth WO_{3ss}.
		1200	2				
		1301	68			No melting	L-MonWO_{3ss}.
				900 [h]	0.25	do	Orth WO_{3ss} + Tet WO_{3ss}.

TABLE 19. *Experimental data for compositions in the binary system* Nb_2O_5–WO_3. *Part I*—Continued.

Composition		Heat treatments				Results	
		Initial [a]		Final[b]		Physical observation	X-ray diffraction analyses[c]
Nb_2O_5	WO_3	Temp.	Time	Temp.	Time		
Mole %	*Mole %*	*°C*	*Hour*	*°C*	*Hour*		
1	99	1200	2	...	...	No melting	WO_{3ss} + L-MonWO_{3ss}.
				1200	90	do	WO_{3ss} + L-MonWO_{3ss}.
				1400	0.083	do	...
				1411	.083	Partially melted	...
				1422	.083	do	...
				1430	.083	do	...
				1435	.083	Completely melted	...
		1200	2	...	...	...	...
		1248	67	...	...	No melting	WO_{3ss} + L-MonWO_{3ss}.
				900 [h]	...	do	WO_{3ss}.
0	100	...	...	1000	10	No melting	WO_3.
				1329	2	do	WO_3 + TriWO_3.
				1351	48	do	WO_{3ss} + TriWO_3.
				1420	0.083	do	...
				1424	.083	do	...
				1430	.083	do	...
				1433	.083	do	...
				1435	.05	Completely melted	...
				1435	.083	do	...
				1436	.166	do	...
				1437	.083	do	...
				1439	.083	do	...
				1453	.083	do	...
				1462	.083	do	...
				1470	.083	do	...
				1485	.083	do	WO_3 + TriWO_3.

Experimental data for compositions in the binary system Nb_2O_5–WO_3. *Part II (less pure end members)*

Composition			Heat treatments				Results	
			Initial [i]		Final		Physical observation	X-ray diffraction analyses [c]
93.75		6.25	...	...	1053	336	No melting	6:1 + Nb_2O_5.
	(15:1)		1354	48	...	...	do	"30:1" + 6:1 (?).
					1053	336	do	"30:1" + 6:1 (?).
92.86		7.14	...	...	1354	40	No melting	"30:1" + 6:1.
	(13:1)							
85.71		14.29	...	...	1100	66	No melting	6:1.
	(6:1)		...	...	1248	64	do	6:1.
					1352	66	do	6:1.
77.78		22.22	...	...	1104	68	No melting	6:1 + 7:3 + 13:4.
	(7:2)		...	...	1203	89	do	6:1 + 13:4 + 7:3 (?).
					1352	21	do	6:1 + 7:3 + 13:4 (tr).
76.19		23.81	...	...	1044	336	No melting	13:4 + 6:1 (?) + 7:3 (?).
	(16:5)		...	...	1109	65	do	13:4 + 6:1 (?) + 7:3 (?).
					1200	138	do	13:4 + 6:1 + 7:3.
					1303	71	do	6:1 + 7:3 + 13:4 (tr).
72.73		27.27	...	...	1201	89	No melting	13:4 + 7:3.
	(8:3)							
70		30	...	...	1097	94	No melting	7:3 + 13:4 (tr).
	(7:3)		...	...	1349	23.5	do	7:3 + 6:1 (tr).
61.54		38.46	...	...	1097	94	No melting	7:3 + 1:1.
	(8:5)		...	...	1201	113	do	8:5 + 7:3 (tr).
					1202	42	do	8:5 + 7:3 + "bronze".
					1255	65	do	8:5 + 7:3 (tr).
					1255	92	do	8:5 + 7:3 (tr).
					1303	16	do	8:5 + 7:3 (tr).
					1350	19	do	8:5 + 7:3 (tr).
			1354	16	...	...	No melting	8:5 + 7:3 (tr).
					1048	336	do	8:5 + 7:3 + "bronze" + 1:1.
60		40	...	...	1203	89	No melting	8:5 + "bronze" (tr).
	(3:2)							
52.94		47.06	...	...	1097	70	No melting	7:3 + 1:1 + "bronze" (tr).
	(9:8)		...	...	1201	113	do	8:5 + "bronze".
					1255	65	do	8:5 + "bronze" + 9:8 (?).
					1303	16	do	9:8 + 8:5 (tr).
					1318	67	do	9:8 + 8:5 (tr).
					1321	19	do	9:8 + 8:5 (tr).
					1348	20	do	9:8 + 8:5 (tr).
					1350	19	do	9:8 + 8:5 (tr).
					1352	21	do	9:8 + 8:5 (tr).
					1352	68	do	9:8 + 8:5 (tr).
			1354	16	...	...	do	9:8 + 8:5 (tr).
					1048	336	do	1:1 + 7:3 + "bronze" + 9:8 (tr) + 8:5 (tr).
50		50	...	...	1098	336	No melting	1:1 + "bronze" + 7:3.
					1101	66	do	1:1 + "bronze" + 7:3.

