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Elucidating the physical properties of the molybdenum oxide Mo_4O_{11} and its tantalum substituted variant $\text{Mo}_2\text{Ta}_2\text{O}_{11}$

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Abstract: Although $\gamma/\eta\text{-Mo}_4\text{O}_{11}$ and $\text{Mo}_2\text{Ta}_2\text{O}_{11}$ are used in a variety of industrial applications and can easily be synthesized in a chemical vapour transport (CVT) process or reactions in silica ampoules, respectively, only few data are available concerning their physical properties. In this paper, we further explore the properties of the three compounds with respect to their thermal and magnetic behavior, surface composition, and Raman spectroscopic properties.

Keywords: heat capacity; magnetic properties; molybdenum; oxide; powder diffraction; Raman spectroscopy; tantalum; thermal expansion; XPS.

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Introduction

Elemental molybdenum comprises a tremendous diversity in its range of applications. Utilization covers i.e. the heavy industry, where molybdenum is used in a mass range of 0.25–8% to drastically increase toughness and significantly decrease brittleness of steel. Another important application of molybdenum is its use as a trace component in plant fertilizers (in form of molybdates) and as a trace element in all living organisms in general. Additionally, elemental molybdenum plays an important part in catalysts used in petrochemical processes and as an anode material in X-ray generators [1–4].

The availability of molybdenum is not that scarce, as large deposits of molybdenum containing ore are known to be situated in China, the USA, Chile, and Canada. However, molybdenum is not available in its genuine form and has to be isolated from naturally occurring molybdenum minerals like Sidwillite, Umohoite, Iseite, Molybdenite, or Ilseemannite. Today, molybdenum is produced by extraction from these minerals as well as by extraction from the copper production process, where it is interspersed in the Chalcopyrite ore and is extracted as a side product. In both processes the ultimately used mineral is Molybdenite (molybdenum disulfide), which is detached from other ores by froth flotation. Subsequently, the molybdenum disulfide is oxidized by roasting to form molybdenum trioxide, which in turn can be reduced with hydrogen via molybdenum dioxide to yield the pure molybdenum. To produce an even purer form of elemental molybdenum, a cleaning step can be introduced, where the molybdenum trioxide is transferred into the ammonium heptamolybdate by reaction with ammonia, before the reduction with hydrogen is proceeded. The reduction process with hydrogen does not work in a simple one step reaction as during the process numerous molybdenum oxides like Mo_4O_{11} , Mo_5O_{14} , Mo_8O_{23} , and Mo_9O_{26} are formed [1, 5–8].

Especially, the binary oxides $\gamma/\eta\text{-Mo}_4\text{O}_{11}$, with γ referring to the phase synthesized at higher temperatures and η to the phase synthesized at lower temperatures, are of

particular interest, as they form in large quantities during the reduction process. The first step of the reduction to elemental molybdenum starts with the molybdenum trioxide (MoO_3), which is reduced to Mo_4O_{11} , and ends with molybdenum dioxide (MoO_2). As of today it is indicated, that the morphology of this first intermediate Mo_4O_{11} is of crucial importance to the morphology of the molybdenum dioxide product and therefore to the elemental molybdenum. The morphology of the final molybdenum product in turn has vital influence on the sinter capabilities of the elemental powder, which is especially important in the general production of molybdenum-based materials [9–11].

The first investigations of molybdenum oxides via X-ray diffraction methods have been conducted in 1944 by Hägg and Magnéli [12]. A wide array of different non-stoichiometric molybdenum oxides has thereby been uncovered. A summary was first given by Kihlberg in 1959 (Figure 1), containing stoichiometry and synthesis temperatures [6]. Years of investigations by Kihlberg, Ekström, and others did further elucidate the field [13–23]. An extensive recapitulation of the known phases and several synthesis methods was given by Blume in his doctoral thesis in 2004 [5].

