

Preparation and Crystal Structure of Re_3O_{10}

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Trirheniumdecaoxide, Re_3O_{10} , was obtained by the reaction of ReO_2 and ReO_3 in an arc-melting furnace. X-ray powder diffraction revealed a tetragonal structure with space group $I\bar{4}m2$ and lattice constants $a = 5.171(1)$ and $c = 13.371(6)$ Å. The crystal structure is built up by layers of corner-sharing $[\text{ReO}_5]$ square pyramids perpendicular to $[001]$ with the apical oxygen pointing up and down alternately. These layers are interconnected by disordered $[\text{ReO}_6]$ octahedra. Early reports on Re_2O_5 are reviewed in the light of our results. © 2001 Academic Press

Key Words: Re_3O_{10} ; rhenium oxide; Rietveld refinement; mixed valence compound.

INTRODUCTION

Rhenium, the 5d element of the manganese group, was discovered in 1925 (1a–1c). Besides other aspects in rhenium chemistry, summarized extensively by R. D. Peacock in 1973 and by G. Rouschias in 1974 (2a, 2b), several groups of researchers worked on preparation, characterization, and crystal structure solution of the rhenium(III–VII)oxides. Preparation methods for rhenium sesquioxide, which always appears as a hydrate, $\text{Re}_2\text{O}_3 \cdot \text{H}_2\text{O}$, were reported in 1933 (3). In the same year a description of the synthesis of black ReO_2 was published (4). ReO_2 is dimorphous. The monoclinic structure ($\alpha\text{-ReO}_2$) with staggered strings of $[\text{ReO}_6]$ octahedra as in brookite connected by shared corners as in rutile was determined in 1957 (5). The orthorhombic high-temperature phase ($\beta\text{-ReO}_2$), formed irreversibly from $\alpha\text{-ReO}_2$ above 460°C, was published in 1969 (6). Its structure consists of zigzag chains of $[\text{ReO}_6]$ octahedra along the c -axis sharing edges, which are connected by sharing corners. The structural relationship between the red compound ReO_3 and WO_3 was first mentioned in 1932 (7a, 7b), but the crystal structure was solved in 1966 and confirmed later (8a, 8b). Several high-pressure modifications

of ReO_3 are also described in the literature (9a, 9b). The crystal structure of the pale yellow Re_2O_7 compound is built up from double-layers of $[\text{ReO}_4]$ tetrahedra sharing corners that are alternately connected by $[\text{ReO}_6]$ octahedra (10a–10c). Re_2O_5 was first mentioned in 1929 as a purplish red compound (1b, 1c). Later works gave additional preparation methods for this red product, but it was supposed to be ReO_3 and not Re_2O_5 (7b, 11a, 11b). In 1965 Re_2O_5 was described as a blue–black compound disproportionating rapidly at room temperature in the presence of water and at 250°C under vacuum into Re_2O_7 and $\alpha\text{-ReO}_2$ (12). Re_2O_5 was prepared by electrochemical reduction of ReO_4^- with Pt electrodes in a bath of 12 M H_2SO_4 and 0.16 M ReO_4^- . X-ray investigations gave evidence for a tetragonal structure with lattice constants $a = 5.80(3)$ Å and $c = 12.87(3)$ Å (12). A similar method with Fe^{2+} or Sn^{2+} as reducing agent was published in 1968 (13), describing Re_2O_5 as a blackish blue and amorphous material, which has been characterized by IR spectroscopy and thermal analysis. The preparation of Re_2O_5 was also proposed by oxidation of $\text{ReO}_2 \cdot 2\text{H}_2\text{O}$, and the following electron microscopic investigation revealed an orthorhombic unit cell related to the cubic ReO_3 with $b \approx c \approx a_c \approx 3.747$ Å and $a \approx 2a_c\sqrt{2} \approx 10.598$ Å (14). However, a complete structure description is still lacking for Re_2O_5 . In this contribution we report on an attempt to synthesize Re_2O_5 and the following structure analysis.

EXPERIMENTAL

A mixture of ReO_2 and ReO_3 (Aldrich, 99.9%) in ratio 1:1 was ground under acetone in an agate mortar and formed into pellets (1 mm in thickness, 13 mm in diameter) under a load of 10 tons. These metallic-purple-colored pellets have been heated in an arc-melting furnace (Bühler Lichtbogenanlage AM) under an argon atmosphere for about 10 s and turned to a blue compound, which became black and wet only a few seconds after opening the furnace.

