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High-Resolution Transmission Electron Microscopy—Investigation of Vanadium–Tungsten Oxides Prepared by Chemical Transport Reactions*

G. HEURUNG AND R. GRUEHN

Institut für Anorganische und Analytische Chemie, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58, D-6300 Giessen, Germany

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Crystalline monophasic samples of three mixed vanadium–tungsten oxides $(V_{0.8}W_{0.2})_3O_7 \approx (V,W)_9O_{21}$, $(V_{0.65}W_{0.35})_2O_5 \approx (V,W)_{16}O_{40}$, and $V_{0.64}W_{0.36}O_{2.60} \approx V_{16}W_9O_{65}$ were prepared by chemical transport reactions. The block structures of these compounds were investigated by high-resolution electron microscopy. They are built up by square blocks with [3 × 3 × ∞], [4 × 4 × ∞], or [5 × 5 × ∞] corner-sharing *M*–O-octahedra. Other block sizes were only observed as defects. The thermal behavior of the compounds was investigated.

Introduction

In the past *M*–Nb_2O_5 (*2*) as well as $(V_{0.65}W_{0.35})_2O_5$ (*3*) were considered as having identical structures consisting of [4 × 4]-blocks connected by corners (Fig. 1a). Our studies (*4*, *5*) of *M*–Nb_2O_5 with high-resolution transmission electron microscopy (HRTEM), however, revealed a disordered arrangement of blocks with different sizes and connections (Figs. 1b,c). *M*–Nb_2O_5 is a case where the X-ray structure determination cannot lead to a correct result. It is also not possible to learn by that method which types of defects are present in the $(V,W)O_x$-structures investigated in this paper. This caused us to reinvestigate the system V/W/O, placing particular emphasis on compounds with block structures.

The building principle of these compounds (*6*) can be described by sections of the ReO_3-structure characterized by *M*–O-octahedra, sharing corners in all three directions. These sections (so-called blocks) are separated from each other by planes of edge-sharing octahedra (so-called crystallographic shear(cs)-planes) limiting the ReO_3 framework in two directions. Adjacent blocks are displaced by half of an octahedron diagonal with regard to the third direction. Blocks at the same height (same line thickness in Fig. 1a) are connected by their corners.

The crystal structures of $(V_{0.8}W_{0.2})_3O_7$ (*7*) and $(V_{0.65}W_{0.35})_2O_5$ (*3*) have been determined from X-ray diffraction data (*7*, *3*). According to recent investigations (*8*) $(V_{0.8}W_{0.2})_3O_7$ has a range of composition from $V_{2.5}W_{0.5}O_7$ to $V_{2.8}W_{0.2}O_7$. Early electron microscope investigations were made on $(V_{0.65}W_{0.35})_2O_5$ at lower resolution (*9*). Recently,

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* Contribution to the Investigation of Inorganic Non-stoichiometric Compounds XXVII. Contribution XXVI: see (*1*).

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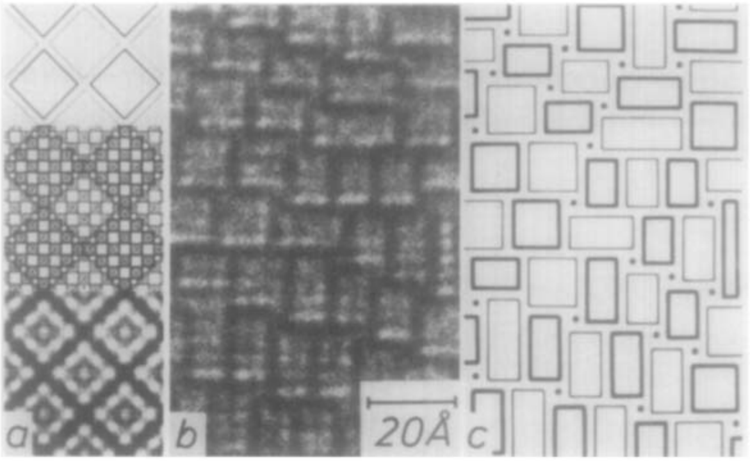

FIG. 1. M–Nb_2O_5. (a) Ideal structure according to (*2, 3*). From top to bottom: the arrangement of the [4 × 4]-blocks, the connection of octahedra, a simulated image. (b) Transmission electron micrograph of the disordered real structure of M–Nb_2O_5 containing a small portion of WO_3. (c) Interpretation of the image (b).