Disregarding the structural characterizations via X-ray diffraction, hardly any investigations into the physical properties of the individual molybdenum oxides were made. The electrical conductivities of both Mo_4O_{11} phases were investigated by Gruber and Krautz [24]. The specific electrical resistivity was given as $0.53 \, \Omega\text{m}$ (metallic) for η - Mo_4O_{11} and $26 \, \Omega\text{m}$ (semiconducting) for γ - Mo_4O_{11} .

In this work, we want to focus on the characterization of the physical properties of the binary oxides γ/η - Mo_4O_{11} and on one of its tantalum substituted forms, the phase $\text{Mo}_2\text{Ta}_2\text{O}_{11}$ [25].

Experimental section

Synthesis

The pure molybdenum oxides were synthesized by the chemical vapour transport (CVT) method. To prevent contamination with oxygen and water vapour, the initial preparations were made in a glovebox. The reactions were performed in evacuated, torch sealed fused silica ampoules ($l=250 \, \text{mm}$, $\varnothing=25 \, \text{mm}$, thickness of the tube walls = $1.8 \, \text{mm}$). A mixture of $1636.5 \, \text{mg}$ MoO_3 ($11.4 \, \text{mmol}$), $363.7 \, \text{mg}$ MoO_2 ($2.8 \, \text{mmol}$) and $176.6 \, \text{mg}$ TeCl_4 ($0.7 \, \text{mmol}$) yielding a final Mo:O ratio of 1:2.80 was thoroughly ground together in an agate mortar and transferred into a silica ampoule. To yield the phase η - Mo_4O_{11} , the oven was kept at 798 – $748 \, \text{K}$ (educt zone – product zone) for 5 days. Afterwards, the oven was subsequently cooled to room temperature. For the phase γ - Mo_4O_{11} , the oven was kept at 923 – $873 \, \text{K}$ for 5 days. Due to the inherent nature of the CVT process, the final product forms as a crystalline compound on the ampoule walls as shown in Figure 2. η - Mo_4O_{11} forms thin layered crystals (up to $3 \, \text{cm}$ in size). The phase γ - Mo_4O_{11} on the other hand, yields smaller and thicker crystals as shown in Figure 3. The deep wine-red colour and bronze reflections are typical for both phases of Mo_4O_{11} .

To obtain the tantalum substituted phase $\text{Mo}_2\text{Ta}_2\text{O}_{11}$, the reaction was performed in an evacuated, torch sealed silica glass ampoule ($l=80 \, \text{mm}$, $\varnothing=25 \, \text{mm}$, thickness of the tube wall = $1.8 \, \text{mm}$). A mixture of $443.3 \, \text{mg}$ MoO_3 ($3.1 \, \text{mmol}$) and $556.7 \, \text{mg}$ Ta_2O_5 ($1.3 \, \text{mmol}$) was ground together in a agate mortar and heated up to a temperature of $1123 \, \text{K}$ and kept there for 15 days. Afterwards, the ampoule was cooled with a rate of $1 \, \text{K min}^{-1}$ to room temperature. The product was obtained as a compressed grey-purple powder (Figure 4). In comparison to the synthesis described in [25], the temperature is higher (about $100 \, \text{K}$)

Fig. 1: Uncovered oxides in the binary system molybdenum-oxygen and their formation temperatures based on data from [5, 6, 13].

Fig. 2: Photograph of the final product η - Mo_4O_{11} retrieved from the ampoule walls. The compound forms large (up to $3 \, \text{cm}$) and thin wine-red platelets.

Fig. 3: Photograph of γ - Mo_4O_{11} under the microscope. The compound forms large ($\varnothing = 0.5$ cm) wine-red crystals.

Fig. 4: Photograph of the product $\text{Mo}_2\text{Ta}_2\text{O}_{11}$ under the microscope ($\varnothing = 0.2$ cm).

and the duration of the heating process longer (compared to 3 h). However, it seems that in contrast to an open air reaction, the silica ampoules enable a reaction without much MoO_3 loss (only 20% MoO_3 excess used), while still yielding the phase pure product $\text{Mo}_2\text{Ta}_2\text{O}_{11}$. The synthesis was therefore very similar to [26], where the phase $\text{Mo}_2\text{Ta}_2\text{O}_{11}$ was falsely described as $\text{Ta}_2\text{O}_5 \cdot 3\text{MoO}_3$ ($\text{Mo}_3\text{Ta}_2\text{O}_{14}$).

