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Lithium Insertion in Reduced Tungsten Oxides

I. $Li_{9.0}W_{19}O_{55}$

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Lithium has been inserted chemically at room temperature into the crystallographic shear phase $W_{19}O_{55}$. Maximum lithium content was $Li_{9.0}W_{19}O_{55}$. X-ray diffraction and electron microscopy show that lithium insertion contracts the lattice and causes the doubling of *a* and *b* parameters of the $W_{19}O_{55}$ unit cell.

Introduction

Although a lot of work has been done on the so-called tungsten bronzes (*1*), in particular on the Na_xWO_3 phases, very little work appears to have been done on alkali–metal insertion in reduced tungsten oxides. Indeed the W–O phase diagram is particularly complicated due to the existence of crystallographic shear phases (CS), pentagonal column-related structures, and other complex crystallographic phases (*2*). It then appears attractive to try to insert cations in the empty tunnels existing within the reduced phases.

In view of the particular interest recently shown lithium inserted bronzes, which appear to allow energy storage (*3*) and interesting devices, we started a program of work aimed at the alkali insertion in reduced oxides of tungsten. We describe in this paper our work on Li insertion in $W_{19}O_{55}$.

Experimental

The sample of overall composition $WO_{2.895}$ was prepared from the starting materials H_2WO_4 and W metal. The WO_3 was obtained by heating at 815°C H_2WO_4 for 3 days. The $W_{19}O_{55}$ was obtained by heating at 950°C a mixture of WO_3 and W powder in quartz tubes sealed under vacuum for 10 days. The product was then homogenized by annealing under vacuum for 7 days at 1050°C.

Lithium was inserted chemically into the $W_{19}O_{55}$ phase by reaction with *n*-butyllithium in hexane: 2 cm^3 of dry hexane was added to approximately 1 g of $WO_{2.895}$ in a nitrogen atmosphere followed by addition of an excess of *n*-butyllithium solution (1.6 *M*). The product was equilibrated at room temperature for 5 days, the liquid decanted, and the remaining solid washed with dry hexane and finally vacuum dried.

The amount of lithium inserted in the host oxide was determined by delithiation reaction, carried out on the lithium-inserted compound with iodine in acetonitrile. The quantity of iodine consumed in the delithiation reaction was determined by titration of the excess with a standard thiosulfate solution.

Reaction products were characterized by

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X-ray diffraction and electron microscopy and diffraction.

For the X-ray powder diffraction pattern a Siemens D-500 diffractometer with radiation Cu$K\alpha$ filtered by Ni was used. Patterns were recorded between 5 and 60°; the peak positions for all samples were calibrated against an internal Si standard.

The electron microscope was a Siemens Elmikop 102; the accelerating potential was 100 Kv. The samples were crushed in an agate mortar, ultrasonically dispersed in *n*-butanol, and then mounted on carbon-coated microgrids.

Results and Discussion

The X-ray pattern of the unlithiated oxide can approximately be indexed on a monoclinic cell with parameters a = 12.13(1) Å, b = 3.793(2) Å, c = 22.45(1) Å, and β = 94.5(1)°, related to an ReO_3-type subcell by the expression $a = (10/10^{1/2})a_r$, $b = a_r$, $c = (19/10^{1/2})a_r$ (the subindex r refers to ReO_3-type subcell: $a_r \simeq 3.8$ Å). This ideal cell gives a c parameter of 22.8 Å; however, it is well known from the structure of $W_{20}O_{58}$ (*4*) that in these CS (103) phases, each octahedron between CS planes contributes 1.175 Å to the distance between them, so that the relation between the number of octahedra (n) and the c parameter is $n = c \sin \beta/1.175$. However the differences between the peak positions of consecutive homologs are too small to unambiguously define the observed n member. For this reason electron microscopy was used to characterize the starting oxide. Figure 1a shows an electron diffraction pattern of the original sample; a 19-fold superstructure is observed along $\overline{g}$ 103_r. Some streaking is also seen on the diagram and this is indicative of some disorder in the crystal. The electron micrograph labeled Fig. 1b indeed shows disorder, although the normal spacing is of the order of 22.5 Å. We conclude that the starting material is, on the average, the n = 19 member of the homologous series W_nO_{3n-2} (*5*). On this basis, the X-ray diffraction pattern can be indexed as in Table I; all peaks were accounted for by the proposed structure. The corresponding unit cell parameters are shown in Table II.

