

# Crystal Structure Studies of Tetragonal Sodium Tungsten Bronzes, $\text{Na}_x\text{WO}_3$ . I. $\text{Na}_{0.33}\text{WO}_3$ and $\text{Na}_{0.48}\text{WO}_3$ \*

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The crystal structures of two sodium tungsten bronzes,  $\text{Na}_{0.33}\text{WO}_3$  and  $\text{Na}_{0.48}\text{WO}_3$ , have been determined by three-dimensional single-crystal X-ray analysis. They were found to crystallize in the tetragonal space groups  $P4_2/m$  ( $a = 12.097$ ,  $c = 3.754 \text{ \AA}$ ,  $Z = 10$ ) and  $P4/mbm$  ( $a = 12.150$ ,  $c = 3.769 \text{ \AA}$ ,  $Z = 10$ ), respectively. The structures were solved by standard Patterson and Fourier techniques and refined by full-matrix least-squares to final conventional discrepancy indices of 8.9% for  $\text{Na}_{0.33}\text{WO}_3$  and 8.4% for  $\text{Na}_{0.48}\text{WO}_3$ . In general, the oxygen atoms were found to be either twofold or fourfold disordered, suggesting that the  $\text{WO}_6$  octahedra do not have axes exactly aligned parallel to the crystallographic  $c$ -axis. The structure found can be viewed as a composite of two kinds of domain structures. These domain structures would require a doubling of the  $c$ -axis along with selection of new  $a$ - and  $b$ -axes along the  $[1\ 1\ 0]$  and  $[\bar{1}\ 1\ 0]$  directions. There exist pentagonal and tetragonal sites in both these sodium tungsten bronzes for sodium atoms occupancy. In  $\text{Na}_x\text{WO}_3$ ,  $x = 0.48$ , all the pentagonal sites are filled and 40% of the smaller tetragonal sites are also occupied. As  $x$  decreases to 0.33 though, only the pentagonal sites are occupied. A relation between the  $x$  value and the  $\text{Na}_x\text{WO}_3$  crystal structures is postulated, extrapolating from the results found in these structure determinations.

## Introduction

The sodium tungsten bronzes,  $\text{Na}_x\text{WO}_3$ , have been found to form in sodium compositions ranging from  $0 \leq x \leq 1.0$ . They were first investigated by Hägg (*1*) and his collaborators and their crystal structures have been studied using X-ray, neutron, and electron-microwave methods. For  $x = 1.0$ , one has the perfect perovskite lattice and as the  $x$  value decreases, electrons are lost from the conduction band in relation to the sodium atom vacancies. These bronzes have been found to exist

in triclinic (2), tetragonal (3, 4), and cubic (5) forms as shown in Table I. However, for the most part, accurate crystal-structure determinations have not been carried out. The crystal structure of the tetragonal form was first determined by Magnéli. However, this determination primarily offered evidence as to the tungsten atom positions and left questions as to the correct space group and accurate positions for the oxygen and sodium atoms, as well as possible sites for the sodium atoms and their occupancy.

Recently these sodium tungsten bronzes and other compounds exhibiting a crystal structure of the "tungsten bronze type" have been found to possess unusual electronic character, i.e., ferroelectricity, semiconductivity, and superconductivity. The superconductivity of tetragonal sodium tungsten bronze was first discovered by Raub et al. (6). Recent results

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TABLE I  
 SOME  $\text{Na}_x\text{WO}_3$  CRYSTAL STRUCTURES

$x$ value	Crystal form	Space group	$a$	$b$	$c$	$\alpha$	$\beta$	$\gamma$	Reference
0.5 <sup>a</sup>	Triclinic	?	8.381	8.162	3.870	90.05	103.11	95.34	2a
0.43 <sup>b</sup>	Triclinic	$P\bar{1}$	7.287	18.474	7.235	95.22	119.64	89.40	2b
0.28	Tetragonal	$P42_1$ or $P\bar{4}2_1m$	12.094	—	3.748	—	—	—	3
0.33	Tetragonal	$P\bar{4}2_1m$	12.097	—	3.754	—	—	—	
0.38	Tetragonal	$P42_1$ or $P\bar{4}2_1m$	12.102	—	3.748	—	—	—	3
0.48	Tetragonal	$P4/mbm$	12.150	—	3.769	—	—	—	
0.1	Tetragonal	$P4/nmm$	5.248	—	3.895	—	—	—	4
1.0	Cubic	?	3.87	—	—	—	—	—	5a
1.0	Cubic	?	3.866	—	—	—	—	—	5b
0.86 ~ 0.59 <sup>c</sup>	Cubic	$I3m3$	3.866	—	—	—	—	—	5c
0.95	Cubic	?	3.857	—	—	—	—	—	5d
0.4	Cubic	?	3.817	—	—	—	—	—	5d

<sup>a</sup>  $\text{Na}_2\text{W}_4\text{O}_{13}$ .

<sup>b</sup>  $\text{Na}_6\text{W}_{14}\text{O}_{45}$ .

<sup>c</sup> Neutron diffraction study. The cell dimensions used were those of (5b).

by Shanks (7) of this Laboratory indicate that the superconducting character of these materials is very greatly influenced by the sodium atom composition. As the  $x$  value of  $\text{Na}_x\text{WO}_3$  decreases and approaches 0.2, the transition temperature for superconductivity is found to increase exponentially. In order to characterize the changes taking place in these materials on the atomic scale better, we decided to carry out accurate three-dimensional X-ray structure analyses of  $\text{Na}_{0.33}\text{WO}_3$  and  $\text{Na}_{0.48}\text{WO}_3$ .

### Experimental

The samples of  $\text{Na}_{0.33}\text{WO}_3$  and  $\text{Na}_{0.48}\text{WO}_3$  were kindly supplied by H. Shanks. Preliminary oscillation and Weissenberg photographs exhibited  $D_{4h}4/mmm$  Laue symmetry and no reflections of the superstructure type reported by Magnéli were observed.

The unit cell parameters and their estimated standard deviations were obtained by a least-squares fit (8) to the  $2\theta$  values of 14 independent high-angle reflections whose centers were determined by half-height techniques on a previously aligned four circle diffractometer. These, along with other crystal data, are listed in Table II.