X-ray structure determination

A STOE Stadi P diffractometer with curved Ge(111)-monochromatized $\text{Mo-K}_{\alpha 1}$ radiation ($\lambda = 70.93$ pm) was used to characterize the polycrystalline samples by X-ray powder diffraction. Diffraction intensities were measured with a Mythen2 1K (Dectris, Switzerland) microstrip detector with 1280 strips. For the measurement, the bulk material was ground to a powder in an agate mortar and fixed between two polyacetate films.

The Rietveld refinements were accomplished with the software package DIFFRACPLUS-TOPAS® 4.2 (Bruker AXS GmbH, Karlsruhe, Germany) [27] based on single-crystal data for η - Mo_4O_{11} (collection code: 82,363) [28], γ - Mo_4O_{11} (collection code: 76,366) [15], and $\text{Mo}_2\text{Ta}_2\text{O}_{11}$ (collection code: 247,163) [25] from the ICSD [29–31]. The reflection shapes were modelled using modified Thompson-Cox-Hastings pseudo-Voigt profiles [32, 33]. Instrumental contributions on reflection profiles were corrected from the refinement of a standard (LaB_6) [34]. The background was fitted with Chebychev polynomials up to the 6th order [35].

Relevant details of the data collections and the refinements using the Rietveld method are listed in Table 1.

Thermal investigations

Heat capacity: The thermal behaviour in the temperature range from 303 to 1103 K was studied under inert conditions with a concurrent thermal analysis apparatus (NETZSCH STA F2 Jupiter®; NETZSCH-Gerätebau GmbH, Selb, Germany). The NETZSCH Applikationslabor (Selb, Germany) conducted the measurements.

In addition, a further measurement was performed using differential scanning calorimetry (DSC) between 298 and 573 K applying a Netzsch DSC 204 F1 Phoenix equipped with a τ -sensor. The sample with a weight of 17.14(2) mg was placed in an Al-crucible. For this measurement, the heating and cooling rate was set to 6 K min^{-1} and helium was used as a protective gas.

Thermal expansion

High-temperature dilatometry of γ - Mo_4O_{11}

The temperature-induced strain was studied between 298 and 720 K on an as grown plane-parallel plate of γ - Mo_4O_{11} using a commercial inductive gauge dilatometer (DIL 402C from Netzsch) equipped with a sample holder made of α - Al_2O_3 , type S thermocouples and a high-temperature furnace (type 6.219.1-26 from Netzsch). The normal of the plane-parallel plate runs parallel to [100] with $a = 2444.9$ pm as determined by X-ray diffraction. The thickness of the sample along [100], which is the direction of the temperature-induced strain measurements, was 1.548 mm and the deviation from plane-parallelism of opposing faces was smaller than 10 μm . The γ - Mo_4O_{11} sample was measured twice in air with heating/cooling rates of 0.6 and 1 K min^{-1} , respectively. The dilatometer was calibrated with standard samples made of α - Al_2O_3 .

High-temperature X-ray (HT-XRD) powder diffraction of η - Mo_4O_{11} and $\text{Mo}_2\text{Ta}_2\text{O}_{11}$

The HT-XRD experiments were conducted using a Rigaku Ultima IV diffractometer with a thermal attachment (Cu-K_{α} , 40 kV and 35 mA, reflection geometry, D/teX Ultra high-speed detector, air atmosphere, $2\theta = 10$ – 80° , temperature range 293–1173 K, step size 10 K). Before the HT-XRD experiments, a Si external standard was measured in the

Tab. 1: Crystal data obtained through the Rietveld refinement of powder diffraction patterns (standard deviations in parentheses).