$V_{16}W_9O_{65}$ was reported in Ref. (*8*) and in our laboratory (*1*). We believe that our electron microscope investigations can provide a comprehensive survey on the known compounds with block structure in this system.

Preparation of Samples

The samples were prepared by chemical transport reactions starting with mixtures of V_2O_5, WO_2, and WO_3 or V_2O_3, V_2O_5, and WO_3. The starting material WO_2 was also made by chemical transport from WO_3 and W with I_2 as transporting agent. V_2O_3 was prepared by reduction of V_2O_5 with H_2. The method of chemical transport (*10*) offers the possibility to obtain crystalline samples at lower temperatures within a few days. The preparations were performed in closed silica ampoules which were heated in an electric two-zone furnace. The mixtures of the oxides were placed at the hotter side T_2 (750 to 850°C) of the ampoule. At the cooler zone at T_1 crystals formed at temperatures between 750 to 800°C (T_2–T_1 ~ 50 to 100°C). HCl (1 atm, 25°C) was used as transporting agent. The crystals grew within 3 or 4 days as black, rectangular, or square tubes and columns with a length of several millimeters (Fig. 2).

Electron Microscope Method (*11*)

The investigations were performed with a Philips electron microscope EM 400, using a high-resolution side-entry goniometer (HMG) stage. The crystals were crushed and the powder placed on a carbon-coated copper grid. Suitable crystal pieces whose short crystallographic axis could be brought into the required orientation parallel to the electron beam were found by selected area diffraction. Lattice images were recorded from areas that were less than 100 Å in thickness. An acceleration voltage of 100 kV electrons and a primary magnification of usually 345,000× were applied.

Results

The images of the investigated compounds exhibit a uniform array of blocks connected by corners and thereby are in

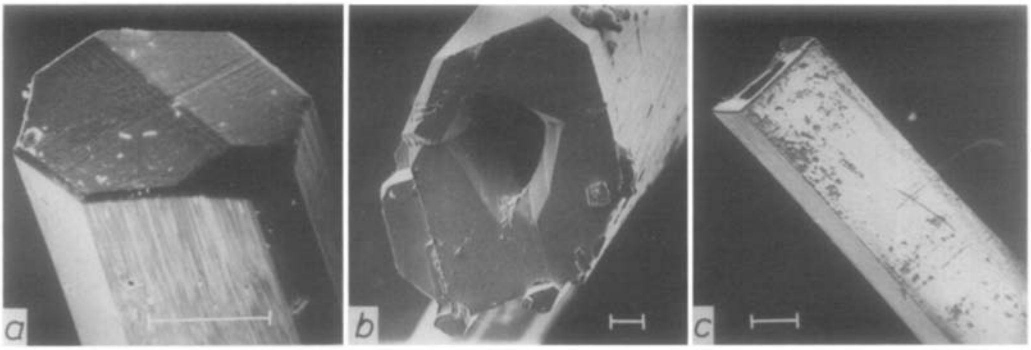

FIG. 2. Micrographs of crystals having the [3 × 3]-, [4 × 4]-, and [5 × 5]-block structures taken with SEM. The white line in these pictures corresponds to a length of 0.1 mm. (a) $(V_{0.8}W_{0.2})_3O_7$; (b) $(V_{0.65}W_{0.35})_2O_5$; (c) $V_{16}W_9O_{65}$.

agreement with the X-ray data (*3*, *7*) and previous electron optical investigations (*9*). The structures are well-ordered with only a few Wadsley-defects. These defects are slices built up by blocks which have a different size from the ones of the main structure. The images correspond to a projection of structure and these slices appear as rows of blocks. Heavily disordered domains comparable with M–Nb_2O_5 are rare.

The structure of [3 × 3]-blocks of $(V,W)_3O_7$ (Fig. 3) is well ordered and nearly without defects. The incorporation of rows of [3 × 4]-blocks (Wadsley-defects) was observed very infrequently.