Chemical analysis of the lithiated sample suggests a composition of $Li_{0.475}WO_{2.895} \Leftrightarrow Li_{9.0}W_{19}O_{55}$. The X-ray diffraction pattern of this sample (Table III) could also be indexed on the same cell, but a displacement toward higher 2θ values was evident in the peaks. This is indicative of a contraction of the structure due to the insertion as can be seen in the unit cell parameters in Table II. Delithiated samples exhibited the same X-ray patterns as the starting materials. In terms of the unit cell volume and composition the above contraction is much larger than that observed in pure, i.e., nonreduced, WO_3. There a maximum lithium in-

TABLE I

X-RAY DIFFRACTION POWDER DATA ($\lambda_{CuK\alpha}$ = 1.5418 Å) FOR $WO_{2.895}$ SAMPLE

$h\ k\ l$	d_{obs} (Å)	I/I_0	d_{calc} (Å)
$\overline{1}\ 0\ 4$	5.234	2	5.229
$\overline{1}\ 0\ 5$	4.303	15	4.302
$\overline{3}\ 0\ 1$	4.028	12	4.025
$\overline{3}\ 0\ 2$	3.893	55	3.892
$0\ 1\ 0$	3.787	72	3.794
$3\ 0\ 2$	3.702	64	3.704
$\overline{1}\ 0\ 6$	3.642	100	3.640
$\overline{1}\ 1\ 4$	3.080	3	3.071
$4\ 0\ 0$	3.024	1	3.026
$\overline{1}\ 1\ 5$	2.845	3	2.846
$2\ 0\ 7$	2.743	86	2.738
$3\ 1\ 1$	2.723	20	2.725
$3\ 1\ 2$	2.650	19	2.650
$\overline{1}\ 1\ 6$	2.627	27	2.627
$2\ 1\ 7$	2.221	17	2.220
$\overline{2}\ 0\ 11$	1.972	19	1.973
$\overline{5}\ 1\ 5$	1.905	19	1.904
$0\ 2\ 1$	1.890	14	1.890
$1\ 0\ 12$	1.817	3	1.819
$\overline{2}\ 1\ 11$	1.748	10	1.750
$\overline{1}\ 0\ 13$	1.722	2	1.721
$\overline{5}\ 1\ 8$	1.701	36	1.702

