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High-Pressure Phases in the System W–O. II. Structure Determination of $WO_{2.625}$ by HRTEM and X-ray Powder Diffraction Analysis

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Abstract

A new type of tungsten oxide has been synthesized from a mixture of W and WO_3 by a solid-phase sintering method under high-pressure conditions. The crystal structure of the new oxide was investigated by HRTEM, selected-area electron diffraction and X-ray powder diffraction. The structure belongs to space group *Pbam* or $P2_12_12$ and has the following unit-cell parameters: $a = 21.431$ (9), $b = 17.766$ (7), $c = 3.783$ (2) Å, $V = 1440$ Å^3, $Z = 32$, $D_x = 8.33$ g cm^{-3}. The structural model and W-cation positions were determined by HRTEM and image processing. X-ray powder analysis and the *SHELX* computer program were used to prove the proposed structural model: $N = 158$, $R = 0.075$, U_{iso}(W) =

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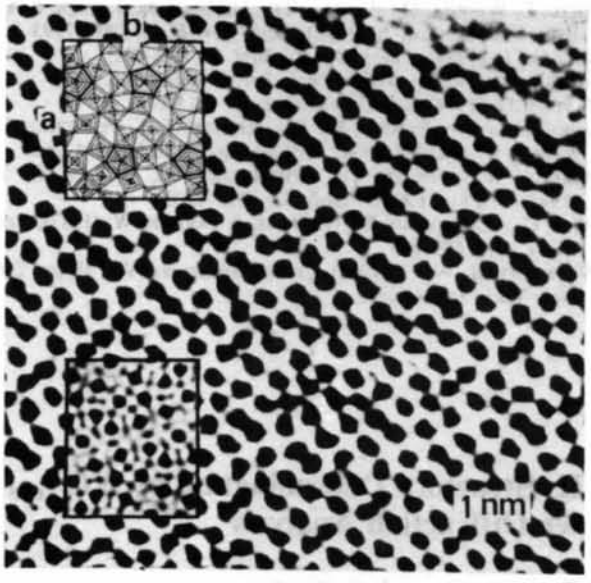
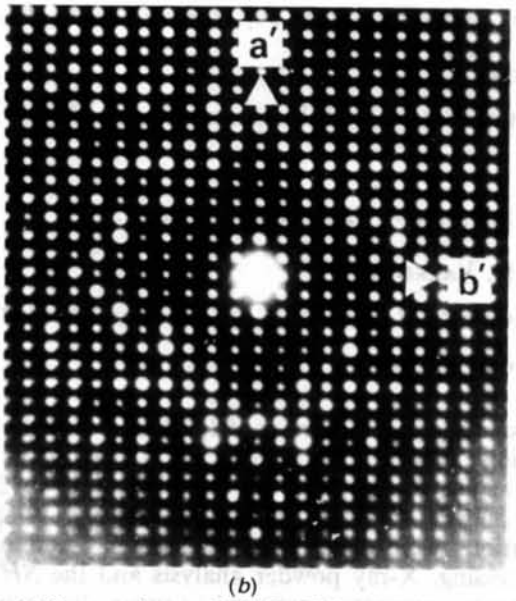
0.019 (3), $U_{iso}(O) = 0.055$ (12) Å^2. The investigated crystal structure is, in fact, similar to $WO_{2.72}$ and is formed by W—O octahedra and pentagonal bipyramids.

1. Introduction

It has been shown (Barabanenkov, Zakharov, Zibrov, Filonenko & Werner, 1992) that the synthesis of WO_x under high-pressure conditions gives rise to the formation of new high-density structures in which some of the W cations can be tetrahedrally coordinated.



(*a*)



(*b*)

Fig. 1. (*a*) Structure image of $W_{32}O_{84}$ ($WO_{2.625}$) taken at Scherzer defocus. (*b*) Selected-area electron diffraction.