The structure of $(V_{0.65}W_{0.35})_2O_5$ consisting of [4 × 4]-blocks is also well ordered in general. Small variations in the ratio O/M (M = V,W) can be compensated in the following manner. In samples with a ratio $O/M < 2.50$ rows of [3 × 4] blocks (marked in Fig. 4) appear as Wadsley-defects within the matrix of the [4 × 4]-blocks. A pure compound built up only from [3 × 4]-blocks

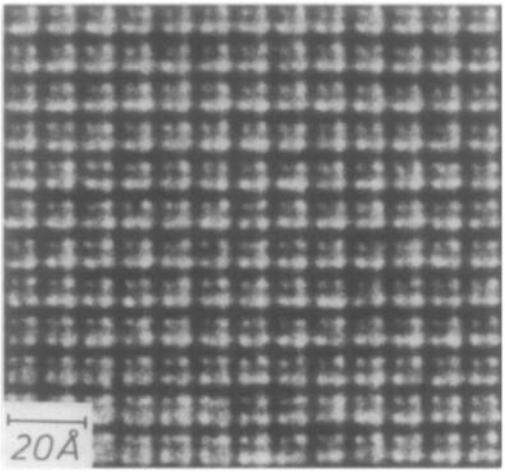

FIG. 3. Transmission electron micrograph of $(V_{0.8}W_{0.2})_3O_7$. The structure is built up by [3 × 3]-blocks. The section shown in the picture contains no defects.

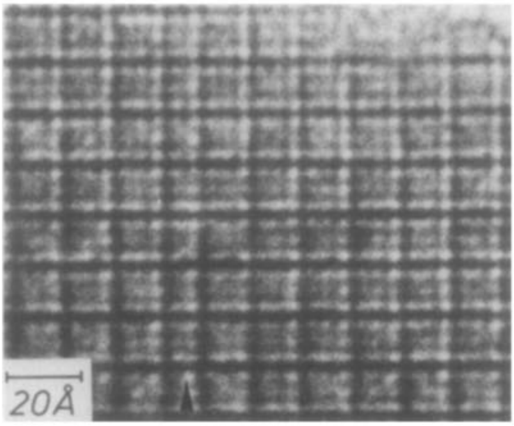

FIG. 4. Transmission electron micrograph of $(V_{0.65}W_{0.35})_2O_5$ with one row of [3 × 4]-blocks (marked by arrow) in the matrix of [4 × 4]-blocks.

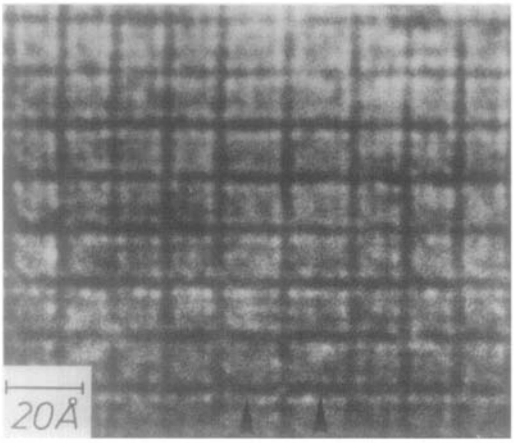

FIG. 5. Transmission electron micrograph of $(V_{0.65}W_{0.35})_2O_5$ with two rows of [5 × 4]-blocks (arrows).

connected by corners could not be found. It would have the composition $(V,W)_{12}O_{29}$. If the samples have a ratio O/M slightly higher than 2.50, caused by an increase of the WO_3-portion, [5 × 4]-blocks can be observed as Wadsley-defects (marked in Fig. 5). A [5 × 4]-block structure of this type has the composition $(V,W)_{20}O_{51}$, i.e., a ratio $O/M = 2.55$. When we tried to prepare this compound as a single phase we always encountered a disproportionation into a mixture of $(V,W)_{16}O_{40}$ and $(V,W)_{25}O_{65}$.

Most of the images of $V_{16}W_9O_{65}$ reveal a well-ordered structure of [5 × 5]-blocks connected by their corners. As an example, Fig. 6 was selected from a series of photographs of different crystal pieces which show a nearly undistorted arrangement. As with the other compounds, some Wadsley-defects could be found. In this case, rows of [5 × 6]-blocks (Fig. 6) and [5 × 4]-blocks (Fig. 7) predominate as defects with the composition $(V,W)_{30}O_{79}$ ($O/M = 2.63$) and $(V,W)_{20}O_{51}$ ($O/M = 2.55$), respectively. In Fig. 6 the row of [5 × 6]-blocks does not run continuously through the crystal, but one part of the row is displaced parallel to the direction of the other. This is equivalent to a shift of a cs-plane by one octahedra diagonal. The [5 × 6]-blocks at the location of this displacement are no longer connected by corners but by their longer edges (marked by circle in Fig. 6).