For data collection, crystals were selected that were in the shapes of parallelepipeds formed with the (1 1 0), ( $\bar{1}$  1 0), and (0 0 1) planes as faces. The crystal dimensions were  $0.050 \times 0.067 \times 0.068$  mm for  $\text{Na}_{0.33}\text{WO}_3$ , and  $0.061 \times 0.065 \times 0.069$  mm for  $\text{Na}_{0.48}\text{WO}_3$ . Data were collected at room temperature using an automated four-circle diffractometer designed and built in the Ames Laboratory. This diffractometer is interfaced to a PDP-15 computer (9) in a real-time mode and is equipped with scintillation counter. For data collection reflected beam graphite-monochromated radiation was used ( $\lambda = 0.70926$  Å). Within a  $2\theta$  sphere of  $70^\circ$  ( $\sin\theta/\lambda = 0.8071$

 TABLE II  
 CRYSTAL DATA FOR  $\text{Na}_{0.33}\text{WO}_3$  AND  $\text{Na}_{0.48}\text{WO}_3$ 

	$\text{Na}_{0.33}\text{WO}_3$	$\text{Na}_{0.48}\text{WO}_3$
Molecular formula	$\text{Na}_{0.33}\text{WO}_3$	$\text{Na}_{0.48}\text{WO}_3$
Molecular weight	239.43	242.88
Space group	$P\bar{4}2_1m$	$P4/mbm$
Cell dimensions	$a = 12.097(2)$ $c = 3.754(2)$	$12.140(2)$ Å $3.767(2)$
$Z$	10	10
Density (calculated)	7.240	7.267 g/cm <sup>3</sup>
Radiation	$\text{MoK}\alpha$	$\text{MoK}\alpha$
Linear absorption coefficient	586.7	580.8 cm <sup>-1</sup>

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR  $\text{Na}_{0.33}\text{WO}_3$ 

H	K	L	F <sub>O</sub>	F <sub>C</sub>	H	K	L	F <sub>O</sub>	F <sub>C</sub>	H	K	L	F <sub>O</sub>	F <sub>C</sub>	H	K	L	F <sub>O</sub>	F <sub>C</sub>
2	0	0	65	65	12	9	0	52	59	17	6	1	79	78	12	4	2	122	133
4	0	0	166	144	14	9	0	102	86	18	6	1	50	49	13	4	2	75	80
6	0	0	59	61	15	9	0	43	41	7	7	1	160	157	14	4	2	44	54
8	0	0	206	156	10	10	0	82	91	8	7	1	59	52	15	4	2	111	111
12	0	0	74	87	11	10	0	78	78	9	7	1	107	112	17	4	2	60	83
14	0	0	279	278	12	10	0	117	109	10	7	1	36	37	5	5	2	326	367
18	0	0	37	37	13	10	0	68	68	11	7	1	114	116	6	5	2	116	105
2	1	0	145	145	14	10	0	119	115	13	7	1	125	112	7	5	2	102	102
3	1	0	319	319	15	10	0	88	60	15	7	1	166	157	8	5	2	51	61
4	1	0	351	331	11	11	0	52	62	16	7	1	46	51	9	5	2	150	168
6	1	0	64	66	13	11	0	86	76	17	7	1	74	70	10	5	2	73	75
7	1	0	417	357	16	11	0	119	111	8	8	1	193	182	12	5	2	42	41
8	1	0	82	75	12	12	0	97	105	9	8	1	35	34	13	5	2	78	84
10	1	0	176	164	13	13	0	112	108	10	8	1	35	36	15	5	2	51	57
11	1	0	79	72	0	0	0	663	673	11	8	1	162	163	15	5	2	43	49
12	1	0	68	69	2	0	1	53	52	12	8	1	89	78	6	6	2	52	53
13	1	0	82	79	4	0	1	135	131	13	8	1	72	71	7	6	2	76	76
14	1	0	104	58	5	0	1	63	56	14	8	1	62	47	8	5	2	106	133
15	1	0	45	42	6	0	1	89	78	16	8	1	54	55	9	6	2	88	107
16	1	0	45	50	8	0	1	145	118	17	8	1	71	61	10	6	2	60	52
17	1	0	128	128	10	0	1	244	236	9	9	1	122	103	11	6	2	126	129
18	1	0	76	72	12	0	1	56	57	10	9	1	128	136	12	6	2	157	164
2	2	0	110	116	14	0	1	243	263	12	9	1	54	58	13	6	2	42	43
3	2	0	295	303	2	1	1	157	161	14	9	1	111	86	15	6	2	60	50
4	2	0	221	231	3	1	1	320	258	10	10	1	94	84	16	6	2	59	61
6	2	0	337	330	4	1	1	294	241	11	10	1	80	71	17	6	2	72	74
7	2	0	80	77	6	1	1	61	55	12	10	1	115	104	7	7	2	133	177
8	2	0	174	161	7	1	1	351	310	13	10	1	72	65	8	7	2	73	76
9	2	0	47	46	8	1	1	56	56	14	10	1	142	110	9	7	2	93	89
10	2	0	143	119	10	1	1	176	161	15	10	1	85	60	10	7	2	45	42
11	2	0	187	183	11	1	1	63	66	11	11	1	71	58	11	7	2	11	103
12	2	0	116	116	12	1	1	77	71	13	11	1	81	73	13	7	2	52	56
13	2	0	108	104	13	1	1	72	75	12	12	1	123	103	15	7	2	129	140
18	2	0	74	69	14	1	1	89	96	13	12	1	37	34	16	7	2	58	51
3	3	0	145	176	15	1	1	37	40	13	13	1	120	102	17	7	2	53	65
4	3	0	41	48	16	1	1	39	49	14	13	1	46	32	8	8	2	176	167
5	3	0	66	68	17	1	1	126	121	0	0	2	597	633	9	8	2	42	39
6	3	0	302	290	18	1	1	79	71	1	0	2	45	47	11	8	2	139	152
7	3	0	39	43	2	2	1	86	117	4	0	2	108	132	12	8	2	67	62
8	3	0	289	261	3	2	1	231	232	5	0	2	99	92	13	8	2	70	72
10	3	0	44	45	4	2	1	216	177	6	0	2	76	75	14	8	2	79	51
11	3	0	137	122	5	2	1	39	34	7	0	2	59	57	16	8	2	55	46
13	3	0	166	158	6	2	1	351	299	8	0	2	141	146	9	9	2	84	97
15	3	0	90	84	7	2	1	128	93	9	0	2	57	55	10	9	2	120	127
16	3	0	160	143	8	2	1	167	143	10	0	2	204	210	12	9	2	55	56
18	3	0	34	36	9	2	1	60	44	12	0	2	43	44	14	9	2	55	67
5	4	0	143	155	10	2	1	130	113	14	0	2	234	225	15	9	2	37	31
8	4	0	81	79	11	2	1	174	166	18	0	2	39	39	16	10	2	68	73
4	4	0	279	279	12	2	1	146	104	2	1	2	144	120	11	10	2	74	66
12	4	0	154	157	13	2	1	55	58	3	1	2	214	220	13	10	2	100	92
13	4	0	90	77	17	2	1	43	43	4	1	2	284	272	13	10	2	80	67
14	4	0	72	65	18	2	1	70	68	5	1	2	39	40	14	10	2	105	103
15	4	0	116	119	3	3	1	102	98	6	1	2	67	64	15	10	2	75	60
16	4	0	40	41	4	3	1	82	66	7	1	2	279	272	11	11	2	59	53
17	4	0	58	60	5	3	1	77	52	8	1	2	70	74	12	11	2	42	37
5	5	0	408	436	6	3	1	313	238	10	1	2	151	153	13	11	2	70	61
6	5	0	116	120	8	3	1	311	239	11	1	2	53	47	12	12	2	128	100
7	5	0	145	142	10	3	1	53	46	12	1	2	78	80	13	12	2	41	40
8	5	0	66	68	11	3	1	130	128	13	1	2	70	60	13	13	2	104	89
9	5	0	212	203	13	3	1	142	151	14	1	2	83	98	0	0	3	351	391
10	5	0	77	65	15	3	1	74	76	15	1	2	37	44	1	0	4	299	297
12	5	0	43	42	16	3	1	128	138	16	1	2	54	52	3	0	3	47	36
13	5	0	81	76	18	3	1	34	38	17	1	2	99	108	4	0	4	52	72
14	5	0	58	56	5	4	1	163	171	18	1	2	57	71	5	0	3	100	108
15	5	0	63	66	7	4	1	34	34	2	2	2	124	109	6	0	3	91	91
18	5	0	58	56	8	4	1	66	69	3	2	2	265	237	7	0	4	54	59
6	6	0	76	85	19	4	1	266	246	4	2	2	182	186	8	0	3	133	129
7	6	0	49	63	14	4	1	38	39	5	2	2	51	53	9	0	3	59	65
8	6	0	157	162	12	4	1	174	152	6	2	2	270	246	10	0	3	191	175
9	6	0	117	117	13	4	1	79	80	7	2	2	67	70	14	0	3	152	175
10	6	0	57	56	14	4	1	60	62	8	2	2	109	119	2	1	3	127	134
11	6	0	137	146	15	4	1	108	115	9	2	2	53	49	3	1	3	153	154
12	6	0	192	201	16	4	1	40	41	10	2	2	94	100	4	1	3	191	206
15	6	0	69	68	17	4	1	60	61	11	2	2	170	167	5	1	3	46	55
16	6	0	73	77	5	5	1	358	374	12	2	2	114	112	6	1	3	60	59
17	6	0	53	60	6	5	1	116	98	13	2	2	105	101	7	1	3	195	199
18	6	0	54	53	7	5	1	123	124	17	2	2	36	41	8	1	3	69	65
7	7	0	142	145	8	5	1	62	59	18	2	2	48	52	1	4	2	148	139
8	7	0	76	75	9	5	1	213	194	3	3	2	134	128	12	1	3	66	81
9	7	0	118	119	10	5	1	65	61	4	3	2	67	73	14	1	3	77	76
11	7	0	146	125	12	5	1	40	40	5	3	2	66	69	15	1	3	45	43
13	7	0	127	121	13	5	1	72	77	6	3	2	241	230	16	1	3	54	50
15	7	0	151	165	14	5	1	58	57	7	3	2	39	40	2	2	3	107	105
16	7	0	53	55	15	5	1	53	62	8	3	2	200	220	3	2	3	175	164
17	7	0	82	73	18	5	1	62	64	10	3	2	46	47	4	2	3	130	135
8	8	0	177	199	6	6	1	50	59	11	3	2	107	111	5	2	3	54	60
13	8	0	158	168	7	6													

