

Neutron Diffraction Studies of Cubic Tungsten Bronzes

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Powder neutron diffraction studies of $\text{Li}_{0.36}\text{WO}_3$, $\text{Na}_{0.73}\text{WO}_3$ and $\text{La}_{0.14}\text{WO}_3$ show them to be isostructural with cubic $\text{D}_{0.53}\text{WO}_3$. Apart from $\text{La}_{0.14}\text{WO}_3$, all have distorted perovskite structures described by a body centered unit cell ($Im\bar{3}$) containing eight formula weights. The distortion, which decreases in the order $D \sim \text{Li} > \text{Na}$ creates two crystallographically inequivalent A sites: 12 coordinate $(0, 0, 0)$ and 4 coordinate $(\frac{1}{2}, \frac{1}{2}, 0)$. Although precise occupation numbers of these sites could not be determined directly, it is probable that the lithium atoms are ordered into the 4 coordinate sites. $\text{La}_{0.14}\text{WO}_3$ has the simple perovskite structure with a random distribution of lanthanum atoms over the 12 coordinate A sites. Comparative features of the cubic tungsten bronze structures are discussed.

Introduction

Cubic tungsten bronzes $M_x\text{WO}_3$ occur with insertion elements $M = \text{Li}, \text{Na},$ and La . All are electronically and structurally related, but complete structure determinations have not hitherto been made.

Previous reports (1-5) on the preparation and properties of lithium tungsten bronze phases Li_xWO_3 ($0 < x \leq 0.5$) show that the unit cell symmetry increases with increasing x and a cubic phase exists for $x \geq 0.26$. Unlike the sodium tungsten bronzes, however, the tetragonal I structure is not formed and the lattice is observed to contract rather than expand with an increase in x content. The lithium and oxygen positions have not been determined previously.

There has been no report of a superlattice of the simple perovskite unit cell but extra reflections are clearly visible on powder X-ray photographs. The positions of the extra reflections corresponded to the strongest superlattice reflections of the cubic D_xWO_3 structure (6) suggesting an analogous WO_3 framework distortion.

Although the cubic sodium tungsten bronze Na_xWO_3 ($0.37 \leq x \leq 0.95$) is the most extensively studied bronze phase, there are still

several features of the crystal structure which are not clearly understood.

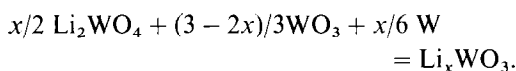
Due to anomalies in the resistivity of cubic Na_xWO_3 (7), Atoji and Rundle undertook a single crystal neutron diffraction study of $\text{Na}_{0.75}\text{WO}_3$ (8). The crystal was grown electrolytically and optical examination showed that twinning occurred with each single domain possessing a very slight tetragonal distortion. The optical results were similar to those found earlier in a more complete study (9). The presence of additional very weak reflections necessitated a double cubic unit cell containing eight molecules. The Laue symmetry of the composite crystal was $m\bar{3}m$ and the data were interpreted by Fourier and least-squares techniques. The final agreement was poor ($R_f = 17\%$, no data given) and the model proposed involved an ordering of the sodium atoms in the $6(b)$ $(\frac{1}{2}, \frac{1}{2}, 0)$ sites of $Im\bar{3}m$ with the $2(a)$ $(0, 0, 0)$ sites empty. The tungsten atoms were arranged on a primitive cubic lattice and the 24 oxygen atoms were statistically distributed over 96 sites corresponding to the superimposition of the individual domains. The structure of a single domain and the mode of intergrowth were not deduced.

All the rare-earth elements form tungsten bronzes with similar structural and electronic properties to the lithium and sodium analogs (10-14). A tetragonal *I* structure is not formed, however, and the change from a deformed perovskite to a cubic phase occurs at lower *x* values ($x = 0.08$ for La_xWO_3), the cubic phase having a relatively small range of homogeneity ($0.08 \leq x \leq 0.19$). Magnetic (10), optical, and Mössbauer (15) measurements indicate that the lanthanide is in the trivalent oxidation state.

The purpose of the present work was to attempt complete structure determinations for the phases $\text{Li}_{0.36}\text{WO}_3$, $\text{Na}_{0.54}\text{WO}_3$, $\text{Na}_{0.73}\text{WO}_3$, and $\text{La}_{0.14}\text{WO}_3$ by powder neutron diffraction.