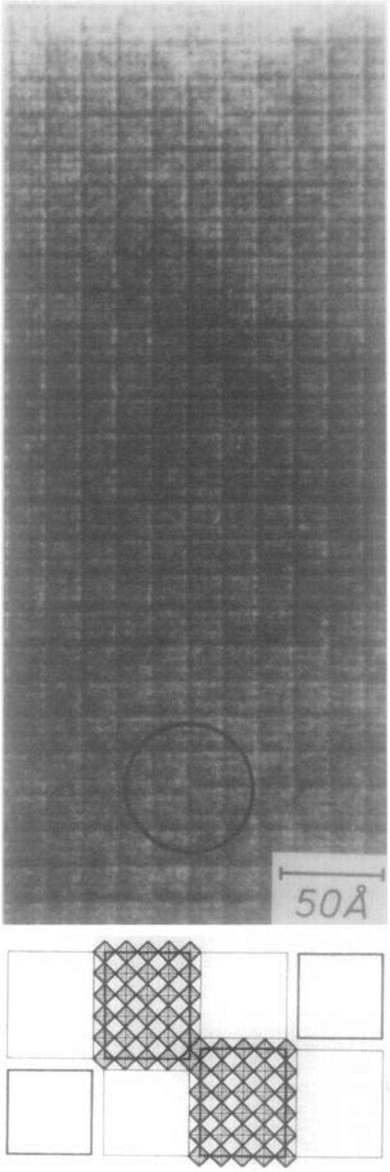

FIG. 6. Transmission electron micrograph of $V_{16}W_9O_{65}$ with one row of [5 × 6]-blocks in the matrix of [5 × 5]-blocks. A displacement of the [5 × 6]-row (encircled) is depicted in detail. The resolution of the image increases toward the upper part corresponding to the thin edge of the crystal.

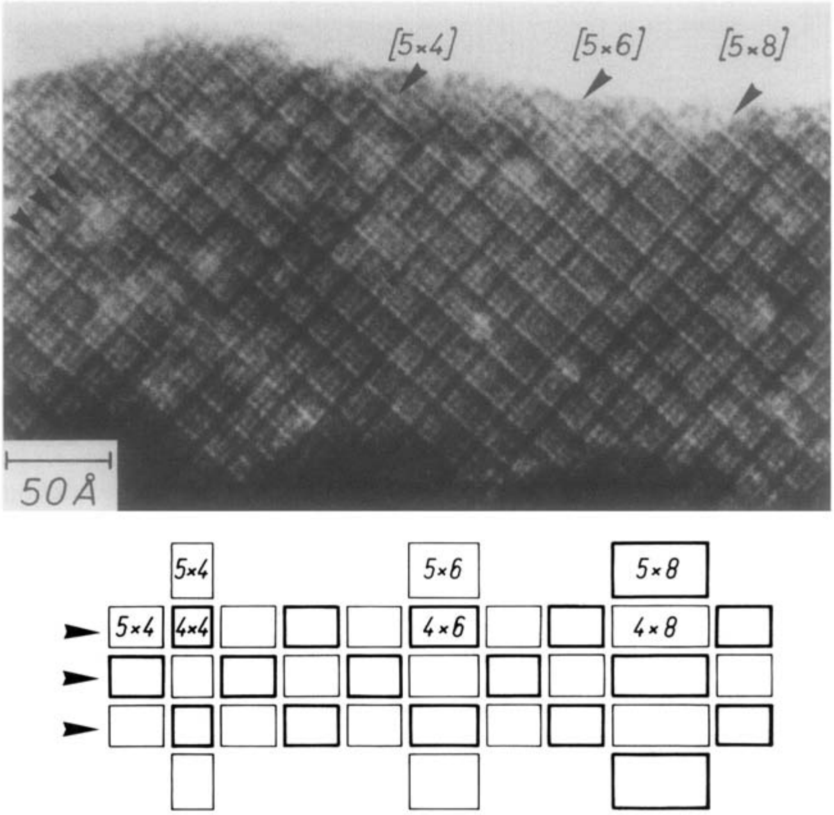

FIG. 7. Transmission electron micrograph of $V_{16}W_9O_{65}$ with Wadsley-defects running in different directions through the matrix of [5 × 5]-blocks. The interpretation shows how unusual block sizes are produced by defect rows intersecting each other.