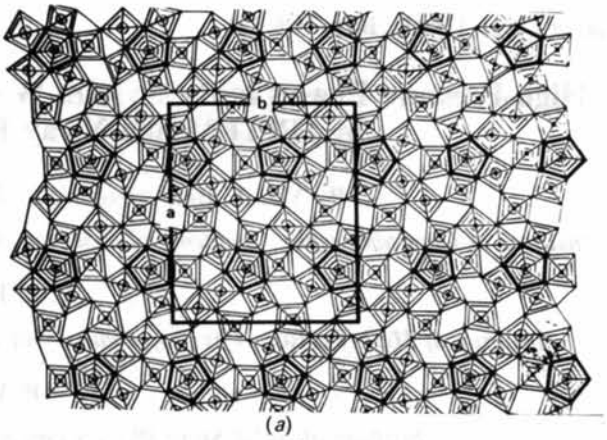
Table 1. *Atomic coordinates for the* $WO_{2.625}$ *structure* ($R = 0.075$)

	x	y	z		x	y	z
W1	0.105	0.069	0.000	O7	0.266	0.417	0.500
W2	0.168	0.259	0.000	O8	0.434	0.360	0.500
W3	0.357	0.248	0.000	O9	0.028	0.129	0.000
W4	0.383	0.031	0.000	O10	0.149	0.158	0.000
W5	0.250	0.101	0.000	O11	0.079	0.279	0.000
W6	0.016	0.352	0.000	O12	0.088	0.437	0.000
W7	0.266	0.417	0.000	O13	0.186	0.352	0.000
W8	0.434	0.360	0.000	O14	0.261	0.238	0.000
				O15	0.201	0.493	0.000
O1	0.105	0.069	0.500	O16	0.343	0.360	0.000
O2	0.168	0.259	0.500	O17	0.349	0.132	0.000
O3	0.357	0.248	0.500	O18	0.462	0.074	0.000
O4	0.383	0.031	0.500	O19	0.453	0.248	0.000
O5	0.250	0.101	0.500	O20	0.438	0.473	0.000
O6	0.016	0.352	0.500	O21	0.180	0.011	0.000

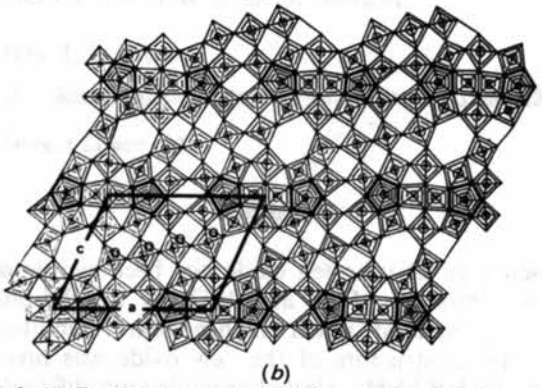
The main goal of this investigation was the determination of the crystal structure of an unknown WO_x high-pressure phase by HRTEM, image processing, selected-area electron diffraction and X-ray powder diffraction.

2. Experimental

A specimen with the average composition $WO_{2.6}$ was prepared from a mixture of W and WO_3 powders by a solid-phase sintering method under the following



(*a*)



(*b*)

Fig. 2. (*a*) Structural model of $W_{32}O_{84}$. (*b*) Structural model of $W_{18}O_{49}$.

conditions: pressure 60 kbar, $T = 1570$ K, annealing time 10 min (Barabanenkov *et al.*, 1992). X-ray powder diffraction measurements were carried out on an HZG-4 diffractometer using Cu $K\alpha$ radiation and Ni filter. The *SHELX* (Sheldrick, 1976) computer program package was used in order to process the diffraction data obtained.

HRTEM structure observations were carried out with a JEM-4000EX electron microscope at 400 kV accelerating voltage and 0.16 nm point-to-point resolution. The resolution level in the experimental images was determined by optical diffraction. The image processing method used was reported in detail earlier (Barabanenkov *et al.*, 1992; Hovmöller, Sjogren, Farrauts, Sundberg & Marinder, 1984).

The composition of the investigated phase was qualitatively controlled by EDX microanalysis and no other cations except W were detected.

3. Results

The sintered $W_{32}O_{84}$ ($WO_{2.625}$) samples were practically single-phase ones, according to X-ray powder diffraction data. Only some of them contained 1–2 mass% $WO_{1.09}$. The $WO_{2.625}$ is, in fact, metastable under normal atmospheric pressure and decomposes yielding stoichiometric amounts of $W_{18}O_{49}$ ($WO_{2.72}$) and WO_2 at elevated temperatures.