Powder diffractometer	STOE Stadi P		
Radiation; wavelength (pm)	Mo- $K_{\alpha 1}$; $\lambda = 70.93$		
Temperature (K)	296(2)		
θ range (°)	2.000–40.385		
Step width (°)	0.015		
Crystal system	Monoclinic	Orthorhombic	Trigonal
Space group	$P2_1/c$ (no. 14)	$Pna2_1$ (no. 33)	$R\bar{3}m$ (no. 166)
Formula units per cell (Z)	4	4	3
Empirical formula	η -Mo ₄ O ₁₁	γ -Mo ₄ O ₁₁	Mo ₂ Ta ₂ O ₁₁
<i>a</i> (pm)	668.992(8)	2446.61(5)	562.541(3)
<i>b</i> (pm)	543.790(7)	545.383(9)	<i>a</i>
<i>c</i> (pm)	2455.74(4)	674.76(2)	2515.06(3)
β (°)	94.2927(9)		
<i>V</i> (nm ³)	0.89087	0.90036	0.68927
Molar mass (g mol ⁻¹)	559.749	559.749	729.769
Calculated density (g cm ⁻³)	4.17	4.13	5.27
<i>R</i> _{exp} (%)	1.06	0.96	0.96
<i>R</i> _{wp} (%)	7.58	9.79	4.67
<i>R</i> _p (%)	5.68	7.30	3.24

temperature range 293–1273 K in order to control the thermal expansion coefficients. The temperatures of the phase transitions were checked using SiO₂ and K₂SO₄. The error in the determination of the temperature did not exceed ± 10 K. Experimental data processing by the Rietveld refinement, approximation of temperature dependencies of lattice parameters, and drawing of the α figures were performed using RietToTensor [36].

Magnetic investigations

The single crystals of γ -Mo₄O₁₁, η -Mo₄O₁₁, and Mo₂Ta₂O₁₁ obtained via chemical vapour transport were ground into fine powders in an agate mortar and subsequently packed into polyethylene (PE) capsules and attached to the sample holder rod of a Vibrating Sample Magnetometer (VSM) for measuring the magnetization $M(T, H)$ in a Quantum Design Physical Property Measurement System (PPMS). The samples were investigated in the temperature range of 3–300 K with an applied external magnetic field of 10 kOe. The recorded susceptibilities were corrected by the diamagnetic contributions caused by the PE capsules.

XPS measurements

X-ray photoelectron spectroscopic (XPS) measurements were carried out using a Thermo Scientific MultiLab 2000 spectrometer with a base pressure in the low 10^{-10} mbar range. The instrument is equipped with a monochromated Al- K_{α} X-ray source, an Alpha 110 hemispherical sector analyzer as well as a flood gun for charge compensation, providing electrons with a kinetic energy of 6 eV. Wherever possible, the C 1s peak (set to 284.8 eV) was used to calibrate the energy axis shift. Survey spectra were collected to determine the surface purity of the samples, whereas high-resolution spectra of the O 1s, C 1s, Ta 4d, and Mo 3d regions were used to derive information of the relevant

oxidation states of the respective elements. Deconvolution was carried out by fitting mixtures of Gaussian and Lorentzian functions (30% Lorentzian character) as peak shapes for each component, limited by several constraints in the fitting process: for each component, the peak splitting was set to a fixed value, depending on the transition and the element. The peak width for the respective spin-orbit components were restricted to the same value. The respective peak area ratios were set to 3:2 for the $d_{5/2}:d_{3/2}$ component and 4:3 for the $f_{7/2}:f_{5/2}$ component. A Shirley-type background was used for baseline correction. For calculation of the surface ion concentration, relative sensitivity factor (RSF) and electron mean free path corrections have been applied. The mean free path correction was based on values from the NIST database.

Raman spectroscopic measurements

The Raman spectroscopic measurements were done on a LabRam HR 800 spectrometer equipped with a 1024×256 CCD detector (Peltier-cooled) combined with an Olympus BX41 microscope. All measurements were carried out using a laser wavelength of 532 nm and a total laser power of approximately 12 mW. The laser wavelength was chosen to avoid resonant effects on Mo₄O₁₁, as observed in [37]. A 300 L mm^{-1} grating (spectral resolution approximately 3.5 cm^{-1}) was used and all spectra were baseline corrected using a second order polynomial and normalized by the unit vector method (both LabSpec 6).