Sample Preparation and Analysis

Li_xWO_3 . Neutron diffraction studies of lithium compounds are severely impeded by the very small lithium scattering length and accordingly a bronze containing the maximum possible lithium content was prepared. The solid-state reaction used was



The dried reagents Li_2WO_4 (Hopkin and Williams), WO_3 , and W (Analar B.D.H.) were reacted together in evacuated gold lined silica tubes at 650°C . A reaction time of 1 week was used and the samples slowly cooled to room temperature. The samples, which were observed to darken over a period of several weeks in air, were stored *in vacuo*. The purity of the product was checked by X-ray diffraction, and the *x* content was determined by thermogravimetric oxidation. The maximum *x* content found for a pure bronze phase was 0.36 ± 0.01 and the X-ray powder pattern (Table I) implied a cubic unit cell with $a = 7.446 \pm 0.001 \text{ \AA}$.

Na_xWO_3 . Large samples ($\sim 25 \text{ g}$) of well-sintered sodium tungsten bronzes were prepared by the solid-state reaction

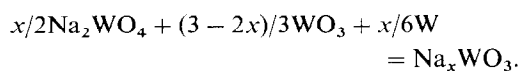


TABLE I
X-RAY POWDER PATTERN OF CUBIC $\text{Li}_{0.36}\text{WO}_3$

Subcell	Double-cell			
	<i>h k l</i>	<i>h k l</i>	<i>d</i> _{obs}	<i>d</i> _{calc}
1 0 0	2 0 0		3.715	3.723
	1 1 0		2.634	2.633
		3 1 0	2.351	2.355
	1 1 1		2.149	2.150
		3 2 1	1.990	1.990
2 0 0	4 0 0		1.861	1.862
2 1 0	4 2 0		1.665	1.665
2 1 1	4 2 2		1.521	1.520
		5 1 0	1.459	1.460
2 2 0	4 4 0		1.317	1.316
		4 3 3	1.280	1.277
3 0 0	6 0 0		1.242	1.241
		5 3 2	1.211	1.208
	3 1 0	6 2 0	1.178	1.177
	3 1 1	6 2 2	1.123	1.123
	2 2 2	4 4 4	1.074	1.075
	3 2 0	6 4 0	1.031	1.033
		6 3 3	1.012	1.013
	3 2 1	6 4 2	0.9934	0.9951
	4 0 0	8 0 0	0.9304	0.9308
	4 1 0	8 2 0	0.9026	0.9030
	4 1 1	8 2 2	0.8773	0.8776
		7 4 3	0.8654	0.8656
	3 3 1	6 6 2	0.8539	0.8542
		7 5 2	0.8431	0.8431
	4 2 0	8 4 0	0.8325	0.8325
	4 2 1	8 4 2	0.8125	0.8125
	3 3 2	6 6 4	0.7938	0.7938
		9 3 0	0.7850	0.7849

Anhydrous Na_2WO_4 was prepared by heating $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (Analar B.D.H.) at 120°C for 12 hr. The reactants were heated in a gold-lined silica tube at 850°C for 1 week and then cooled slowly to room temperature.

Two samples were prepared with nominal *x* values of 0.55 and 0.75 and the corresponding cubic lattice constants were 3.828 ± 0.001 and $3.845 \pm 0.001 \text{ \AA}$. A powder photograph of the sample with largest *x* content did reveal an extremely small splitting of the highest angle reflection. This was more clearly observed using a Phillips PW1051 diffractometer and an estimate of $c/a = 3.844/3.847 = 0.9992$ was made.

The accurate compositions of the bronzes were determined by several independent methods. Thermogravimetric oxidation (to $\text{Na}_2\text{W}_2\text{O}_7$ and $\text{Na}_2\text{W}_4\text{O}_{13}$) gave x contents of 0.73 ± 0.01 and 0.54 ± 0.01 . These values compare well with estimates of 0.74 ± 0.02 and 0.53 ± 0.02 made by use of Brown and Banks linear relationship between composition and lattice constant (16, 17). In the case of the bronze with highest sodium content, a further check was made. The mean oxidation state of tungsten was determined by the reducing power method of Choain and Marion (18). Assuming no oxygen deficiency, an x value of 0.730 ± 0.002 was deduced. The compositions of the two bronzes were taken as $\text{Na}_{0.73}\text{WO}_3$ and $\text{Na}_{0.54}\text{WO}_3$.