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To protect this very hygroscopic reaction product from moisture the whole furnace was operated under an argon atmosphere in a glove bag. Hereby, the sample could be collected from the ground plate of the furnace and stored under an argon atmosphere. Based on color and decomposition behavior, the product was assumed to be Re_2O_5 as described in the literature (12, 13). For structure determination the material was poured into a 0.5-mm glass capillary and investigated by X-ray powder diffraction using a STOE STADI-P diffractometer in Debye-Scherrer mode with germanium-monochromatized $\text{CuK}\alpha_1$ radiation and a position-sensitive detector with 6° aperture.

STRUCTURE ANALYSIS

The powder pattern recorded directly after synthesis is shown in Fig. 1 and gave the impression of a rather amorphous material. Only the reflections of metallic rhenium could be identified. Ten weeks later the same sample was measured again and the appearance of the powder pattern had changed strikingly (Fig. 2). This behavior is reproducible, but the amount of metallic rhenium in the reaction product was not always the same. The sample with the lowest metallic rhenium content was used for structure determination. All reflections could be indexed based on a tetragonal unit cell with $a = 5.171(1) \text{ \AA}$ and $c = 13.371(6) \text{ \AA}$. Note that all reflections $(00l)$ are considerably broadened. The lattice constants are close to those reported for Re_2O_5 (12), supporting the assumption of having prepared Re_2O_5 . Therefore it was tried to solve the crystal structure from powder data and hereby confirm the proposed stoichiometry.

For the selection of a specific space group it is important that no extinction rules in addition to body centering are

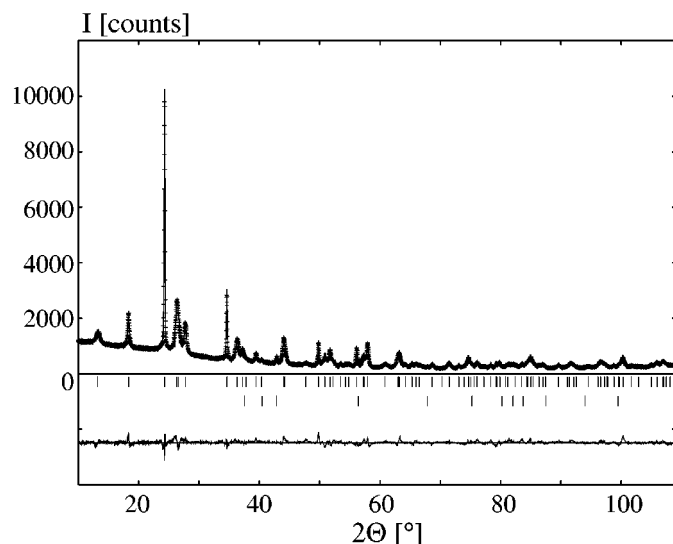


FIG. 2. Observed and calculated profiles for Re_3O_{10} and difference plot after 10 weeks of annealing. The lower line of reflection marks belongs to metallic rhenium.

observed. Only one or two Re sites are allowed based on the cell volume and chemical constraints. Considering the relative intensities of all $(00l)$ reflections makes it possible to distinguish the symmetry elements 4 and $\bar{4}$. In the case of a $\bar{4}$ -axis the following relation holds,

$$I^{00l} \sim (f^l)^2 [\cos(2\pi lz_1) + \rho \cos(2\pi lz_2)]^2,$$

while for a 4-axis:

$$I^{00l} \sim (f^l)^2 [\exp(2\pi ilz_1) + \rho \exp(2\pi ilz_2)]^2.$$

f^l is the X-ray form factor for rhenium atoms, z_1 and z_2 are the fractional coordinates of the two rhenium sites along the c -axis, and ρ is the relative multiplicity of both sites, i.e., $\frac{1}{4}$, $\frac{1}{2}$, or 1. The relative intensities of the $(00l)$ reflections indicate a $\bar{4}$ axis most probable and thus only the three space groups $I\bar{4}$ (No. 82), $I\bar{4}m2$ (No. 119) and $I\bar{4}2m$ (No. 121) were retained. Furthermore, $z_1 \sim 0$, $z_2 \sim \frac{1}{4}$, and $\rho = \frac{1}{2}$ can be deduced from the relative intensities of the $(00l)$ reflections alone.

To determine all atom positions additional considerations were necessary. With the volume of the unit cell being around 360 \AA^3 the volumes per atom for all possible stoichiometries Re_xO_y ($x = 2-5$) were calculated. The density of the new compound had to be lower than that of ReO_3 , the volume per atom higher than that in ReO_3 ($13 \text{ \AA}^3/\text{atom}$), and therefore the number of atoms lower than $N = 28$. Odd formula units Z are excluded by I -symmetry; at least two rhenium sites are necessary. All possible compositions are shown in Table 1.