The measurements of Mo₂Ta₂O₁₁ were carried out on a powder sample using an Olympus $\times 50$ LNPlanFLN objective (NA = 0.5). The measurements of both the monoclinic and orthorhombic η/γ -Mo₄O₁₁ modification were done on a platelet sample using an Olympus $\times 10$ MPlanN objective (NA = 0.25). The two different orientations of the sample relative to the laser polarisation were achieved by turning the sample by 90°. For the measurement of the third orientation of monoclinic η -Mo₄O₁₁, the sample was embedded upright in an epoxy resin and polished to give a smooth surface.

Elemental analysis

Elemental analyses were conducted for all three compounds to determine the composition with regard to molybdenum and oxygen for the binary compounds and with regard to molybdenum, tantalum, and oxygen for $\text{Mo}_2\text{Ta}_2\text{O}_{11}$. The analyses were executed via the Mikroanalytisches Labor Pascher (Remagen, Germany).

Results and discussion

The compounds discussed in this paper are very similar with respect to their crystal structures. Both phases, γ - and η - Mo_4O_{11} , exhibit condensed MoO_6 octahedra forming bands along the c -axis, which are connected through MoO_4 tetrahedra. In the case of η - Mo_4O_{11} , the orientation of the octahedra stays the same throughout the structure, whereas in the case of γ - Mo_4O_{11} the orientation changes from band to band (see Figure 5; top and middle).

As investigated in [28], the phase η - Mo_4O_{11} is prone to twinning along [001]. In the twinning intergrowth area, building failures can occur, resulting in the orientation change of the octahedra, as observed in γ - Mo_4O_{11} . Additionally, the molybdenum atoms are not situated in the centre of the octahedra, but rather moved towards one of the octahedra side planes, therefore yielding three longer (γ : $\varnothing = 206.7$ pm; η : $\varnothing = 206.6$ pm) and three shorter (γ : $\varnothing = 181.9$ pm; η : $\varnothing = 181.9$ pm) Mo–O distances (overall average: γ : 194.3 pm; η : 194.2 pm) [15, 28]. This effect is most prevalent in those octahedra connected to the tetrahedral MoO_4 entities, whereby the shortest Mo–O distances (γ : $\varnothing = 175.8$ pm; η : $\varnothing = 176.3$ pm) are found in the tetrahedra [15, 28]. Concluding from the Mo–O distances, the molybdenum in the tetrahedra is a Mo(VI) atom and the octahedra are statistically occupied by Mo(V) and Mo(VI) atoms in a ratio of 2:1.

In comparison to the Mo–O distances given above, the Mo–O distances in the binary molybdenum oxide MoO_3 , consisting exclusively of MoO_6 octahedra, range from 167.8

Fig. 5: Crystal structures of η - Mo_4O_{11} (top), γ - Mo_4O_{11} (middle), and $\text{Mo}_2\text{Ta}_2\text{O}_{11}$ (bottom) depicted with their distinct metal-oxygen polyhedra [15, 19, 25].

Tab. 2: Comparison of the experimentally obtained phase composition (elemental analysis) and theoretical values in mass-%.

	η - Mo_4O_{11}	γ - Mo_4O_{11}	$\text{Mo}_2\text{Ta}_2\text{O}_{11}$
$\text{Mo}_{\text{exp}}/\text{Mo}_{\text{theo}}$	67.4/68.6	68.0/68.6	26.0/26.3
$\text{O}_{\text{exp}}/\text{O}_{\text{theo}}$	33.1/31.4	32.2/31.4	24.3/24.1
$\text{Ta}_{\text{exp}}/\text{Ta}_{\text{theo}}$			48.7/49.6

to 232.7 pm ($\emptyset = 198.1$ pm) [38, 39]. The major distortion in MoO_3 is expressed by two very short (167.8 and 173.8 pm), two medium (2×194.9 pm), and two longer (224.3 and 232.7 pm) Mo–O distances. In contrast, CaMoO_4 singularly consists of MoO_4 tetrahedra with Mo–O distances of

4×175.5 pm [40]. Therefore, the conclusions drawn above agree well with the coordination dependent Mo–O distances found in the literature.