Experimental data for compositions in the binary system Nb_2O_5–WO_3. *Part II (less pure end members)*—Continued.

Composition		Heat treatments				Results	
		Initial [i]		Final		Physical observation	X-ray diffraction analyses [c]
		1348	20			do	9:8 + "6:11"[f].
				1044	336		8:5 + "6:11" + 1:1.
42.31	57.69			1157	89	No melting	"bronze" + 1:1 + 8:5.
(11:15)				1305	22	do	"6:11" + 9:8.
35.14	64.86			1105	67	No melting	"6:11".
(13:24)				1305	22	do	"6:11".
30	70			1105	67	No melting	4:9 + "bronze" (?).
(3:7)				1301	70	do	4:9 + "bronze" (?).
25	75			1097	70	No melting	"bronze" + WO_3 (tr).
(1:3)				1300	44	Partially melted (?)[g]	"bronze".
				1300	70	do	"bronze".
23.17	76.83			1202	24	No melting	"bronze" + WO_{3ss} (?).
(19:63)				1279	46	Partially melted (?)[g]	
11.11	88.89			1202	24	No melting	"bronze" + L-MonWO_{3ss} + WO_{3ss}.
(1:8)				1279	46	Partially melted (?)[g]	"1:11" + "bronze".
				1300	44	do	"1:11" + 2:7.

[a] All specimens were initially calcined at 700 °C for 19 hr with heating and cooling rates of approximately 4 °C/min. Small portions of this calcine were then reheated for the designated time at one or more designated higher temperatures and generally quenched in sealed Pt tubes.

[b] After the initial heat treatment(s) all specimens were reheated at the indicated temperature and quenched in sealed Pt tubes, unless otherwise specified.

[c] The phases identified are given in the order of amount present at room temperature. The phases are not necessarily those present at the temperature to which the specimen was heated.

(?) = interpretation is not certain.
ss = solid solution.
(tr) = trace just barely discernible in x-ray pattern.
"30:1" = a phase of unknown structure occurring at a mole ratio of approximately 30:1 Nb_2O_5: WO_3.
(unknown) = extra peaks in the x-ray pattern which cannot be assigned to any recognized phase.
6:1 = $6Nb_2O_5 \cdot WO_3$ ($WNb_{12}O_{33}$).
low Nb_2O_5 = nonequilibrium phase (similar to the low temperature form of Nb_2O_5), when quenched from above the liquidus and examined at room temperature.
7:3 = $7Nb_2O_5 \cdot 3WO_3$ ($W_3Nb_{14}O_{44}$).
13:4 = $13Nb_2O_5 \cdot 4WO_3$ ($W_4Nb_{26}O_{77}$).
"bronze" = a metastable disordered phase having a variable composition and an undistorted tetragonal-tungsten-bronze type x-ray pattern (designated as "3:8" on the phase diagram).
8:5 = $8Nb_2O_5 \cdot 5WO_3$ ($W_5Nb_{16}O_{55}$).
9:8 = $9Nb_2O_5 \cdot 8WO_3$ ($W_8Nb_{18}O_{69}$).
1:1 = $Nb_2O_5 \cdot WO_3$ (WNb_2O_8).
"6:11" = a tungsten bronze type phase of orthorhombic symmetry and with superstructure lines indicative of the unit cell being tripled in the *a* and *b* directions.
Q – liq = metastable phase or phases which form only from the quenched liquid and give very poorly defined x-ray powder patterns, having the general appearance of the ReO_3 subcell characteristic of most of the compounds in this system.
4:9 = $4Nb_2O_5 \cdot 9WO_3$ ($Nb_8W_9O_{47}$).
L-MonWO_{3ss} = the monoclinic polymorph of WO_3 reported [30] to occur below –40 °C "stabilized" by a small amount of solid solution of Nb_2O_5 in WO_3.
2:7 = $2Nb_2O_5 \cdot 7WO_3$ ($W_7Nb_4O_{31}$).
"1:11" = Magneli "shear" phase having the approximate composition $1Nb_2O_5$:$11WO_3$.
"1:15" = Magneli "shear" phase having the approximate composition $1Nb_2O_5$:$15WO_3$.
Tet WO_{3ss} = the high temperature polymorph of WO_3 stabilized by solid solution of Nb_2O_5 in WO_3.
Orth WO_{3ss} = the orthorhombic polymorph of WO_3 ordinarily stable between about 320 °C and ~ 745 °C, "stabilized" by addition of Nb_2O_5 in solid solution.
Tri WO_3 = the polymorph of WO_3 which is stable just below room temperature and occurs at room temperature when pure WO_3 is ground in a mortar and pestle for a short time.