La_xWO_3 . Several of the lanthanides are not suitable for neutron studies as they have extremely large absorption cross sections. Lanthanum was chosen as it has a small absorption coefficient and a large scattering length. A solid-state reaction



was carried out at 1020°C for 3 days in a sealed silica tube. The blue-violet product was characterized (by X-ray diffraction) as a pure cubic phase of lattice constant $a = 3.833 \pm 0.001 \text{ \AA}$. A nominal composition of 0.14 ± 0.01 was confirmed by the weight change on oxidation. There was no indication from the powder photograph of either high-angle splitting or the existence of a superlattice.

Neutron Diffraction

Neutron Bragg intensities were measured at room temperature on a powder diffractometer at the reactor "Pluto" A.E.R.E. Harwell. The samples were contained in vanadium cans and data were collected in the 2θ angular range $5\text{--}85^\circ$. The lithium and lanthanum bronzes were studied using neutrons of wavelength 1.105 \AA from a copper monochromator. To improve the counting statistics for the weak superlattice reflections in the sodium tungsten bronzes a very long monitor count was employed together with a neutron wavelength of 1.46 \AA . The longer wavelength was obtained by reflection from the 311 planes of a

crushed germanium monochromator and a take-off angle of 72° .

Refinements

$\text{Li}_{0.36}\text{WO}_3$. All the reflections could be indexed on the cubic X-ray unit cell subject to systematic absences when $h + k + l = 2n + 1$ (Table I). The superlattice reflections were very strong and their intensity distribution was very similar to that found for cubic $\text{D}_{0.53}\text{WO}_3$ (6) which adopts a structure described by the space group $Im\bar{3}$ with 24O in 24(g) $(0, y, z)$ and 8W in 8(c) $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$.

Full-matrix least-squares refinements in the space group $Im\bar{3}$ were made using a computer program (19) which minimizes the quantity

$$M = \sum_i w_i (I_{\text{obs}_i} - I_{\text{calc}_i})^2.$$

TABLE II
OBSERVED AND CALCULATED
INTENSITIES FOR $\text{Li}_{0.36}\text{WO}_3$

hkl	I_{calc}	I_{obs}	$\sigma(I_{\text{obs}})$
200	46.76	46.50	0.28
310	27.94	28.35	0.25
130			
222			
222	11.01	11.70	0.20
321	29.88	29.58	0.26
231			
400	28.53	28.43	0.26
420	39.47	39.70	0.36
240			
422	5.22	5.49	0.36
431	10.17	9.42	0.23
341			
510			
150			
512	7.38	6.91	0.28
152			
440	13.99	13.86	0.27
433	28.02	28.02	0.30
530			
350			
442	16.39	16.78	0.30
600			
532	34.40	34.45	0.32
352			
611			

TABLE III
ATOM PARAMETERS FOR $\text{Li}_{0.36}\text{WO}_3^a$

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (\AA^2)	Atoms per unit cell
Li(1)	2(<i>a</i>)	0.0	0.0	0.0	2.8(1.3)	0.0
Li(2)	6(<i>b</i>)	0.5	0.5	0.0	2.8(1.3)	2.88
O	24(<i>g</i>)	0.205(1)	0.292(1)	0.0	0.67(7)	24.0
W	8(<i>c</i>)	0.25	0.25	0.25	0.3(2)	8.0

^a Estimated standard deviations in parentheses.

Thirteen peak intensities were calculated and w_i was taken as $1/\sigma_i^2$ where σ_i is the standard deviation of the *i*th intensity as estimated from counting statistics. Neutron scattering lengths of $b_{\text{Li}} = -0.214 \times 10^{-12}$ cm, $b_{\text{W}} = 0.477 \times 10^{-12}$ cm, $b_{\text{O}} = 0.580 \times 10^{-12}$ cm were used (20).