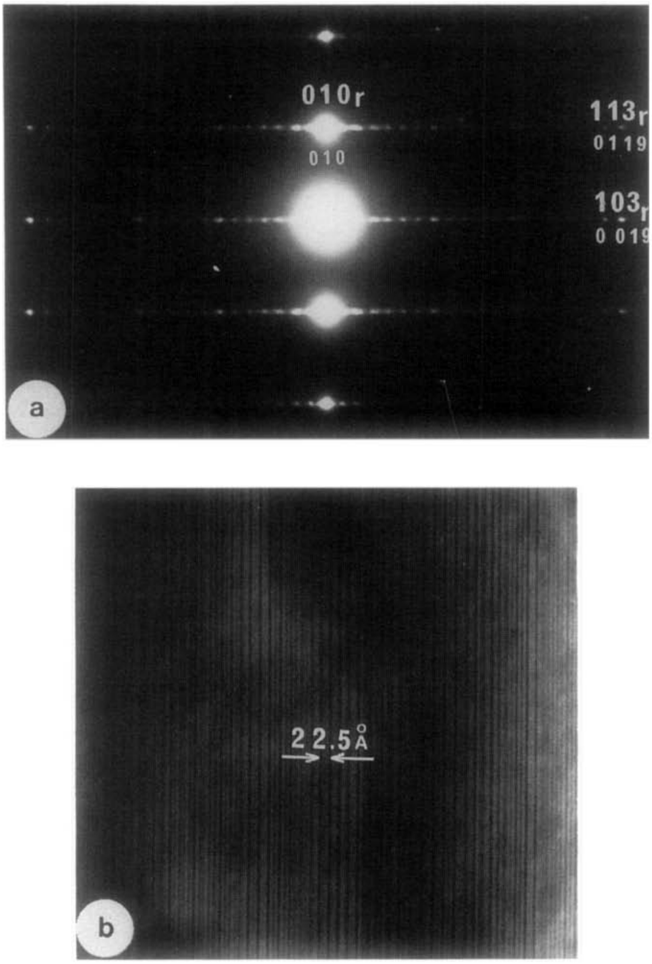

FIG. 1. (a) Electron diffraction pattern of $WO_{2.895}$ along the |100| zone axis. (b) Corresponding electron micrograph showing disorder along the *c* axis.

sertion of $Li_{0.67}WO_3$ (*6*) induces a contraction of approximately 2%, while in the present case, a smaller—but equivalent, see below—lithium concentration, $Li_{0.475}WO_{2.895}$, produces a contraction of approximately 5%. This seems to imply that the CS-based structure is less rigid than pure WO_3, a remarkable result.

TABLE II

UNIT CELL PARAMETERS OF THE MONOCLINIC PHASES $W_{19}O_{55}$ AND $Li_{9.0}W_{19}O_{55}$

Phase		*a* (Å)	*b* (Å)	*c* (Å)	*β* (°)	*V* (Å³)
$W_{19}O_{55}$	Calculated	12.0	3.8	22.8	90	—
$W_{19}O_{55}$	Experimental	12.13(1)	3.793(1)	22.45(1)	94.5(1)	1.030(1)
$Li_{9.0}W_{19}O_{55}$	Experimental	11.94(1)	3.753(4)	21.97(1)	94.6(1)	981(1)

TABLE III

X-RAY DIFFRACTION POWDER DATA ($\lambda_{CuK\alpha}$ = 1.5418 Å) FOR THE $Li_{0.475}WO_{2.895}$ PHASE[a]

$h\ k\ l$	$h_1\ k_1\ l_1$	d_{obs} (Å)	I/I_0	d_{calc} (Å)
$\bar{1}$ 0 4	$\bar{2}$ 0 4	5.120	2	5.131
$\bar{1}$ 0 5	$\bar{2}$ 0 5	4.216	12	4.221
$\bar{3}$ 0 1	$\bar{6}$ 0 1	3.948	10	3.954
$\bar{3}$ 0 2	$\bar{6}$ 0 2	3.844	51	3.839
0 1 0	0 2 0	3.751	52	3.753
3 0 2	6 0 2	3.642	51	3.635
$\bar{1}$ 0 6	$\bar{2}$ 0 6	3.580	100	3.570
2 0 5	4 0 5	3.392	2	3.399
4 0 0	8 0 0	2.969	1	2.972
$\bar{1}$ 1 5	$\bar{2}$ 2 5	2.804	4	2.805
3 1 1	6 2 1	2.690	64	2.686
3 1 2	6 2 2	2.610	22	2.611
$\bar{1}$ 1 6	$\bar{2}$ 2 6	2.588	40	2.587
2 1 7	4 2 7	2.182	27	2.182
$\bar{2}$ 0 11	$\bar{4}$ 0 11	1.933	16	1.935
$\bar{5}$ 1 5	$\overline{10}$ 2 5	1.874	30	1.874
1 0 12	2 0 12	1.786	4	1.783
$\bar{2}$ 1 11	$\bar{4}$ 2 11	1.719	8	1.720
$\bar{1}$ 0 13	$\bar{2}$ 0 13	1.687	6	1.687
$\bar{5}$ 1 8	$\overline{10}$ 2 8	1.675	45	1.674

[a] Subindex 1 refers to a double unit cell with parameters a = 23.84(2) Å, b = 7.51(1) Å, c = 21.97(1) Å, β = 94.6(1)°.