Figure 7 deals with the same sample as Fig. 6, but it was one of the very rare examples which reveal a surprising variety of defects. Different Wadsley-defects run perpendicular to each other. At the intersection of these different rows single blocks with unusual sizes appear. The existence of [5 × 8]-blocks is extraordinary. These building units have the composition $(V,W)_{40}O_{107}$, corresponding to a ratio $O/M = 2.675$ and are an example of an extreme internal disproportionation (5) because the octahedra at the corners of the blocks have a formal ratio O/M of only 2.0. They, therefore, differ considerably from the [5 × 5]-blocks of the matrix with the composition $(V,W)_{25}O_{65} \triangleq O/M = 2.60$. Parallel to the one row of [5 × 8]-blocks, two additional Wadsley-defects, one row of [5 × 6]- and one of [5 × 4]-blocks can be detected. Perpendicular to these rows there are three parallel adjacent rows of [5 × 4]-blocks. At the intersection of the rows of [5 × 4]-blocks necessarily [4 × 4]-blocks occur.

The crossing of the [5 × 4]-blocks with the [5 × 6]-blocks generates [4 × 6]-blocks having the composition $(V,W)_{24}O_{62}$ ($O/M = 2.583$). The intersection of the [5 × 4]- with the [5 × 8]-blocks cannot be seen on the image in Fig. 7 because the crystal is already too thick in this part, but, one can assume that there are [4 × 8]-blocks with the composition $(V,W)_{32}O_{84}$ ($O/M = 2.625$).

All these different kinds of nonsquare

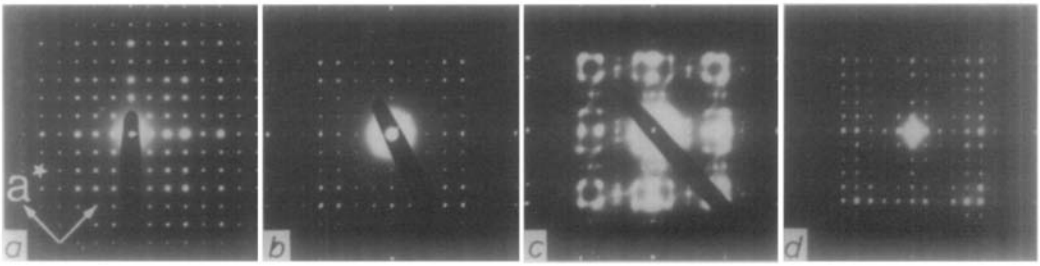

FIG. 8. Electron diffraction pattern (*h k* 0) of (a) $(V_{0.8}W_{0.2})_3O_7$ with [3 × 3]-blocks; (b) $(V_{0.65}W_{0.35})_2O_5$ with [4 × 4]-blocks; (c) *M*–Nb_2O_5 having a disordered structure of Fig. 1b; (d) $V_{16}W_9O_{65}$ with [5 × 5]-blocks.

blocks with the characteristic connection by corners could only be found in defects but, never as sole building elements of a pure phase. Therefore, $(V,W)_9O_{21}$ with [3 × 3]-, $(V,W)_{16}O_{40} \triangleq (V_{0.65}W_{0.35})_2O_5$ with [4 × 4]- and now $V_{16}W_9O_{65}$ with [5 × 5]-blocks are the only compounds with block structure that could be prepared in the system V/W/O up to the present. In Fig. 8 the diffractograms of these compounds are shown and can be compared with the pattern of *M*–Nb_2O_5.

Thermal Behavior

All these phases are very sensitive to heat treatment and oxidation. Already at ~530°C $(V,W)_9O_{21}$ is oxidized and decomposes by heating in air as is demonstrated by using a continuous high temperature Guinier camera. The oxidized material only shows WO_3- and weak and diffuse V_2O_5-reflections on the Guinier diagram. $(V_{0.65}W_{0.35})_2O_5$ decomposes under these same conditions at about 550°C. Only WO_3-reflections remain on the Guinier diagram.

The oxidation of $V_{16}W_9O_{65}$ in air begins at about 560°C and only WO_3-reflections remain on the Guinier diagram above 600°C. When $V_{16}W_9O_{65}$ is heated under vacuum at 820°C for 24 hr, the compound decomposes into WO_3 and the two modifications of $(V_{0.65}W_{0.35})_2O_5$. One consists of [4 × 4]-blocks and the other one has a *R*–Nb_2O_5 (*12, 13*) like structure with [2 × ∞ × ∞]-building elements (*14*). Heating under vacuum at 920°C for 24 hr leads to WO_3 and $(V_{0.65}W_{0.35})_2O_5$. Under these conditions the latter compound exclusively appears as the [2 × ∞ × ∞]-block modification. These results are in good agreement with (*8*). The decomposition under vacuum is not in contradiction to our result that $V_{16}W_9O_{65}$ can be prepared by chemical transport at the same temperature, since one has to take into consideration that the compound is stabilized by the gas phase of the transport system (*15*).

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