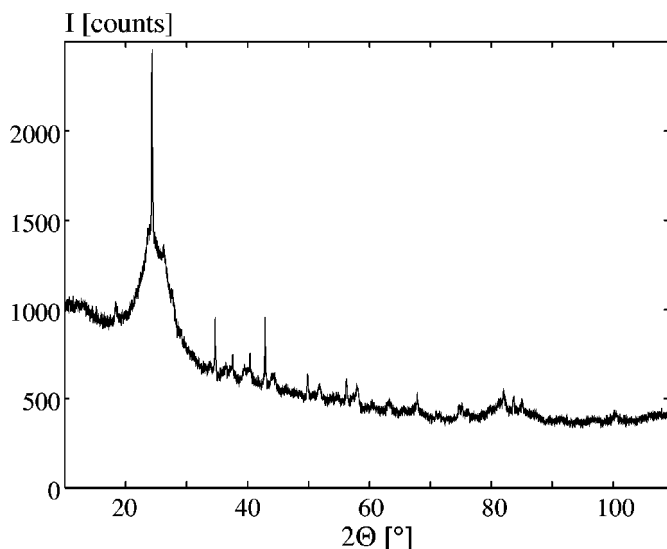


FIG. 1. X-ray powder pattern of the as-prepared sample.

TABLE 1
Summary of All Considered Compositions

Oxides	Cell volume (Å ³)	ρ_v (g/cm ³)	Volume per oxygen (Å ³)
Re ₂ O ₇	1035.5	6.21	18.5
ReO ₃	52.7	7.39	17.6
ReO ₃ (9 Gpa)	91.2	8.53	15.2
Re ₂ O ₅	432.9	6.94	21.6
α ReO ₂	124.9	11.61	15.6
β ReO ₂	128.4	11.29	16.1
Re ₆ O ₁₈ \equiv 6ReO ₃	357.6	6.53	19.9
Re ₈ O ₂₀ \equiv 4Re ₂ O ₅	357.6	8.41	17.9
Re ₆ O ₂₀ \equiv 2Re ₃ O ₁₀	357.6	6.68	17.9
Re ₇ O ₂₂	357.6	7.69	16.3

The cell parameters for the blue unknown oxide Re_xO_y, although close to the Tribalat's ones for Re₂O₅, are sufficiently different to give a cell volume $V = 357.6 \text{ \AA}^3$ much smaller than that of Re₂O₅, i.e., 433 \AA^3 . So before creating any hypothesis about possible sites for Re and O atoms we tried to appreciate via the classical volume of oxygen atoms in oxides ($\sim 16\text{--}17 \text{ \AA}^3$) and also the corresponding volumic mass ρ_v , to propose by comparison with known rhenium oxides, a reasonable formula. This information is summarized in Table 1. The oxygen number y is even (space group symmetry) and should be around $y = 18$, $y = 20$, or $y = 22$, which gives a reasonable volume per oxygen (V/O), i.e., 19.9, 17.9, and 16.3 \AA^3 . The first solution leads to the Re₆O₁₈ formula, which could be a polymorph of ReO₃; taking into account that ReO₃ is already a rather open structure, it seems unreasonable, in a first attempt, to have such a large V/O and correlatively such a low ρ value. (Note also that the powder color is deep blue.) The last y value gives Re₇O₂₂ and corresponds to a mixed valence oxide Re₂⁷⁺Re₅⁶⁺O₂₂, which gives too low a value for V/O to be in agreement with our procedure of synthesis. In addition, it is also moisture sensitive. Finally we are left with two possibilities:

— Re₈O₂₀, which could correspond to the Re₂O₅ oxide, but we note that the ρ value is extremely high, which is not expected after such synthesis; or

— Re₆O₂₀, which corresponds to a mixed valence oxide Re₃O₁₀ or Re₂⁷⁺Re₄⁶⁺O₁₀, such a formula being reasonable for the color of the powder and the V/O and ρ values.

The relative intensities of reflections (00 l) strongly indicate $\bar{4}$ symmetry with two Re sites Re1 and Re2 at z_1 and z_2 with corresponding multiplicities $m_1 : m_2 = 2 : 1$.

The 8g and 8i sites were not reasonable positions for rhenium atoms. Since $a_0/\sqrt{2} = 3.66 \text{ \AA}$ is close to Re–Re distances, the 4e site (0, $\frac{1}{2}$, z) or the equivalent 4f site (0, 0, z) with z close to 0 is reasonable for the rhenium atom Re1.