The *Im*3 model was used to describe the position of eight formula weights in the unit cell and the 2.88 lithium atoms were distributed randomly on the perovskite *A* sites, i.e., 0.72 Li in 2(*a*) (0,0,0) and 2.16 in 6(*b*) ($\frac{1}{2}, \frac{1}{2}, 0$). Unit isotropic temperature factors were assigned and the undistorted structure gave an R_I index ($[\sum_i w_i(I_{\text{obs}_i} - I_{\text{calc}_i})]/\sum I_{\text{obs}_i}$) of 65%. Displacement of the oxygen atoms and refinement of three temperature factors reduced the R_I index dramatically to 1.36% with an agreement factor, $\{[\sum_i w_i(I_{\text{obs}_i} - I_{\text{calc}_i})]/(m-n)]^{1/2}$, where m = number of observations (13) and n = number of parameters (5),

of 2.32. Refinement of the lithium occupation numbers of the 2(*a*) and 6(*b*) sites, with the sum constrained to the composition, gave an agreement factor of 2.35 ($R_I = 1.35$). The final agreement between observed and calculated

TABLE V
OBSERVED AND CALCULATED
INTENSITIES FOR $\text{Na}_{0.73}\text{WO}_3$

<i>h k l</i>	I_{calc}	I_{obs}	$\sigma(I_{\text{obs}})$
2 0 0	72.09	72.30	0.34
2 2 0	2.92	2.83	0.19
3 1 0	5.75	5.73	0.19
1 3 0			
2 2 2	111.38	111.26	0.39
3 2 1	8.04	7.89	0.20
2 3 1			
4 0 0	171.43	171.12	0.46
4 2 0	62.32	62.59	0.30
2 4 0			
4 3 1	6.12	6.43	0.20
3 4 1			
5 1 0			
1 5 0	3.47	3.06	0.19
5 1 2			
1 5 2	166.63	166.86	0.47
4 4 0			
4 3 3	6.72	6.84	0.20
4 3 3			
5 3 0			
3 5 0	45.08	44.80	0.30
4 4 2			
6 0 0	11.88	11.88	0.23
5 3 2			
3 5 2			
6 1 1			

TABLE IV

BOND ANGLES AND DISTANCES FOR $\text{Li}_{0.36}\text{WO}_3$

Bond distances (\AA)		Bond angles ($^\circ$)	
W1-W2	3.723(1)	W1-W2-OI	13.8
W1-OI	1.917(2)	W1-OI-W2	152.3
OI-OII	3.053(5)	OI-W1-OIII	88.5
OI-OII'	3.098(5)	OI-W1-OIV	88.2
OI-OIII	2.675(3)	OI-W1-OV	91.0
Li-OI	2.175(2)	OIII-W1-OIV	92.3
Li-OIV	2.657(3)		
Li-OV	3.075(3)		

TABLE VI
ATOM PARAMETERS FOR $\text{Na}_{0.73}\text{WO}_3$

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (\AA^2)	Atoms per unit cell
Na(1)	2(<i>a</i>)	0.0	0.0	0.0	1.6(1)	2.00(34)
Na(2)	6(<i>b</i>)	0.5	0.5	0.0	1.6(1)	3.84(34)
O	24(<i>g</i>)	0.2382(2)	0.2618(2)	0.0	0.56(4)	24.0
W	8(<i>c</i>)	0.25	0.25	0.25	0.20(7)	8.0

intensities are listed in Table II and the corresponding positional and thermal parameters in Table III. The structural parameters obtained are compatible with the weakness of the reflections not included in the refinement.

Further relaxation involving displacement of the lithium atoms from the *A* sites and reduction of the symmetry of the WO_3 framework did not significantly improve the agreement.

$\text{Na}_{0.73}\text{WO}_3$. Thirteen intensities from 25 independent reflections were chosen for refinement together with a sodium scattering length (*l*) of 0.362 and unit isotropic temperature factors.

An ideal perovskite structure containing a random distribution of sodium atoms (i.e., 1.46 Na in 2(*a*) (0,0,0) and 4.38 Na in 6(*b*) ($\frac{1}{2}, \frac{1}{2}, 0$)) gave an R_I index of 9.7%. Displacement of the oxygen atoms along $\langle 110 \rangle$ in *Im*3 and refinement of three temperature factors gave $R_I = 0.38\%$ and an agreement factor

(A.F.) = 1.31 (five parameters). This may be compared with the two possible fully ordered models: (i) 5.84 Na in 6(*b*), (2(*a*) empty), $R_I = 0.83\%$ A.F. = 3.11; (ii) 2 Na in 2(*a*), 3.84 Na in 6(*b*), $R_I = 0.38\%$ A.F. = 1.18.