[d] Specimen heated and cooled at about 4 °C/min rather than quenched.

[e] Nonequilibrium, probably due to incomplete reaction.

[f] Nonbinary equilibrium, postulated as being due to reduction.

[g] Metastable melting.

[h] Pt tube not sealed.

[i] Did not receive preliminary 700° heat treatment.

5. Reduction

As has been previously mentioned there is some tendency for WO_3 to reduce on heating to high temperatures, even in the sealed Pt tubes. This tendency is greatly enhanced by subjecting the specimens to high temperatures for extended periods of time. The problem of reduction of WO_3 is apparently carried into the Nb_2O_5-WO_3 system to such an extent that the system may not be completely binary at high temperatures.

The experimental data indicate that the system probably remains essentially binary as long as no melting occurs. However, above the solidus, reduction very likely takes place and the measured liquidus values may not represent binary equilibrium. The melting relations around the ordered bronze-type phases, from about 60 to 80 mole percent WO_3, were particularly difficult to obtain experimentally. The three compounds at "6:11", 4:9 and 2:7 all appeared to melt congruently with binary solidus relations between them. However, the liquidus values appear to form smooth curves between these congruent melting points without any indication of a change in slope toward a eutectic composition. The phenomena is characteristic of a nonbinary system. For the sake of simplicity, the phase diagram has been drawn to indicate the most likely binary relationships and liquidus curves have been dashed to illustrate the uncertainty in values.

Another indication of reduction occurs in the melting relations of the $B_{nm+1}O_{3nm-(n+m)+4}$ homologous series compounds. The phases $W_3Nb_{14}O_{44}$, $W_5Nb_{16}O_{55}$, and $W_8Nb_{18}O_{69}$ were all observed to melt incongruently. Experimentally these compound compositions were observed to begin to form a second phase at about 1440°, 1385°, and 1375°, respectively. However, compositions in two-phase regions between these compounds did not begin to form the new phase until considerably higher temperatures, even though the specimen may have shown an appearance of partial melting. This apparent increase in the stability temperature of the phases is dependent on the amount of time the specimen is held at temperature, and binary melting relationships can be approximated by only holding the experimental specimens for relatively short periods of time. It may therefore be concluded that reduction takes place in these specimens, when held above the solidus temperatures. However, it has previously been concluded [1–4] that the crystal structure of these compounds precludes any appreciable nonstoichiometry. Therefore, it appears likely that, as the W^{+6} ion is reduced, the Nb/W ratio of these phases shifts towards higher tungsten content, maintaining an essentially constant cation: anion ratio.

In addition to the relatively large amount of reduction which apparently takes place above melting, there is possibly some tendency towards reduction at lower temperatures. The amount of reduction which can take place experimentally below melting is probably several orders of magnitude less than that which occurs above melting because it seems in no way to affect the equilibrium relationships. The only indication of this minor reduction is in a tendency for discoloration of the specimens. Almost any composition in the system, held for long periods of time in a sealed Pt tube will show a much darker green or blue color than does the same composition either held for shorter periods or not sealed. This darker color can always be lightened by annealing the specimen in an open Pt tube, at about 1000 °C.

It is intriguing to postulate that the Nb_2O_5-WO_3 system might more closely approach binary conditions if the experiments were performed under conditions of high oxygen pressure, such as that utilized by Van Hook [39]. Such studies will probably become more common in the near future.