$\text{\AA}^{-1}$ ), all data in the  $hkl$  octant were measured using an  $\omega$ -scan method. Of the 1467 reflections examined, 1445 had positive peak intensity for  $\text{Na}_{0.33}\text{WO}_3$ , while the corresponding numbers for  $\text{Na}_{0.48}\text{WO}_3$  were 1468 and 1223.

The two compositions were found to conform to different space groups. In  $\text{Na}_{0.33}\text{WO}_3$ , the following systematic absences were observed:  $h00$  when  $h$  was odd and  $0k0$  when  $k$  was odd, indicating possible space groups  $P4_212$  or  $P4_21m$ . On the other hand, for  $\text{Na}_{0.48}\text{WO}_3$ , systematic absences in  $h0l$  and

$0kl$  reflections when  $h$  and  $k$  were odd were observed, implying  $P4/mbm$ ,  $P4bm$ , or  $P4b2$  as the space group.

Intensity data were corrected for Lorentz-polarization and absorption effects (10), and the estimated error in each intensity was calculated by

$$\sigma_I^2 = C_T + 2C_B + (0.04C_T)^2 + (0.04C_B)^2 + (0.04C_I)^2 T_a^2,$$

where  $C_T$ ,  $C_B$ ,  $C_I$ , and  $T_a$  are the total count, the background count, the net count, and the