Therefore a structure with Re1 on the 4f site was chosen as a starting model for Rietveld refinements. Because $c = 13.3 \text{ \AA}$, additional rhenium atoms Re2 had to be placed on the 2d site (0, $\frac{1}{2}$, $\frac{1}{4}$). This model gave convergence, and the refinements led to $z = -0.023$ for the Re1 atoms. Any other model with more or less than six rhenium atoms in the unit cell gave poorer agreement after refinement. However, a significant improvement was achieved by including a disorder of Re2, (2d) (0, $\frac{1}{2}$, $\frac{1}{4}$) sof = 1 \rightarrow (8h) (x , $\frac{1}{2}$ + x , $\frac{1}{4}$) sof = 1/4 with x refined to -0.08 , corresponding to a deviation of nearly 0.6 \AA from the 'ideal' $x = 0$ site. The Re sites are in agreement with those derived from the Patterson functions, calculated based on either space group $I\bar{4}$ or $I\bar{4}m2$, which also indicated two heavy atom sites at (0, $\frac{1}{2}$, 0) and (0, $\frac{1}{2}$, $\frac{1}{4}$).

Based on the Re substructure oxygen positions were successively searched by difference Fourier analysis, revealing O1 at (8g) (x , x , 0), $x \approx 0.25$ and O2 at (4g) (0, $\frac{1}{2}$, z), $z \approx 0.12$. Another oxygen position O3 was found at $z \approx \frac{1}{4}$, but appeared to be disordered. Note that the disorder for Re2 is only introduced to simulate a huge thermal displacement. Reasonable bond lengths are only obtained for Re2 at the center 2d (0, $\frac{1}{2}$, $\frac{1}{4}$). The best results of the Rietveld refinement with FULLPROF (15) are summarized in Table 2, and observed and calculated profiles are compared in Fig. 2. The effect of absorption has been calculated numerically and was taken into account as additional factors to the calculated intensities at each 2Θ point.

TABLE 2
Structural details of Re₃O₁₀

Composition	Re ₃ O ₁₀
Radiation	CuK α_1
2θ range, $\Delta 2\theta$	$10^\circ\text{--}109^\circ$, 0.02°
Molecular weight	718.6 g/mol
Space group	$I\bar{4}m2$
Unit cell data	$a = 5.171(1) \text{ \AA}$ $c = 13.371(6) \text{ \AA}$ $V = 357.5(3) \text{ \AA}^3$ $\rho_x = 6.68 \text{ g/cm}^3$ $Z = 2$
FWHM (00 l)	$0.8 \dots 1.2^\circ$
FWHM ($hk0$)	$0.15 \dots 0.75^\circ$
Atom sites, Wyckoff notation x/a , y/b , z/c , sof	Re1 4f $0 \frac{1}{2} - 0.023(2)$ sof = 1 Re2 8h $- 0.082(2)$ $0.418(2) \frac{1}{4}$ sof = 1/4 O1 8g $0.293(6)$ $0.293(6)$ 0 sof = 1 O2 4f $0 \frac{1}{2}$ $0.115(2)$ sof = 1 O3 16j $0.14(2)$ $0.15(2)$ $0.23(3)$ sof = 1/2
No. of refined parameters	33
Residuals	$\chi^2 = 4.01$ $R_F = 5.88$ $R_{ex} = 4.25$

Note. Estimated standard deviations are in agreement with [16].

DISCUSSION

The crystal structure of the mixed valence (VII,VI) rhenium oxide Re_3O_{10} is built up by $(\text{ReO}_3)_n$ layers of $[\text{ReO}_5]$ corner-sharing square pyramids. These layers are linked to each other by $[\text{ReO}_6]$ octahedra, sharing the apical oxygen of the square pyramids and oxygens of the opposite octahedra. The structure is shown in Fig. 3 and the two alternative coordinations of Re2 with O3 due to the disorder of O3 are displayed in Fig. 4. The $[\text{ReO}_6]$ octahedra are rather regular, but the Re2 ion is highly disordered. The higher symmetric space group $I\bar{4}m2$ was preferred, although a very similar structure can be obtained for space group $I\bar{4}$. On one hand, the disorder of O3 is eliminated by the use of $I\bar{4}$; on the other hand four more refineable coordinates are introduced, which give only a minor improvement between the observed and calculated diffraction patterns: R_F changes from 5.88 to 5.74, and χ^2 from 4.01 to 3.65. However, it cannot be excluded that $I\bar{4}$ is more appropriate for the crystal structure of Re_3O_{10} . To the authors' knowledge there is no similar structure described in the literature. This is probably due to the very unusual formal oxidation state of $6\frac{2}{3}$ per rhenium ion—maybe a unique feature of this rhenium oxide. The uncertainty in the bond lengths for Re2 does not even allow the assignment of Re(+VI) for Re1 and Re(+VII) for Re2.