Electron diffraction of the lithium-inserted material also shows a 19-fold superstructure along $\bar{g}$ 103_r (Fig. 2); other orientations, however, show evidence of a unit cell multiple with respect to the fresh material. Figure 3a shows the |201| zone axis of the $WO_{2.895}$, while in Fig. 3b the same zone axis of the lithium-inserted material shows additional spots that imply the doubling of $\bar{a}$ and $\bar{b}$ (with respect to the $W_{19}O_{55}$ cell), i.e., $2 \times 10/10^{1/2}a_r$, $2 \times a_r$, $19/10^{1/2}\ a_r$, with respect to the ReO_3-type cell. Systematic extinctions for h, k, l, with $h + k = 2n + 1$, suggest a C-centered cell.

From the structural principles established for $W_{20}O_{58}$ and the corresponding W_nO_{3n-2} family (5, 7), it is clear that the structure of $W_{19}O_{55}$ can approximately be described as formed by ReO_3-type octahedra sections, $|\infty \times \infty \times 19|$ in extent, separated by ordered CS planes where octahedra share edges in groups of 19 (Fig. 4). In this structure there are two types of tunnels: square tunnels similar to those found in WO_3 and double rectangular tunnels formed in the CS plane. The number of lithium positions in the tunnels is 0.789/W atom of square type and 2 × 0.053/W atom in the rectangular ones. The maximum lithium content in the tunnels will then correspond to $Li_{15+2}W_{19}O_{55}$ ⟨ ⟩ $Li_{0.894}WO_{2.895}$. According to chemical analysis the composition is $Li_{0.475}WO_{2.895}$ ⟨ ⟩ $Li_{9.0}W_{19}O_{55}$.

It appears then that, as in the case of

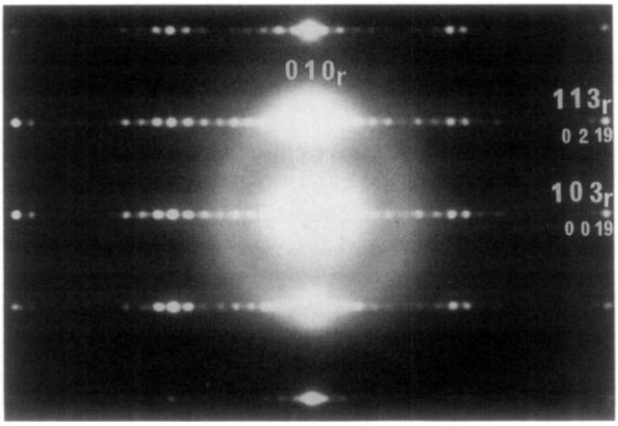

FIG. 2. Electron diffraction pattern of $Li_{0.475}WO_{2.895}$ along the |100| zone axis.