TABLE IV  
OBSERVED AND CALCULATED STRUCTURE FACTORS FOR  $\text{Na}_{0.48}\text{WO}_3$

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	0	0	46	58	11	6	0	143	161	13	2	1	101	98	12	5	1	78	78	12	6	2	191	188
4	0	0	149	151	12	6	0	235	234	17	2	1	57	53	11	11	1	59	63	15	6	2	53	44
6	0	0	47	49	15	6	0	67	76	18	2	1	90	91	13	14	1	102	93	16	6	2	69	72
8	0	0	162	157	16	6	0	82	86	3	3	1	101	103	12	12	1	139	122	17	6	2	60	80
10	0	0	257	273	17	6	0	116	94	4	3	1	49	48	13	13	1	126	125	7	7	2	169	169
12	0	0	90	76	7	7	0	204	192	3	3	1	43	42	0	0	2	705	541	8	7	2	69	66
14	0	0	276	307	8	7	0	89	84	6	3	1	232	250	2	0	2	48	34	9	7	2	104	104
2	1	0	115	145	9	7	0	141	131	8	3	1	227	232	4	0	2	124	104	11	7	2	111	106
3	1	0	228	302	11	7	0	150	133	10	3	1	52	51	6	0	2	60	54	13	7	2	116	111
4	1	0	225	344	13	7	0	183	138	11	3	1	139	146	8	0	2	138	133	15	7	2	170	166
6	1	0	60	67	15	7	0	158	199	13	3	1	176	171	10	0	2	229	218	17	7	2	47	67
7	1	0	363	375	16	7	0	44	59	15	3	1	91	88	12	0	2	53	84	8	8	2	174	171
8	1	0	16	76	17	7	0	84	76	16	3	1	163	166	14	0	2	267	250	11	8	2	162	154
10	1	0	176	179	8	8	0	226	212	18	3	1	51	48	2	1	2	127	104	12	8	2	89	81
11	1	0	55	88	9	8	0	44	39	5	4	1	164	175	3	1	2	214	215	13	8	2	45	60
12	1	0	86	76	11	8	0	218	184	8	4	1	56	50	4	1	2	260	259	14	8	2	49	50
13	1	0	95	93	12	8	0	116	102	9	4	1	242	257	6	1	2	53	50	9	9	2	111	113
14	1	0	127	97	13	8	0	87	70	11	4	1	44	35	7	1	2	276	281	10	9	2	136	131
15	1	0	49	51	14	8	0	45	54	12	4	1	187	168	8	1	2	64	56	14	9	2	78	87
16	1	0	66	57	16	8	0	84	71	13	4	1	97	99	10	1	2	160	149	10	10	2	54	80
17	1	0	154	156	17	8	0	56	72	14	4	1	68	70	11	1	2	69	67	11	10	2	79	71
18	1	0	105	97	9	9	0	147	139	15	4	1	145	140	12	1	2	64	62	12	10	2	126	114
2	2	0	104	118	10	9	0	166	156	16	4	1	65	58	13	1	2	81	71	13	10	2	84	78
3	2	0	228	302	12	9	0	67	64	17	4	1	68	69	14	1	2	76	82	14	10	2	129	118
4	2	0	210	244	14	9	0	107	103	5	5	1	281	373	15	1	2	50	45	15	10	2	78	72
6	2	0	322	337	10	10	0	113	97	6	5	1	104	108	16	1	2	51	48	11	11	2	62	61
7	2	0	77	78	11	10	0	105	85	7	5	1	128	134	17	1	2	139	135	13	11	2	66	80
8	2	0	165	181	12	10	0	150	138	8	5	1	62	60	18	1	2	66	83	12	12	2	89	109
9	2	0	44	47	13	10	0	101	92	9	5	1	207	212	2	2	2	109	91	0	0	3	439	373
10	2	0	144	145	14	10	0	159	142	10	5	1	61	58	3	2	2	216	219	4	0	3	89	73
11	2	0	186	197	15	10	0	64	85	12	5	1	45	33	4	2	2	183	190	6	0	3	84	71
12	2	0	125	124	11	11	0	90	75	13	5	1	89	85	5	2	2	248	250	8	0	3	115	104
13	2	0	127	117	13	11	0	110	99	14	5	1	46	54	7	2	2	71	63	10	0	3	168	163
17	2	0	45	55	16	11	0	152	144	15	5	1	78	72	8	2	2	143	137	14	0	3	166	195
18	2	0	95	98	12	12	0	138	124	16	5	1	64	73	10	2	2	129	118	2	1	3	97	89
3	3	0	143	170	13	13	0	130	131	6	6	1	63	58	11	2	2	161	163	3	1	3	177	159
4	3	0	42	56	0	0	1	778	671	7	6	1	53	54	12	2	2	102	107	4	1	3	187	164
5	3	0	83	88	2	0	1	66	65	8	6	1	160	146	13	2	2	93	96	7	1	3	204	197
6	3	0	269	294	4	0	1	126	132	9	6	1	110	114	18	2	2	62	80	10	1	3	125	123
7	3	0	45	41	6	0	1	91	89	10	6	1	63	52	3	3	2	145	131	11	1	3	50	46
9	3	0	285	270	8	0	1	137	131	11	6	1	159	151	4	3	2	50	43	12	1	3	53	49
10	3	0	27	53	10	0	1	248	243	12	6	1	212	205	5	3	2	67	61	13	1	3	44	51
11	3	0	156	141	12	0	1	53	53	15	6	1	64	71	6	3	2	222	222	14	1	3	48	68
13	3	0	153	179	14	0	1	303	289	16	6	1	94	82	8	3	2	203	212	17	1	3	50	104
15	3	0	58	97	2	1	1	150	153	17	6	1	109	90	11	3	2	92	115	2	2	3	94	82
16	3	0	167	176	3	1	1	249	270	7	7	1	172	173	13	3	2	156	146	3	2	3	186	181
5	4	0	156	170	4	1	1	224	232	8	7	1	61	59	15	3	2	56	80	4	2	3	146	122
8	4	0	81	85	6	1	1	47	46	9	7	1	126	125	16	3	2	166	149	6	2	3	204	178
9	4	0	278	251	7	1	1	257	317	11	7	1	125	121	5	4	2	135	133	7	2	3	68	59
12	4	0	193	182	8	1	1	45	42	13	7	1	138	129	8	4	2	66	62	8	2	3	104	90
13	4	0	115	98	10	1	1	167	176	15	7	1	203	192	9	4	2	236	235	10	2	3	73	87
14	4	0	83	78	11	1	1	83	77	17	7	1	85	72	12	4	2	158	148	11	2	3	158	123
15	4	0	148	147	12	1	1	65	70	7	8	1	180	186	13	4	2	80	84	12	2	3	94	86
17	4	0	72	70	13	1	1	90	86	10	8	1	47	39	14	4	2	44	62	13	2	3	84	70
5	5	0	353	451	14	1	1	97	95	11	8	1	178	175	15	4	2	142	125	3	3	3	104	75
6	5	0	122	122	15	1	1	43	45	12	8	1	105	98	17	4	2	49	60	4	3	3	43	32
7	5	0	121	151	16	1	1	54	50	13	8	1	58	70	5	5	2	296	344	6	3	3	168	159
8	5	0	82	80	17	1	1	155	147	14	8	1	63	55	6	5	2	101	68	8	3	3	172	156
9	5	0	236	218	18	1	1	92	93	16	8	1	61	66	7	5	2	117	114	11	3	3	99	94
10	5	0	96	79	2	2	1	116	123	17	8	1	62	68	8	5	2	69	64	13	3	3	132	115
11	5	0	44	34	3	2	1	204	234	9	9	1	129	122	9	5	2	189	176	16	3	3	99	121
13	5	0	96	90	4	2	1	169	168	10	9	1	160	147	10	5	2	56	64	5	4	3	133	115
14	5	0	76	60	6	2	1	275	292	12	9	1	59	82	13	5	2	74	81	0	4	3	183	178
15	5	0	83	74	7	2	1	52	93	14	9	1	107	97	6	6	2	80	74	12	4	3	122	115
6	6	0	106	110	8	2	1	142	143	10	10	1	94	86	7	6	2	48	48	13	4	3	60	72
7	6	0	44	60	9	2	1	47	44	11	10	1	74	74	9</									

TABLE V

FINAL POSITIONAL AND THERMAL PARAMETERS<sup>a</sup> AND THEIR ESTIMATED STANDARD DEVIATIONS<sup>b</sup> FOR Na<sub>0.33</sub>WO<sub>3</sub><sup>c</sup>

Atom	G	x	y	z	B <sub>iso</sub>
W1	1.0	0.0777(1)	0.2063(1)	0.5087(5)	—
W2	1.0	0.0	0.5	0.4550(6)	—
Na	0.825	0.331(2)	0.168	-0.007(19)	5.4(7)
O1A	0.25	0.047	0.211	0.0	5.0
O1B	0.25	0.063	0.172	0.0	5.0
O1C	0.25	0.109	0.211	0.0	5.0
O1D	0.25	0.063	0.234	0.0	5.0
O2	0.5	-0.040(4)	0.460	-0.040(27)	7.2(14)
O3A	0.5	0.142(4)	0.065(4)	0.391(9)	-0.7(5)
O3B	0.5	0.142(4)	0.068(4)	0.563(11)	1.0(8)
O4A	0.5	0.214(3)	0.286	0.467(10)	-0.5(7)
O4B	0.5	0.230(4)	0.270	0.568(14)	0.1(7)
O5A	0.5	0.005(4)	0.350(4)	0.405(11)	-0.3(5)
O5B	0.5	-0.009(4)	0.356(4)	0.560(12)	0.6(7)

Atom	B <sub>11</sub>	B <sub>22</sub>	B <sub>33</sub>	B <sub>12</sub>	B <sub>13</sub>	B <sub>23</sub>
W1	0.00161(6)	0.00168(6)	0.0101(6)	0.00003(5)	0.0004(3)	0.000(3)
W2	0.00149(8)	0.00149	0.015(2)	0.0	0.0	0.0

<sup>a</sup> The parameters with no estimated standard deviation are not refined.<sup>b</sup> In this and subsequent tables, the values in parentheses denote the estimated standard deviations in the last digits.<sup>c</sup> Anisotropic thermal parameters are of the form of  $\exp(-B_{11}h^2 - \dots - 2B_{12}hk - \dots)$ .