X-ray powder diffraction patterns were indexed in the orthorhombic system. The $0kl$, $0k0$, $h0l$ and $h00$ reflections with $h,k = 2n$ were observed in the X-ray powder diffraction patterns taken from $WO_{2.625}$. Thus, according to the observed extinctions rule only two space groups are appropriate – D_{2h}^9–*Pbam* and D_2^3–$P2_12_12$. It should be noted that in the case of W-layer puckering [*i.e.* W atoms slightly shifted along the c axis from the xy plane in an alternating sequence (Magnéli, 1951)], the crystal structure would belong to space group $P2_12_12$ ($h,k = 2n$ for the $h00$ and $0k0$ reflections).

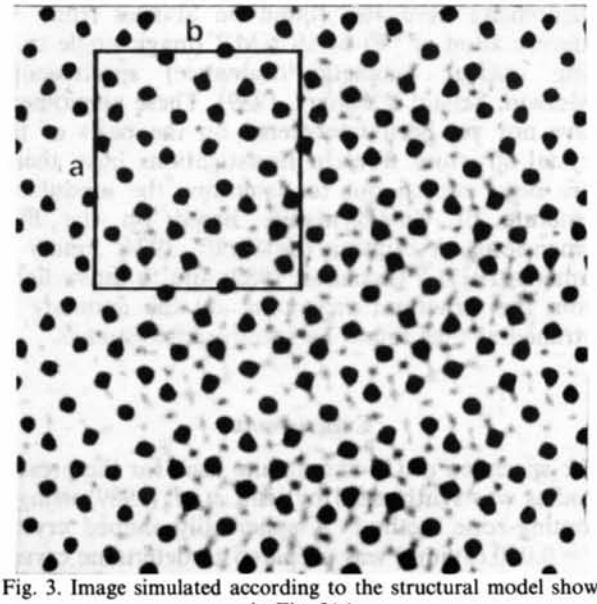


Fig. 3. Image simulated according to the structural model shown in Fig. 2(*a*).

The EM structure image of an unknown phase taken near the Scherzer defocus conditions ($\Delta f \simeq -48.5$ nm, $C_s = 1$ mm, $\theta_c = 1$ mrad, $E = 400$ kV) and selected-area electron diffraction is shown in Fig. 1. Black dots in this image correspond to individual W cation positions. According to the observed contrast the structural model shown in Fig. 2(*a*) (see Table 1) was proposed. The theoretical image calculated according to this model (Fig. 3) was in rather good agreement with the experimental one, thus confirming the proposed model. This model is also in good agreement with X-ray powder diffraction data [number of reflections $N = 158$, $R = 0.075$, $U_{iso}(W) = 0.019$ (3), $U_{iso}(O) = 0.055$ (12) Å^2].

4. Discussion

Thus, it has been shown that annealing of a W and WO_3 mixture with the average composition $WO_{2.6}$ under a pressure of 60 kbar gives rise to the formation of two new phases – $WO_{1.09}$ and $WO_{2.625}$. The sintered specimen consisted mainly (98%) of the $WO_{2.625}$ phase. The composition of the investigated oxide is rather close to $WO_{2.72}$ (Magnéli, 1949); therefore, it would be interesting to compare their structures (Figs. 2*a*, 2*b*). It is evident that the structure of $WO_{2.72}$ is more loose than that of $WO_{2.625}$ due to the presence of large hexagonal channels. It should be noted that the $WO_{2.625}$ structure can be easily derived from that of $WO_{2.72}$ by extracting only four O octahedra (Fig. 2*b*) from a $WO_{2.72}$ unit cell and shifting the rows of a pentagonal bipyramid by 5.3 Å in the c direction. One can see that in the $WO_{2.625}$ structure the pentagonal bipyramids are slightly rotated with respect to the row axis in an alternating sequence.

It has been shown in this paper that a combination of HRTEM, selected-area electron diffraction and X-ray powder diffraction methods can be very fruitful in the structure analysis of finely dispersed crystalline materials.

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