The phase $\text{Mo}_2\text{Ta}_2\text{O}_{11}$ was first described by Berendts et al. [25]. The fundamental building block is derived from the ReO_3 type and is built up of $\text{Ta}^{\text{V}}\text{O}_6$ octahedra ($3 \times 197(2)$ and $3 \times 189.9(3)$ pm) and $\text{Mo}^{\text{VI}}\text{O}_4$ tetrahedra (178(3) and $3 \times 182(2)$ pm). The compound forms a layer like structure stacking along the c -axis (see Figure 5; bottom).

For all three compounds, elemental analysis were performed as depicted in Table 2. The experimentally determined values agree well with the theoretical ones, at least within the accuracy of the methods utilized. The phase $\text{Mo}_2\text{Ta}_2\text{O}_{11}$ has already been examined before, yielding

Fig. 6: Rietveld refinement data. Top to bottom: the observed powder patterns are given in black (η - Mo_4O_{11} , γ - Mo_4O_{11} , and $\text{Mo}_2\text{Ta}_2\text{O}_{11}$), the best fit profiles in red, and the difference curves in blue.

Tab. 3: Comparison of lattice parameters known from the literature for Mo_4O_{11} .

Formula	Space group (no.)	a/b/c (pm)	Year of publication	Reference
η - Mo_4O_{11}	$P2_1/c$ (14)	670.1/543.9/2454, and $\beta = 94.28^\circ$	1963	[19]
η - Mo_4O_{11}	$P2_1/c$ (14)	670.1/543.3/2454, and $\beta = 94.28^\circ$	1980	[24]
η - Mo_4O_{11}	$P2_1/c$ (14)	669.5(1)/544.0(1)/2457.3(3), and $\beta = 94.31(8)^\circ$	1995	[28]
η - Mo_4O_{11}	$P2_1/c$ (14)	670.7(3)/544.2(3)/2454(1), and $\beta = 94.37(5)^\circ$	1996	[41]
η - Mo_4O_{11}	$P2_1/c$ (14)	670(0)/543(9)/2454(8), and $\beta = 94.3(1)^\circ$	1998	[42]
γ - Mo_4O_{11}	$Pnma$ (62)	2440/545/670	1948	[43]
γ - Mo_4O_{11}	$Pna2_1$ (33)	2440/545/670	1950	[44]
γ - Mo_4O_{11}	$Pnma$ (62)	2449/545.7/675.2	1963	[19]
γ - Mo_4O_{11}	$Pna2_1$ (33)	2449/545.7/675.2	1980	[24]
γ - Mo_4O_{11}	$Pna2_1$ (33)	2448.7(1)/675.2(1)/545.7(1)	1985	[45]
γ - Mo_4O_{11}	$Pna2_1$ (33)	2470/677/659	1986	[46]
γ - Mo_4O_{11}	$Pna2_1$ (33)	2449/675/546	1988	[47]
γ - Mo_4O_{11}	$Pna2_1$ (33)	2447(1)/545(4)/674(9)	1998	[42]
γ - Mo_4O_{11}	$Pna2_1$ (33)	2447.56(5)/675.16(1)/545.72(1)	1999	[48]
γ - Mo_4O_{11}	$Pna2_1$ (33)	2407.23(5)/664.83(1)/535.69(1)	1999	[49]
γ - Mo_4O_{11}	$Pna2_1$ (33)	2447.9(13)/673.87(27)/545.66(20)	2005	[50]

an oxygen content of 24.6 wt.-% and a molybdenum to tantalum ratio of 1.03(3) [25]. These results are in good agreement with our findings of 24.3 wt.-% oxygen and a molybdenum to tantalum ratio of 1.01(5).

Powder diffraction data

The Rietveld refinements of the experimental products are shown in Figure 6. The experimental data is shown in black, the best fit profiles in red, and the difference curves in blue. The experimental data agrees well with the single crystal data from the ICSD, a short comparison of these phases is given in Table 3.