TABLE VI

FINAL POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR Na<sub>0.48</sub>WO<sub>3</sub>

Atom	G	x	y	z	B <sub>iso</sub>
W1	1.0	0.0772(1)	0.2065(1)	0.5	—
W2	1.0	1.0	0.5	0.5	—
Na1	1.0	0.331(3)	0.169	0.0	3.8(9)
Na2	0.4	0.0	0.0	0.0	3.1(11)
O1	1.0	0.084(4)	0.209(4)	0.0	4.6(11)
O2	0.5	-0.013(4)	0.487	0.0	3.4(15)
O3	0.5	0.135(3)	0.067(3)	0.459(13)	0.8(6)
O4	0.5	0.219(3)	0.281	0.474(24)	1.2(7)
O5	0.5	-0.004(3)	0.348(3)	0.435(10)	1.0(6)

Atom	B <sub>11</sub>	B <sub>22</sub>	B <sub>33</sub>	B <sub>12</sub>	B <sub>13</sub>	B <sub>23</sub>
W1	0.00105(9)	0.00097(9)	0.0261(1)	-0.00004(6)	0.0	0.0
W2	0.0008(1)	0.0008(9)	0.043(3)	0.0	0.0	0.0

TABLE VII

METAL-OXYGEN DISTANCES AND OXYGEN-METAL-OXYGEN ANGLES FOR  $\text{Na}_{0.33}\text{WO}_3(\text{I})$  AND  $\text{Na}_{0.48}\text{WO}_3(\text{II})$ 

Symmetry <sup>a</sup>			(I)	(II)	Symmetry			(I)	(II)	
W1-O1A	(1, 1)	1.95(6)	1.89(5)	Na1-O1A	(1, 9)	3.00(7)	3.04(6)			
W1-O1A	(1, 2)	1.88(6)		Na1-O1C	(1, 1)	2.74(7)				
W1-O1B	(1, 1)	1.96(6)		Na1-O2	(1, 9)	2.21(7)		2.68(6)		
W1-O1B	(1, 2)	1.90(6)		Na1-O3A	(1, 2)	3.00(6)		3.19(6)		
W1-O1C	(1, 1)	1.95(6)		Na1-O4A	(1, 1)	2.69(6)		2.62(6)		
W1-O1C	(1, 2)	1.88(6)		Na1-O4B	(1, 1)	2.77(6)				
W1-O1D	(1, 1)	1.95(6)		Na1-O4A	(1, 3)	2.81(6)		2.76(6)		
W1-O1D	(1, 2)	1.88(6)		Na1-O4B	(1, 3)	2.36(6)				
W1-O3A	(1, 1)	1.93(5)		1.84(4)	Na1-O5A	(1, 9)		2.58(6)	2.60(6)	
W1-O3B	(1, 1)	1.86(5)		Na1-O5B	(1, 9)	2.85(6)				
W1-O3A	(1, 4)	1.93(5)	1.96(4)	Na1-O5B	(1, 10)	2.58(6)	2.58(6)			
W1-O3A	(1, 4)	1.95(5)	1.95(4)	Na2-O1	(1, 1)	—	2.74(6)			
W1-O4A	(1, 1)	1.92(4)	1.95(4)	Na2-O3	(1, 1)	—	2.52(6)			
W1-O4B	(1, 1)	2.01(5)	2.00(4)	Na2-O3	(1, 10)	—	2.74(6)			
W1-O5A	(1, 1)	1.99(5)								
W1-O5B	(1, 1)	2.10(5)								
W2-O2	(1, 1)	1.98(6)	1.90(5)							
W2-O2	(1, 3)	2.02(6)								
W2-O5B	(1, 1)	1.79(5)	1.86(4)							
W2-O5A	(1, 1)	1.83(5)								
O1A-W1-O1C	(2, 1, 1)	177(3)	175(2)	O1C-W1-O4A	(1, 1, 1)	84(2)	90(2)			
O1A-W1-O3A	(2, 1, 1)	83(2)	85(2)	O1C-W1-O5B	(1, 1, 1)	89(2)	83(2)			
O1A-W1-O4A	(2, 1, 1)	94(2)	84(2)	O1C-W1-O3A	(1, 1, 4)	90(2)	88(2)			
O1A-W1-O5B	(2, 1, 1)	88(2)	97(2)	O3A-W1-O4A	(1, 1, 1)	95(2)	95(2)			
O1A-W1-O3A	(2, 1, 4)	92(2)	97(2)	O3A-W1-O5B	(1, 1, 1)	170(2)	172(2)			
O1C-W1-O3A	(1, 1, 1)	100(2)	95(2)	O3A-W1-O3A	(1, 1, 4)	93(2)	87(2)			
O4A-W1-O5B	(1, 1, 1)	90(2)	92(2)	O3B-W1-O4A	(1, 1, 1)	96(2)	95(2)			
O4A-W1-O3A	(1, 1, 4)	171(2)	178(2)	O3B-W1-O3A	(1, 1, 4)	89(2)	86(2)			
O5B-W1-O3A	(1, 1, 4)	83(2)	86(2)	O4A-W1-O5A	(1, 1, 1)	86(2)	92(2)			
O1A-W1-O3B	(1, 1, 1)	90(2)	85(2)	O5A-W1-O3A	(1, 1, 4)	90(2)	87(2)			
O1A-W1-O4B	(1, 1, 1)	93(2)	90(2)	O1B-W1-O3A	(2, 1, 1)	94(2)	95(2)			
O1A-W1-O5A	(1, 1, 1)	94(2)	97(2)	O1B-W1-O4B	(2, 1, 1)	94(2)	90(2)			
O1A-W1-O3B	(1, 1, 4)	88(2)	88(2)	O1B-W1-O5B	(2, 1, 1)	93(2)	83(2)			
O1C-W1-O3B	(2, 1, 1)	93(2)	95(2)	O1B-W1-O3B	(2, 1, 4)	88(2)	88(2)			
O1C-W1-O4B	(2, 1, 1)	85(2)	84(2)	O1D-W1-O3A	(1, 1, 1)	88(2)	85(2)			
O1C-W1-O5A	(2, 1, 1)	82(2)	83(2)	O1D-W1-O4B	(1, 1, 1)	97(2)	84(2)			
O1C-W1-O3B	(2, 1, 4)	93(2)	97(2)	O1D-W1-O5B	(1, 1, 1)	84(2)	97(2)			
O3B-W1-O4B	(1, 1, 1)	87(2)	95(2)	O1D-W1-O3B	(1, 1, 4)	81(2)	97(2)			
O3B-W1-O5A	(1, 1, 1)	175(2)	172(2)	O3A-W1-O4B	(1, 1, 1)	90(2)	95(2)			
O3B-W1-O3B	(1, 1, 4)	92(2)	86(2)	O3A-W1-O3B	(1, 1, 4)	89(2)	87(2)			
O4B-W1-O5A	(1, 1, 1)	95(2)	92(2)	O4B-W1-O5B	(1, 1, 1)	97(2)	92(2)			
O4B-W1-O3B	(1, 1, 4)	178(2)	178(2)	O5B-W1-O3B	(1, 1, 4)	85(2)	86(2)			
O5A-W1-O3B	(1, 1, 4)	85(2)	87(2)	O2-W2-O2	(1, 1, 3)	180(-)	180(-)			
O1B-W1-O1D	(1, 1, 2)	169(3)	175(2)	O2-W2-O5B	(1, 1, 1)	87(2)	87(2)			
O1B-W1-O3B	(1, 1, 1)	88(2)	95(2)	O2-W2-O5A	(1, 1, 8)	98(2)	93(2)			
O1B-W1-O4A	(1, 1, 1)	96(2)	84(2)	O2-W2-O5B	(3, 1, 1)	92(2)	93(2)			
O1B-W1-O5A	(1, 1, 1)	87(2)	83(2)	O2-W2-O5A	(3, 1, 8)	82(2)	87(2)			
O1B-W1-O3A	(1, 1, 4)	91(2)	97(2)	O5B-W2-O5B	(1, 1, 7)	80(2)	86(2)			