6. Metastable Phases and Nonequilibrium

6.1. Metastable Melting

It can be seen from table 19, that all compositions containing more than about 72 mole percent WO_3 were calcined for about 2 hr at 1200 °C prior to attempting to obtain equilibrium data. This was because the few preliminary heat treatments, performed at temperatures above 1250 °C, without the 1200 °C calcine, exhibited some indication of melting, whereas those with a prior 1200 °C calcine did not show melting until much higher temperatures.

The metastable melting apparently is due to a eutectic type reaction between the metastable bronze-type solid solution (labeled "3:8" on fig. 1) and pure WO_3. It must be emphasized that in order to obtain equilibrium products in the region 72 to 100 mole percent WO_3, this preliminary calcine at 1200 °C is imperative. Without such preliminary heat treatment, neither the 2:7 compound nor the "Magneli-shear" structures can be prepared as single phases.

6.2. Metastable Phases

The bronze-type solid solution previously mentioned ("3:8" of fig. 1) has been interpreted as a metastable phase for several reasons. It appears to be responsible for very low temperature metastable melting which takes place between about 72 and 100 mole percent WO_3. The x-ray powder pattern of the bronze-type solid solution shows no superstructure and the phase must contain disordered pentagonal bypyramid polyhedra. It must be concluded that the disordered phase is metastable because it dissociates on heating to two ordered phases. All compositions between about the 6:11 and 2:7 ratios, when quenched from above the liquidus exhibit the tetragonal bronze-type "disordered" phase with no indication of any superstructure peaks in the x-ray diffraction powder pattern. In addition, many specimens also show a small amount of a quenched liquid phase which exhibits a poorly defined x-ray pattern characteristic of a disordered ReO_3 structure, the basic building unit of all the compounds in the system.

From about 5 mole percent WO_3 to at least 15 mole percent WO_3 another metastable phase is formed from the quenched liquid. This phase has an x-ray pattern, characteristic of the orthorhombic low-temperature form of Nb_2O_5. The diffraction pattern shows diffuse peaks and little or no superstructure lines. This phase never appears below the melting point and only forms as a single phase if the quenching temperature is considerably above the liquidus. The ability of a specimen to be quenched as a phase with a powder pattern similar to the low-temperature form of Nb_2O_5 seems to be dependent on cooling rate and composition. This phenomena has been previously reported for other niobate systems [23, 40].

As shown in table 19, another unknown phase has been found occasionally in nonequilibrium mixtures between about 7 and 25 mole percent Nb_2O_5. All efforts to establish an equilibrium region for this phase have proved negative. It is possible that the unknown compound may represent a complex structure involving a mixture of 3 × 3 blocks along with the 3 × 4 and/or 4 × 4 blocks normally found in other compounds occurring in this composition range. Such a structure would contain a considerable number of Nb^{+5} ions in tetrahedral coordination and would not be expected to form a stable assemblage.

It has been previously mentioned [1] that $WNb_{12}O_{33}$ *appears* to have a small region of homogeneity, in that the 8:1 composition showed only a single phase. However, no change in lattice parameters could be detected. This apparent region of solid solution is most likely due to the very similar powder patterns of the 6:1 compound and the "30:1" phase. A solid solution structure containing either a considerable number of oxygen vacancies or cation interstitials (in either the tetrahedral or octahedral position) would be expected to cause some measurable change in the lattice parameters. One other possible mechanism which has been suggested for solid solution [41] is again raised by the appearance of the "ordered intergrowth" structure of the 13:4 compound, and the suggested possible structure of a 25:1 or 20:1 compound. It is possible that a "disordered intergrowth" of double 3 × 4 blocks might occur in association with the isolated 3 × 4 blocks of the $WNb_{12}O_{33}$ compound [24]. Such a disordered structure or "compositional stacking fault" would cause only a slight broadening of some of the lines of an x-ray diffraction powder pattern, as would a mixture of a small amount of the ordered second phase. It is problematical as to whether such a picture of solid solution would represent a stable or only a metastable condition. Nevertheless, proof of such a postulated disorder would necessarily depend upon other data, outside the scope of this project. A careful electron diffraction and/or electron microscope study might prove of value in deciphering the nature of any possible disorder of this type.