Refinement of the sodium occupation number to 2.00 (± 0.34) Na in 2(*a*) and 3.84

TABLE VIII
OBSERVED AND CALCULATED
INTENSITIES FOR $\text{Na}_{0.54}\text{WO}_3$

<i>h k l</i>	I_{calc}	I_{obs}	$\sigma(I_{\text{obs}})$
2 0 0	71.90	72.22	0.35
3 1 0	4.24	4.72	0.20
1 3 0			
2 2 2	84.12	84.18	0.35
3 2 1	5.89	5.80	0.22
2 3 1			
4 0 0	136.33	135.27	0.43
4 2 0	60.18	60.74	0.31
2 4 0			
4 3 1	4.48	4.50	0.19
3 4 1			
5 1 0	2.61	3.27	0.19
1 5 0			
5 1 2	131.59	132.16	0.43
1 5 2			
4 4 0	4.87	4.47	0.18
4 3 3			
5 3 0	42.63	42.21	0.29
3 5 0			
4 4 2	8.49	8.37	0.21
6 0 0			
5 3 2	6 1 1		
3 5 2			

TABLE VII

BOND ANGLES AND DISTANCES FOR $\text{Na}_{0.73}\text{WO}_3$
(FIG. 1)

Bond distances (\AA)		Bond angles ($^\circ$)	
W1-W2	3.845(1)	O1-W1-OIII	89.9
W1-O1	1.927(1)	O1-W1-OV	90.1
O1-OII	3.664(1)	W1-W2-O1	3.8
O1-OIII	2.722(1)	W1-O1-W2	172.4
OIII-OIV	2.725(1)		
Na-O1	2.591(1)		
Na-OIV	2.722(1)		
Na-OV	2.847(1)		

TABLE IX
ATOM PARAMETERS FOR $\text{Na}_{0.54}\text{WO}_3$

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)	Atoms per unit cell
Na(1)	2(<i>a</i>)	0.0	0.0	0.0	1.2(3)	1.08
Na(2)	6(<i>b</i>)	0.5	0.5	0.0	1.2(3)	3.24
O	24(<i>g</i>)	0.2386(2)	0.2614(2)	0.0	0.8(1)	24.0
W	8(<i>c</i>)	0.25	0.25	0.25	0.1(1)	8.0

(± 0.34) Na in 6(*b*) gave $R_I = 0.38\%$ A.F. = 1.26 (six parameters).

It is seen that all modes of sodium ordering give extremely small discrepancy factors. The agreement for an ordering of sodium atoms in 2(*a*) is shown in Table V and the corresponding atom parameters in Table VI. Further refinements did not suggest a more complex structure.

$\text{Na}_{0.54}\text{WO}_3$. Twelve intensities from 24 independent reflections were used in the refinements. A simple perovskite structure with a random distribution of sodium atoms and unit isotropic temperature factors gave an R_I index of 9%. Displacement of the oxygen atoms along $\langle 110 \rangle$ in $Im\bar{3}$ together with refinement of three temperature factors reduced the R_I index to 0.86% (A.F. = 2.34 (five parameters)). The two ordered models gave: (i) 2.0 Na in (0,0,0), 2.32 Na in ($\frac{1}{2}, \frac{1}{2}, 0$), $R_I = 0.85\%$, A.F. = 2.30; (ii) 4.32 Na in ($\frac{1}{2}, \frac{1}{2}, 0$), (0,0,0) empty, $R_I = 0.89\%$, A.F. = 2.08.

Refinement of the sodium occupation numbers resulted in occupation parameters of 0.20 ± 0.41 Na in (0,0,0) and 4.12 ± 0.41 Na in ($\frac{1}{2}, \frac{1}{2}, 0$) with $R_I = 0.86\%$, A.F. = 2.20 (six parameters).