TABLE VII (continued)

	Symmetry	(I)	(II)		Symmetry	(I)	(II)
O1D-W1-O3B	(2, 1, 1)	95(2)	85(2)	O5B-W2-O5A	(1, 1, 8)	171(2)	(180-)
O1D-W1-O4A	(2, 1, 1)	94(2)	90(2)	O5B-W2-O5A	(1, 1, 6)	93(2)	94(2)
O1D-W1-O5A	(2, 1, 1)	90(2)	97(2)	O5A-W2-O5A	(6, 1, 8)	93(2)	94(2)
O1D-W1-O3A	(2, 1, 4)	78(2)	88(2)				

<sup>a</sup> Symmetry codes: 1 = ( $x, y, z$ ); 2 = ( $x, y, z + 1$ ); 3 = ( $x, y, z - 1$ ); 4 = ( $-y, x, 1 - z$ ); 5 = ( $-x, 1 - y, z + 1$ ); 6 = ( $\frac{1}{2} - y, \frac{1}{2} - x, z$ ); 7 = ( $y - \frac{1}{2}, x - \frac{1}{2}, z$ ); 8 = ( $-x, 1 - y, z$ ); 9 = ( $y, -x, -z$ ); 10 = ( $y, -x, 1 - z$ ).

transmission factor, respectively. The factor 0.04 represents an estimate of nonstatistical error. The estimated deviations in the structure factors were calculated by the finite-difference method (11). Of the 1445 reflections in  $\text{Na}_{0.33}\text{WO}_3$ , 916 were considered observed ( $>4\sigma_I$ ). The corresponding numbers for  $\text{Na}_{0.48}\text{WO}_3$  were 1223 and 882.

### Structure Determination and Refinement

The approximate positions of the two symmetry-independent tungsten atoms from both compounds were easily obtained from analyses of the respective sharpened three-dimensional Patterson maps (12). A comparison of these positions shows them to be almost identical in both structures. Since the  $z$  coordinates of the two tungsten atoms in  $\text{Na}_{0.33}\text{WO}_3$  are very close to  $z = \frac{1}{2}$ , the Fourier syntheses computed from these positions using either the space group  $P4_212$  or  $P\bar{4}2_1m$  show pseudosymmetry as if the space group were  $P4/mbm$ . In order to obtain more accurate initial coordinates of the tungsten atoms, two-dimensional Patterson maps were calculated using first of all the  $h0l$  reflections, and then only  $h0l$  reflections with  $h = 2n + 1$ . Consideration of the differences between these two maps suggested that the more suitable space group was  $P\bar{4}2_1m$  rather than  $P4_212$  and that the  $z$  coordinate of one tungsten atom, the one on the twofold axis parallel to  $c$ , deviated slightly from  $\frac{1}{2}$ . As a result, the initial tungsten atomic positions were determined as follows: W(1) (0.08, 0.21, 0.5) and W(2) (0.0, 0.5, 0.45). In the case of  $\text{Na}_{0.48}\text{WO}_3$ , Patterson analysis indicated  $P4/mbm$  as the appropriate space group.

A study of the electron density and difference synthesis in both compounds obtained by using least-squares refined tungsten parameters indicated that all oxygen atoms at  $z \approx \frac{1}{2}$  could be best represented by replacing each with two half oxygen atoms separated along the  $c$ -axis by 0.6 Å. In  $\text{Na}_{0.33}\text{WO}_3$ , the two oxygen atoms at  $z \approx 0$  were also disordered to two- or fourfold sites, but only one oxygen atom of the  $z \approx 0$  type was twofold disordered in  $\text{Na}_{0.48}\text{WO}_3$ .

There are two possible sites for the sodium atoms. One is of a distorted pentagonal geometry in which each sodium would be surrounded by five oxygen atoms, while the other has four closest oxygen contacts. In  $\text{Na}_{0.33}\text{WO}_3$  a difference electron density synthesis demonstrated that the sodium atoms reside only in the pentagonal site. Indeed any sodium atom in the tetragonal site would find itself in very close proximity to oxygen atoms (1.8 to 2.1 Å). In  $\text{Na}_{0.48}\text{WO}_3$ , with its somewhat larger tetragonal site, sodium atoms were found to be located in both types of sites. However, the electron density of the pentagonal site was much larger than that of the tetragonal site. Occupancy factors were refined using several thermal parameters to reduce correlation effects. This procedure strongly suggested that the pentagonal sites were completely filled while only approximately 40% of the tetragonal sites were occupied.

The atomic positions were first refined isotropically via a full-matrix least-squares technique (13) minimizing the function  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 1.0/\sigma_F^2$  to conventional discrepancy indices of  $R = 11.8\%$  for  $\text{Na}_{0.33}\text{WO}_3$  and  $R = 11.5\%$  for  $\text{Na}_{0.48}\text{WO}_3$ .

In  $\text{Na}_{0.33}\text{WO}_3$ , the oxygen atom that was distributed over four sites did not converge to reasonable positions, probably due to the small amount of electron density associated with each site and correlation effects due to their close proximity to one another; therefore, these positions were fixed from consideration of the difference synthesis map, and isotropic thermal parameters were estimated. Anisotropic thermal parameters were introduced for the tungsten atoms, and the  $R$  indices dropped to 11.0% for  $\text{Na}_{0.33}\text{WO}_3$  and 10.8% for  $\text{Na}_{0.48}\text{WO}_3$ . Agreement with space group equivalent reflections were then checked. In the pairs with  $|F(hkl) - F(khl)| > 2.5(\sigma_F(hkl) + \sigma_F(khl))$ ,  $\sim 10\%$  of the data and particularly at large  $\theta$ , a reflection which had larger residual from the calculated structure factor than its symmetry equivalent partner was eliminated from the data set. Successive refinements using this new data set reduced the  $R$  indices to 9.9% for  $\text{Na}_{0.33}\text{WO}_3$  and 9.6% for  $\text{Na}_{0.48}\text{WO}_3$ . It was also noted that for large reflections the calculated structure factors had larger magnitudes than the observed structure factors, indicating that extinction was making an appreciable effect. Therefore, a correction for extinction was made by Zachariasen's method (14), the values of the extinction parameter being  $3.8(5) \times 10^{-4}$  for  $\text{Na}_{0.33}\text{WO}_3$  and  $3.1(4) \times 10^{-4}$  for  $\text{Na}_{0.48}\text{WO}_3$  on an absolute scale. The possibility of appreciable anisotropic extinction was also checked but such effects did seem prevalent here. Also the structure factors for  $\text{Na}_{0.33}\text{WO}_3$  were computed for the enantiomorph image in order to check for a significant absolute configuration effect. However, no significant difference was recognizable.