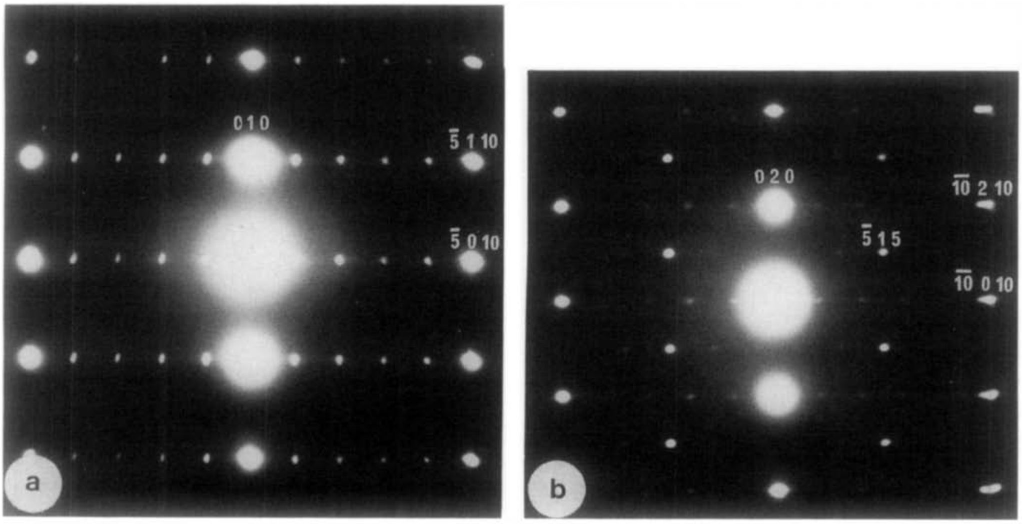

FIG. 3. (a) Electron diffraction pattern of $WO_{2.895}$ along the |201| zone axis. (b) Electron diffraction pattern of $Li_{0.475}WO_{2.895}$ along the |201| zone axis referred to the $W_{19}O_{55}$ unit cell (zone axis of the multiple cell: |101|).

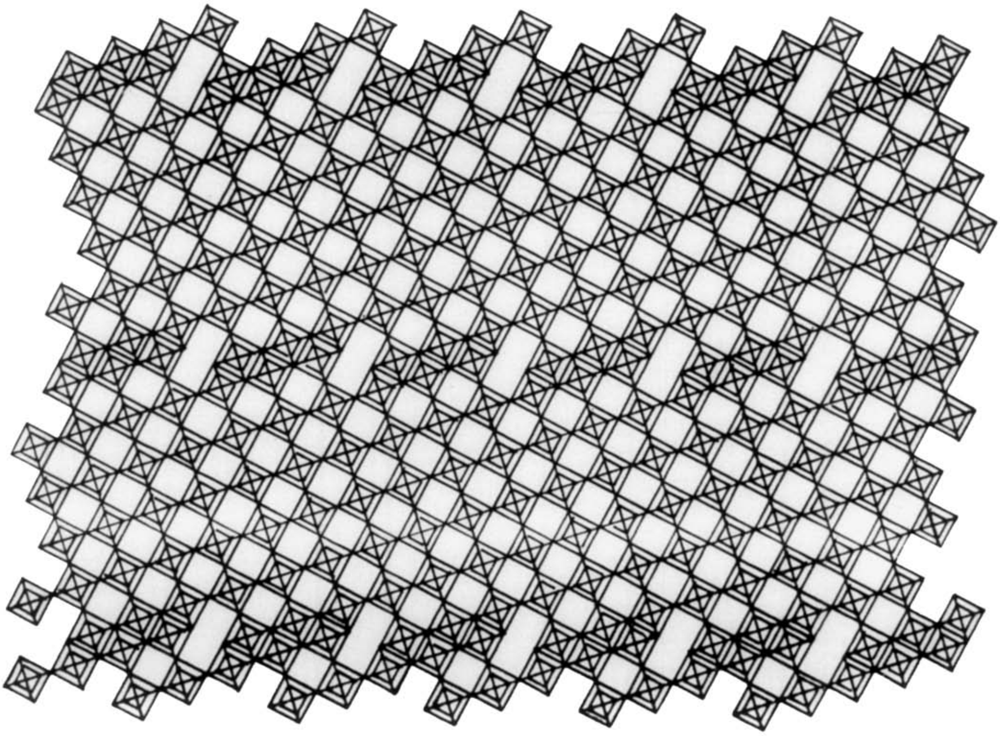

FIG. 4. Idealized structure of $W_{19}O_{55}$ along the *b* axis.

$Li_{0.36}WO_3$ (*8*), the presence of lithium produces a superstructure which is presumably due to the lithium ordering. A full-crystal structure determination is in progress.

A final point worthy of comment is that maximum lithium insertion obtained in this mild-soft chemistry condition is very close to that attained in WO_3, when we express it in terms of the average oxidation states of tungsten which (*6*) are $W = 5.33$ for $Li_{0.67}WO_3$ and $W = 5.315$ for $Li_{0.475}WO_{2.895}$. Thus oxidation state appears to control the maximum possible insertion.

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