The agreement between observed and calculated intensities for the random model is listed in Table VIII and the corresponding structure parameters in Table IX. Displacement of the sodium ions off the *A* sites and further deformation of the WO_3 framework did not improve the agreement.

$\text{La}_{0.14}\text{WO}_3$. There was no evidence of any superlattice reflections and the intensities and errors of 10 reflections were determined. A

neutron scattering length of $b_{\text{La}} = 0.83 \times 10^{-12}$ cm was used (20).

The atoms were placed at the special sites of the ideal perovskite unit cell (space group

TABLE X
BOND ANGLES AND DISTANCES FOR $\text{Na}_{0.54}\text{WO}_3$

Bond distances (Å)		Bond angles (°)	
W1-W2	3.828(1)	OI-W1-OIII	89.9
W1-OI	1.918(1)	OI-W1-OV	90.1
OI-OII	3.653(3)	W1-W2-OI	3.7
OI-OIII	2.710(2)	W1-OI-W2	172.6
OIII-OIV	2.715(2)		
Na-OI	2.583(2)		
Na-OIV	2.710(2)		
Na-OV	2.830(2)		

TABLE XI
OBSERVED AND CALCULATED
INTENSITIES FOR $\text{La}_{0.14}\text{WO}_3$

<i>hkl</i>	I_{calc}	I_{obs}	$\sigma(I_{\text{obs}})$
1 0 0	13.83	13.81	0.19
1 1 1	12.94	12.79	0.20
2 0 0	20.45	20.49	0.20
2 1 0	10.20	10.36	0.17
2 2 0	19.35	19.37	0.20
3 0 0 } 2 2 1 }	6.55	6.44	0.16
3 1 1	9.61	9.65	0.17
2 2 2	8.18	8.05	0.24
3 2 0	3.37	3.36	0.14
4 0 0	4.41	4.42	0.14

TABLE XII
ATOM PARAMETERS FOR $\text{La}_{0.14}\text{WO}_3$

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)	Atoms per unit cell
La	1(<i>a</i>)	0.0	0.0	0.0	0.0(2)	0.14
O	3(<i>c</i>)	0.0	0.5	0.5	0.80(3)	3.0
W	1(<i>b</i>)	0.5	0.5	0.5	0.8(1)	1.0

TABLE XIII
BOND ANGLES AND DISTANCES FOR $\text{La}_{0.14}\text{WO}_3$

Bond distances (Å)		Bond angles (°)	
W1-W1	3.833(1)	OI-W1-OIII	90.0
W1-OI	1.917(1)	W1-W2-OI	0.0
OI-OII	3.833(1)		
OI-OIII	2.710(1)		
La-OI	2.710(1)		

Pm3m) with a fractional occupancy of the *A* position. Isotropic temperature factors of 0.5 were allocated and the scale factor was refined. This resulted in an R_I index of 3.45% and an agreement factor of 2.52. Refinement of the three temperature factors reduced these values to 0.63% and 0.63. The observed and calculated intensities are given in Table XI and the atom parameters and bond distances in Tables XII and XIII.

Discussion

$\text{Li}_{0.36}\text{WO}_3$. Some important bond angles and distances for $\text{Li}_{0.36}\text{WO}_3$ are listed in Table IV (refer to Fig. 1). The WO_6 octahedra are tilted 13.8° from the cube axis (cf. $\text{D}_{0.53}\text{WO}_3$ 11° (6)) resulting in a relaxation of four oxygen atoms towards the 6(*b*) ($\frac{1}{2}, \frac{1}{2}, 0$) sites to form a rectangular environment of $3.050 \times 3.096 \text{ \AA}^2$. By comparison an expansion of the 12 oxygen atoms around the 2(*a*) (0,0,0) sites occurs. The structure analysis does not determine the lithium site occupancies precisely, but it is most likely that the 2.88 Li atoms are ordered into the 6(*b*) sites since the coordination is then fourfold with an Li-O

distance of 2.175 Å close to the sum (2.0 Å) of the ionic radii (21). In the 2(*a*) (0,0,0) sites the Li atoms would be 12 coordinate with an Li-O distance of 2.657 Å. The WO_6 octahedra remain essentially regular with six W-O bond lengths of 1.917 Å, and bond angles close to 90° .