The final agreement factors obtained were:  $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.089$  ( $\text{Na}_{0.33}\text{WO}_3$ ) and 0.084 ( $\text{Na}_{0.48}\text{WO}_3$ ),  $R_w = [\sum (|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.116$  ( $\text{Na}_{0.33}\text{WO}_3$ ) and 0.119 ( $\text{Na}_{0.48}\text{WO}_3$ ). Several oxygen atoms in  $\text{Na}_{0.33}\text{WO}_3$  showed slightly negative thermal parameters as is indicated in Table V, but this is not considered unusual in view of the disordering of these atoms. The atomic scattering factors used were those of Hanson *et al.* (15), modified for the real and imaginary parts of anomalous dispersion (16). The observed and calculated

structure factors are listed in Tables III and IV, and the fractional coordinates and thermal parameters are listed in Tables V and VI, respectively.

## Results and Discussion

The tungsten-oxygen distances and associated angles are listed in Table VII. The distances in  $\text{Na}_{0.33}\text{WO}_3$  range from 1.79(5) Å for W2-O5B to 2.10(5) Å for W1-O5B. The corresponding values in  $\text{Na}_{0.48}\text{WO}_3$  are 1.84(4) Å for W1-O3 and 2.00(4) Å for W1-O5. Such a variation in distances is not unexpected due to the poor determination of the oxygen positions caused by disordering.

An axis of the  $\text{WO}_6$  octahedron is not strictly parallel with the  $c$ -axis, and the angle of tilt is greater in the case of  $\text{Na}_{0.33}\text{WO}_3$  than in  $\text{Na}_{0.48}\text{WO}_3$ , namely  $14^\circ$  compared to  $11^\circ$ . A similar situation has been found in several compounds previously determined with crystal structure of the "tungsten-bronze" type; for example in  $\text{Ba}_{(4\pm x)}\text{Na}_{(2-2x)}\text{Nb}_{10}\text{O}_{30}$  (17), the angle was found to range from  $4.9^\circ$  to  $8.2^\circ$ . The tungsten atoms in the two independent  $\text{WO}_6$  octahedra in  $\text{Na}_{0.33}\text{WO}_3$  are displaced by 0.201 Å relative to each other in the  $c$  direction, but in  $\text{Na}_{0.48}\text{WO}_3$  they have identical  $c$  coordinates. The Na-O distance in  $\text{Na}_{0.33}\text{WO}_3$  ranges from 2.21(9) Å for Na-O2 to 3.00(9) Å for Na-O1A. In  $\text{Na}_{0.48}\text{WO}_3$  on the other hand, the corresponding values are 2.52(6) Å for Na2-O3 and 3.19(6) Å for Na1-O3. Also in  $\text{Na}_{0.33}\text{WO}_3$ , one oxygen located approximately at  $z=0$  is disordered over four sites, while the corresponding oxygen atom in  $\text{Na}_{0.48}\text{WO}_3$  is not significantly disordered, although its thermal parameter is appreciably larger than the others. All evidence therefore points to the crystal structure of  $\text{Na}_{0.33}\text{WO}_3$  being more distorted than that of  $\text{Na}_{0.48}\text{WO}_3$ .

The  $\text{WO}_6$  octahedra are linked together via sharing a corner. This process produces three kinds of interstitial sites in the framework. These are pentagonal, tetragonal, and trigonal in nature, each site having oxygen atoms as nearest neighbors. From consideration of the sodium and oxygen ionic radii, it is found to be possible to locate the sodium atoms only on the



first two types of sites. However, the volume of the pentagonal site is much larger than that of the tetragonal site, the radius of the latter being somewhat shorter than the sum of ionic radii. Hence, it would be expected that sodium atoms would first fill the pentagonal sites and

subsequently, the tetragonal ones. In the crystal structure of  $\text{Na}_{0.48}\text{WO}_3$ , sodium atoms are found in both types of sites with occupancy of 1.0 for the pentagonal site and 0.4 for the tetragonal one. On the other hand, in the structure of  $\text{Na}_{0.33}\text{WO}_3$  it is only the pentag-

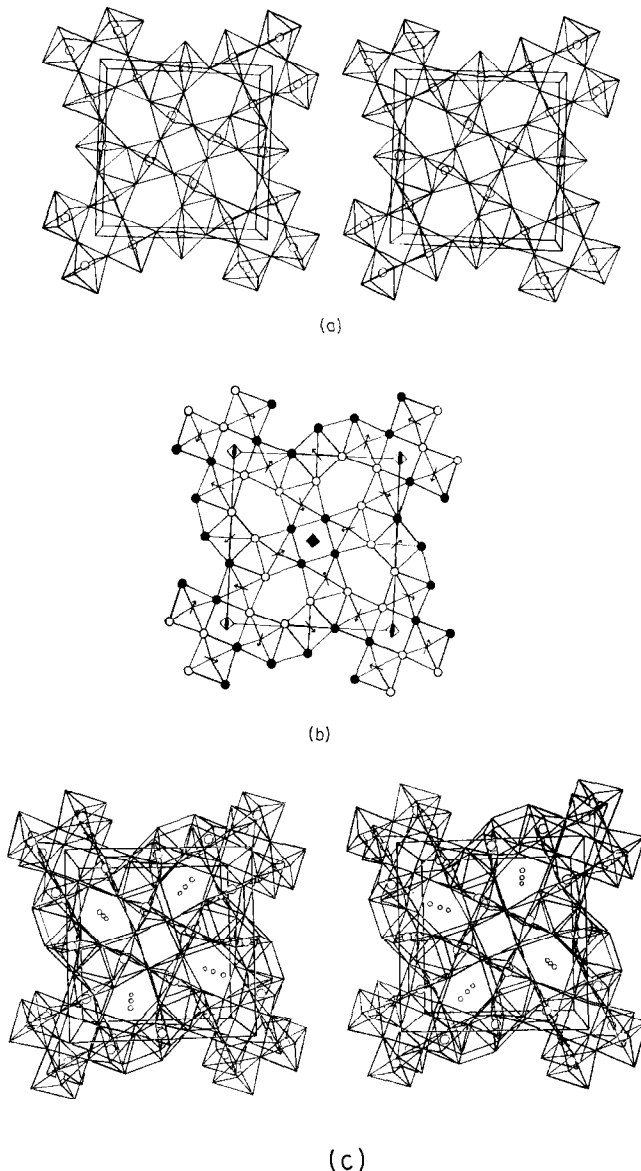
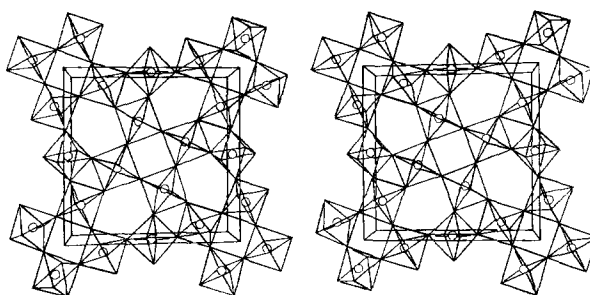
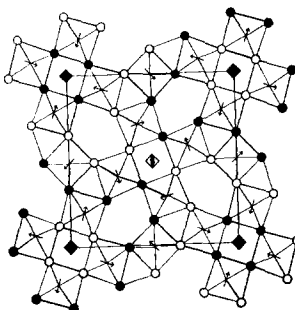