7. References

[1] R. S. Roth and A. D. Wadsley, Acta Cryst. **19,** 26 (1965).

[2] R. S. Roth and A. D. Wadsley, Acta Cryst. **19,** 32 (1965).

[3] R. S. Roth and A. D. Wadsley, Acta Cryst. **19,** 38 (1965).

[4] R. S. Roth and A. D. Wadsley, Acta Cryst. **19,** 42 (1965).

[5] H. J. Goldschmidt, Metallurgia **62,** 241 (1960).

[6] L. M. Kovba and V. K. Trunov, Dokl. Adad. Nauk. SSR **147,** 622 (1962).

[7] L. J. Fiegel, G. P. Mohanty, and J. H. Healy, J. Chem. and Eng. Data **9,** 365 (1964).

[8] G. P. Mohanty and L. J. Fiegel, Acta Cryst. **17,** 454 (1964).

[9] L. M. Kovba, V. K. Trunov, and Y. P. Simanov, Zh. Neorgan. Khim. **9,** 1930 (1964).

[10] H. Schäfer and R. Gruehn, private communication to A. D. Wadsley, 4/14/65.

[11] E. J. Felten, private communication to R. S. Roth, 12/2/64.

[12] H. F. Stimson, J. Res. NBS **65A** (Phys. and Chem.) No. 3, 139 (1961).

[13] G. Brauer, Z. anorg. u. allgem. Chem. **248,** 1 (1941).

[14] F. Holzberg, A. Reisman, M. Berry, and M. Berkenblit, J. Am. Chem. Soc. **79,** 2039 (1957).

[15] M. W. Shafer and R. Roy, Z. Krist. **110,** 241 (1958).

[16] H. J. Goldschmidt, J. Inst. Metals **87,** 235 (1958–59).

[17] A. Reisman and F. Holzberg, J. Am. Chem. Soc. **81,** 3182 (1959).

[18] B. M. Gatehouse and A. D. Wadsley, Acta Cryst. **17,** 1545 (1964).

[19] R. S. Roth, J. Res. NBS **62,** 27 (1959) RP2925.

[20] R. S. Roth and J. L. Waring, J. Res. NBS **66A** (Phys. and Chem.) No. 6, 451 (1962).

[21] R. S. Roth, A. D. Wadsley, and S. Andersson, Acta Cryst. **18,** 643 (1965).

[22] R. Gruehn and H. Schäfer, Naturwissenschaften **50,** 642 (1963).

[23] J. L. Waring and R. S. Roth, J. Res. NBS **69A** (Phys. and Chem.) No. 2, 119 (1965).

[24] A. D. Wadsley, S. Andersson, and W. G. Mumme, Acta Cryst. (to be published).

[25] S. Andersson, Acta Chem. Scand. **18,** 2339 (1964).

[26] M. Lundberg and S. Andersson, to be published.

[27] A. Sleight and A. Magneli, Acta Chem. Scand. **18,** 2007 (1964).

[28] N. Stephensen, private communication.

[29] A. Magneli, Arkiv Kemii **1,** 513 (1950).

[30] R. Veda and T. Ichinokawa, Phys. Rev. **82,** 563 (1951).

[31] J. Wyart and M. Föex, Compt. Rend. 2459 (1951).

[32] S. Tanisaki, J. Phys. Soc. Japan **15,** 566 (1960).

[33] B. T. Mathias and E. A. Wood, Phys. Rev. **84,** 1255 (1951).

[34] S. Levine, R. Corwin, and H. L. Blood, Bull. Am. Phys. Soc. Series II, **1,** [5], 255 (1956).

[35] P. H. Fang, private communication.

[36] E. M. Levin, J. Am. Ceram. Soc. **48,** 491 (1965).

[37] F. M. Jaeger and H. C. Germs, Z. anorg. u. allgem. Chem. **190,** 145 (1921).

[38] B. Phillips and L. Chang, Trans. Met. Soc. AIME **230,** 1203 (1964).

[39] H. J. Van Hook, Rev. Sci. Instr. **36,** 1119 (1965).

[40] E. M. Levin, J. Research NBS **70A** (Phys. and Chem.), No. 1, 5 (1966).

[41] A. D. Wadsley, in Non-stoichiometric Compounds, ed. L. Mandelcorn ch. 3, (Academic Press, N.Y., 1964).

(Paper 70A4–404)