$\text{Na}_{0.54}\text{WO}_3$ and $\text{Na}_{0.73}\text{WO}_3$. The extremely small discrepancies between observed and calculated intensities confirms the correctness of the *Im3* model for both $\text{Na}_{0.54}\text{WO}_3$ and $\text{Na}_{0.73}\text{WO}_3$. Bond angles and distances are listed in Tables VII and X. The distortion from the regular perovskite structure is much smaller than for $\text{D}_{0.53}\text{WO}_3$ and $\text{Li}_{0.36}\text{WO}_3$, the octahedra being almost perfect and in both cases tilted approximately 4° from the W-W

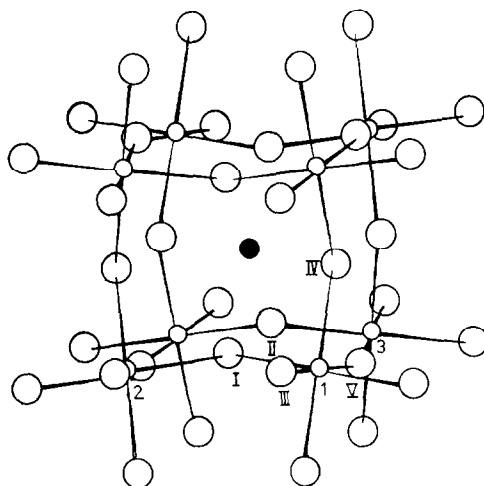


FIG. 1. The eight WO_6 octahedra surrounding $(0, 0, \frac{1}{2})$ in $\text{Li}_{0.36}\text{WO}_3$; large circles, oxygen atoms; small circles, tungsten atoms; closed circles, lithium atoms.

direction. The W–O bond length is significantly larger in $\text{Na}_{0.73}\text{WO}_3$ (1.927(1) Å) than in $\text{Na}_{0.54}\text{WO}_3$ (1.918(1) Å). Since the tilting of regular octahedra destroys the cubic symmetry, the slight tetragonal distortion might indicate that the octahedra are indeed perfect. Such a small distortion can be accommodated in the symmetry related orthorhombic space group *Immm* (as the deformation eliminates the fourfold axes of symmetry the space group cannot be tetragonal). Thermal expansion measurements of sodium tungsten bronzes have indicated a transition, possibly to the true cubic phase, at about 200°C (22, 23).

Recently, a sodium manganese bronze, $\text{NaMn}_7\text{O}_{12}$, has been prepared at 80 kbar pressure and shown to possess the same structure (24). Fourier and least-squares analysis of 142 single-crystal reflections implied the structural formula $(\text{Na}_{0.25}\text{Mn}_{0.75})\text{MnO}_3$ with atomic parameters in *Im3* of 2Na in 2(*a*) (0, 0, 0); 6Mn in 6(*b*) ($\frac{1}{2}, \frac{1}{2}, 0$); 8Mn in 8(*c*) ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$); and 24O in 24(*g*) (0, 0.1828, 0.3132). The distortion is much larger than found in the sodium tungsten bronzes. The sodium atoms completely fill the 12 coordinate 2(*a*) sites, whereas the four coordinate 6(*b*) sites are occupied by manganese atoms.

It is therefore necessary to explain the discrepancy between the interpretations of the powder and single-crystal work. The diffraction symmetry of the crystal was *m3m* which contains fourfold axes of symmetry that are not present in the *Im3* model. The extra symmetry elements must be introduced by the twinning of the crystal, and it is noteworthy that crystals of isostructural $\text{Sc}(\text{OH})_3$ exhibit identical behavior (25). A Fourier projection of the Na_xWO_3 structure necessarily showed (statistical) atom positions with the higher symmetry, but these positions did not provide a good fit between $|F_{\text{obs}}|$ and $|F_{\text{calc}}|$. This is indicative of incoherent twin intergrowth since a Fourier projection of a coherent twin should describe the average cell contents accurately. In the incoherent case, each single domain diffracts independently and each reflection is a composite one from inequivalent planes. The Fourier inversion of such "single"-crystal data does not yield the

correct superimposition of domain arrangements. It is, of course, possible that powdered samples are also twinned in a similar manner. This will not affect the structure analysis as such reflection overlap already occurs due to reflection from nonequivalent planes in separate crystallites.