FIG. 1. (a) A stereographic drawing of one of two possible domain structures of  $\text{Na}_{0.33}\text{WO}_3$  as deduced from this study. The  $c$ -axis is coincident with a 4-axis. (b) An alternate illustration of the first domain structure emphasizing the positions of the oxygen atoms. Those indicated by unfilled circles are above the  $z = \frac{1}{2}$  plane, and those by filled circles are below. (c) A stereographic drawing of the unit cell illustrating the positions of the sodium ions in the pentagonal sites.



(a)



(b)

FIG. 2. (a) A stereographic drawing of the second domain structure. The  $c$ -axis is coincident with a 4-axis. (b) An alternate illustration of the second domain structure. The labeling of the atoms is identical to that of Fig. 1b.

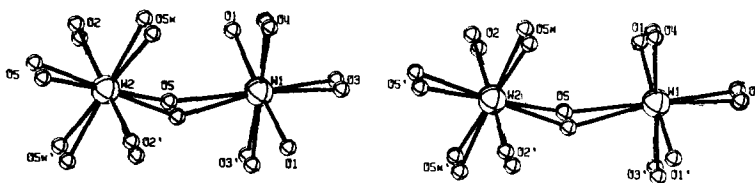


FIG. 3. Disordered  $\text{WO}_6$  octahedra for  $\text{Na}_{0.48}\text{WO}_3$ .

onal sites that are filled with an occupancy of 0.825.

The disordered arrangement found in  $\text{Na}_{0.33}\text{WO}_3$  may be viewed as the superposition of two kinds of ordered arrangements as illustrated in Figs. 1 and 2 (18). If one assumes that the ordered model still possesses the 4-axis, then a fourfold axis is produced in the center of the unit cell. The disordered arrangement found could then be obtained by superimposing a second ordered cell shifted by one-half in the  $a$  and  $b$  directions. Thus, the disordered cell could be viewed as a random

combination of these two kinds of domain structures, or alternately, might be viewed via a twinning model whose twinning plane is the  $(001)$  and the origin of one domain structure coincides with the point  $(0.5, 0.5, 0.0)$  of the other domain structure. It is impossible to distinguish these two possibilities by consideration of the final result. In any case a completely ordered arrangement leads to the doubling of the  $c$ -axis and selection of new  $a$ - and  $b$ -axis along the  $[110]$  and  $[\bar{1}10]$  directions, respectively. A similar situation would occur in  $\text{Na}_{0.48}\text{WO}_3$  (Fig. 3).

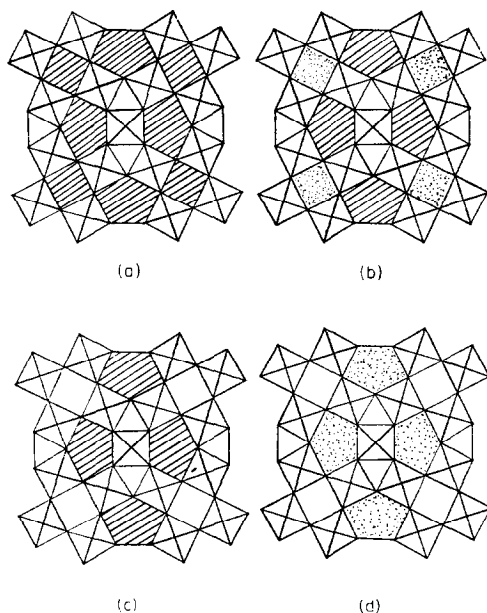


FIG. 4. The relation between the  $x$ -value in  $\text{Na}_x\text{WO}_3$  and their crystal structures. (a)  $x = 0.6$ . Pentagonal ( $P$ ) and tetragonal ( $T$ ) sites are filled up Na atoms.  $P = 1.0$ ,  $T = 1.0$ . Space group is  $P4/mbm$ . (b)  $0.4 < x < 0.6$ . Sodium vacancies increase in tetragonal site.  $P = 1.0$ ,  $T = 5(x - 0.4)$ . Space group is  $P4/mbm$ . (c)  $x = 0.4$ . Tetragonal site is perfectly empty.  $P = 1.0$ ,  $T = 0.0$ . Space group is  $P\bar{4}2_1m$ . (d)  $0.2 < x < 0.4$ . Sodium vacancies increase in pentagonal tunnel at intervals of 1.  $P = 2.5x$ ,  $T = 0.0$ . Space group is  $P\bar{4}2_1m$ .

As noted earlier, when the  $x$  value in  $\text{Na}_x\text{WO}_3$  is in the range of  $0.6 \geq x \geq 0.2$ , the bronze has been reported to crystallize in the tetragonal I form. Our work has shown that this tetragonal form really consists of two different tetragonal space groups, which we will term tetragonal I and tetragonal I'. One can view the changes that take place as the  $x$  value is decreased as follows (see Fig. 4): at  $x = 0.6$ , one can assume that all the pentagonal and tetragonal sites are completely filled with sodium atoms. In the region of  $0.6 \geq x \geq 0.4$ , the appropriate space group is  $P4/mbm$  with the two independent  $\text{WO}_6$  octahedra having their centers on the same plane. As the  $x$  value is decreased, sodium vacancies occur in the tetragonal sites and the angle between the  $c$ -axis and the octahedron axis increases with decreasing  $x$ . The unit cell parameters all decrease. At  $x = 0.4$ , all the sodium atoms are

depleted from the tetragonal sites. A further decrease in  $x$  causes a space group change from  $P4/mbm$  to  $P\bar{4}2_1m$ , and sodium vacancies begin to appear in the pentagonal tunnel along with a further increase in the angle between the  $c$ -axis and the closest octahedron axis. This increase in the angle produces some abnormally short Na-O distances in the pentagonal tunnel at intervals of one unit cell repeat in the  $c$ -direction. (This distance is  $2.21(9) \text{ \AA}$  in  $\text{Na}_{0.33}\text{WO}_3$  and  $2.67(7) \text{ \AA}$  in  $\text{Na}_{0.48}\text{WO}_3$ .) At the same time, the two symmetry independent tungsten atoms move slightly apart in the  $c$ -direction. These distortions coupled with a further decrease in cell dimensions partially compensate for the sodium site vacancies. It is therefore reasonable to assume that those sites with the abnormally short sodium oxygen distances are the most likely ones where vacancies will occur. At  $x = 0.2$  sodium atoms exist only in the pentagonal tunnel at intervals of one  $c$  direction repeat distance. As the  $x$  value is decreased below 0.2, there is a phase transition from the tetragonal I' type to tetragonal II with space group  $P4/nmm$  (4).

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