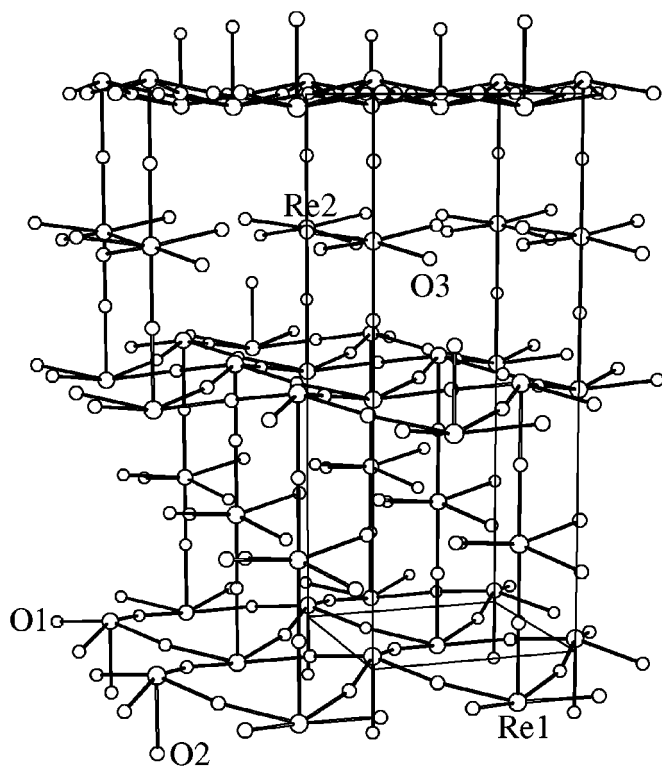


FIG. 3. Perspective view on the crystal structure of Re_3O_{10} .

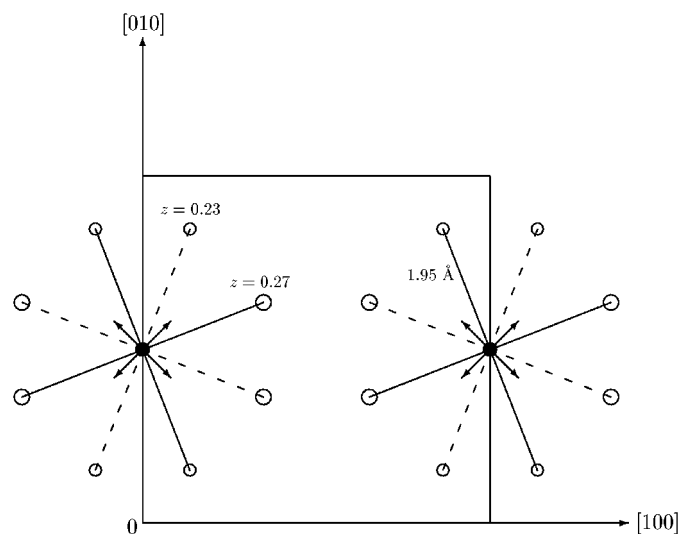


FIG. 4. View on the ab plane as $z \sim \frac{1}{4}$. The two alternative coordinations of Re2 at $(0, \frac{1}{2}, \frac{1}{4})$ and $(1, \frac{1}{2}, \frac{1}{4})$ with O3 are shown as solid and dashed lines, respectively. The arrows indicate the four disordered positions of Re2.

CONCLUSION

The highly hygroscopic trirheniumdecaoxide was prepared from ReO_2 and ReO_3 in an arc-melting furnace under an Ar atmosphere. The as-prepared material appeared rather amorphous, but crystallized during 10 weeks of annealing at room temperature. The composition Re_3O_{10} and its crystal structure were solved from X-ray powder diffraction, and Re_3O_{10} is the first example of five-fold coordinated Re. Lattice parameters, color, and instability in the presence of H_2O are very similar for Re_3O_{10} and Tribalat's Re_2O_5 ; both oxides are probably mixed valence ones. The crystallographic data are sufficiently different to let us suppose that further investigations are necessary to isolate Re_2O_5 and to settle its crystal structure. However, it is also possible that Tribalat's Re_2O_5 was actually Re_3O_{10} as the composition Re_2O_5 was based on electrochemical methods only.

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