The superlattice intensities from Na_xWO_3 are weak and very insensitive to a variation in sodium occupation numbers. All values of the occupation numbers gave very small residuals ($R_t < 1\%$) and at such a level of accuracy it is dangerous to apply simple statistical tests. This is particularly true for $\text{Na}_{0.54}\text{WO}_3$, although in $\text{Na}_{0.73}\text{WO}_3$ it appears that the sodium atoms are not completely ordered into 6(*b*) ($\frac{1}{2}, \frac{1}{2}, 0$).

Single-crystal neutron work on a single domain crystal is necessary to determine precise occupancies. As the distortion is very small the 2(*a*) and 6(*b*) site environments are little different which, coupled with the low mobility of sodium in the structure (26), may make the degree of ordering critically dependent on the method of preparation. Inconclusive evidence for long-range sodium atom ordering has been obtained from electrical and optical studies on electrolytically grown single crystals (7, 27). The crystals may be imperfect and also not stoichiometric in oxygen content (9), and similar measurements on carefully annealed crystals have shown different behavior (28, 29). Short-range ordering of the sodium atoms has also been suggested (30).

$\text{La}_{0.14}\text{WO}_3$. The structure analysis shows that unlike the other tungsten bronzes, $\text{La}_{0.14}\text{WO}_3$ has the simple perovskite structure with no tilt of the octahedra. The lanthanum atoms randomly occupy the perovskite *A* sites and are coordinated by 12 oxygen atoms at a distance of 2.710 Å. This is exactly the sum of the lanthanum and oxygen ionic radii (21).

General Comparison of Cubic Tungsten Bronze Structures

Table XIV summarizes the structural results for the cubic tungsten bronzes studied

TABLE XIV
STRUCTURAL DATA FOR THE CUBIC TUNGSTEN BRONZES

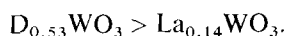
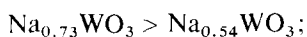
	$D_{0.53}WO_3$	$Na_{0.73}WO_3$	$Na_{0.54}WO_3$	$Li_{0.36}WO_3$	$La_{0.14}WO_3$
W-W subcell	3.781(1)	3.845(1)	3.828(1)	3.723(1)	3.833(1)
Variation with x	Decrease	Increase	Increase	Decrease	Increase
W oxidation state	5.47	5.27	5.46	5.64	5.58
W-O distance	1.926(1)	1.927(1)	1.918(1)	1.917(2)	1.917(1)
W-O tilt	11.0	3.8	3.7	13.8	0
O-O distance	3.264(2)	3.664(1)	3.653(3)	3.053(5) 3.098(5)	3.833(1)
A-O distance	1.10	2.591(1) 2.722(1)	2.583(2) 2.710(2)	2.175(2)	2.710(1)
Ionic radius of A (O = 1.4 Å)	-0.38	1.0	1.0	0.59	1.32
Coordination number of A(2)	1(+1)	4(+8)	4(+8)	4	12
	A(1)	12	12		

by the authors. Three comparative features may be emphasized:

(i) The tilting of the octahedra is in the order of decreasing ionic radius, i.e., La < Na < Li, D. As the tilting increases the 2(a) (0,0,0) and 6(b) ($\frac{1}{2}, \frac{1}{2}, 0$) site environments become more disparate and ordering is more likely, e.g., La disordered, Na probably partially ordered, Li and D ordered.

(ii) Changes in the W-O distances do not necessarily parallel changes in the W-W distances (subcell lattice constants). This is caused by the differences in degree of tilting of the octahedra.

(iii) The W-O distance is increased by a decrease in the tungsten oxidation state, e.g.,



The lattice parameter variation with composition within a cubic phase may be explained by a combination of these factors. The decrease in oxidation state of tungsten, effected by an increase in x content, will cause an increase in the W-O bond distance, and hence, an increase in the lattice parameter, e.g., cubic Na_xWO_3 (16) and La_xWO_3 (11). This may be offset by a small A ion as the average tilt will increase with x content thereby decreasing the W-W distance, e.g., the lattice contraction for cubic Li_xWO_3 (1).

Complete structure determinations of lower symmetry tungsten bronzes are now in progress.

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