Thermal investigations

Heat capacity

In the initial heating process for the phase η - Mo_4O_{11} , a mass loss of 0.9% was observed. The change was attributed to volatile substances adhered to the surface of the sample. After confirming mass consistency by conducting a second heating run, the heat capacity was measured. The heat capacity for η - Mo_4O_{11} was determined to be $0.507 \text{ J g}^{-1} \text{ K}^{-1}$ at 373 K. The heat capacity of the phase γ - Mo_4O_{11} showed a non-linear trend with a pronounced peak at 443 K stemming from a phase transition to a yet unidentified phase. This phase transition is fully reversible exhibiting no significant hysteresis and can be classified to be of weakly first order. The heat capacity of

γ - Mo_4O_{11} could therefore only be measured up to 443 K and was determined to be $0.584 \text{ J g}^{-1} \text{ K}^{-1}$ at 373 K. For the tantalum substituted phase $\text{Mo}_2\text{Ta}_2\text{O}_{11}$, the heat capacity was determined to be $0.459 \text{ J g}^{-1} \text{ K}^{-1}$ at 373 K. The temperature dependence of the heat capacity for all three substances is depicted in Figure 7. The differential scanning calorimetry (DSC) depicted in Figure 8 indicates the reversibility of the phase transition occurring at 443.4 K, as the peak in the DSC-signal can be observed in the heating curve (red) and the cooling curve (blue).

Thermal expansion

High-temperature dilatometry of γ - Mo_4O_{11}

The temperature-induced strain ϵ_{11} of γ - Mo_4O_{11} was directly determined from the longitudinal strain along

Fig. 7: Determined temperature dependence of the heat capacity of η - Mo_4O_{11} (red), γ - Mo_4O_{11} (black), and $\text{Mo}_2\text{Ta}_2\text{O}_{11}$ (blue).

Fig. 8: Differential scanning calorimetry (DSC) measurement of γ - Mo_4O_{11} . Heating and cooling run through the phase transition at about 445–450 K.

Fig. 9: Temperature induced strain along [100] of γ - Mo_4O_{11} as observed by dilatometry.

[100]. Heating and cooling runs exhibit reversible discontinuities at ca. 440 K, which are hints to a phase transition of weakly first order (Figure 9). The thermal expansion of γ - Mo_4O_{11} is non-linear (Figure 9); thus, second-order polynomials of the type $\varepsilon_{11}(T) = \alpha_{11}\Delta T + \beta_{11}(\Delta T)^2$ with $\Delta T = T - T_0$ are required for a proper approximation of the strain ε_{11} over a temperature range between 330 and 436 K. $T_0 = 400$ K denotes the reference temperature and $\alpha_{11} = 7.2(4) \cdot 10^{-6} \text{ K}^{-1}$ and $\beta_{11} = 3.4(1) \cdot 10^{-8} \text{ K}^{-1}$ are the corresponding coefficients of linear and squared thermal expansion referring to 400 K. The reproducibility of the linear thermal expansion coefficient α_{11} is of the order of 5%.

High-temperature X-ray powder diffraction of η - Mo_4O_{11} and $\text{Mo}_2\text{Ta}_2\text{O}_{11}$

Both oxides undergo an assumable solid-phase decomposition (Figure 10). η - Mo_4O_{11} decomposes to the oxide MoO_3 due to the oxidation of Mo^{5+} to Mo^{6+} , which occurs at approximately 693 K. The final temperature of the decomposition is equal to 743 K. The difference between the temperatures of the oxidation determined by HT-XRD and thermal analysis can be due to the different experimental conditions. $\text{Mo}_2\text{Ta}_2\text{O}_{11}$ starts to decompose at approximately 1033 K into the oxide $\text{MoTa}_{12}\text{O}_{33}$ and an insignificant amount of an unidentified phase. No structural phase transitions are observed for both compounds. The temperature dependencies of the unit cell parameters of η - Mo_4O_{11} and $\text{Mo}_2\text{Ta}_2\text{O}_{11}$ are given in Figure 11. The unit cell parameters for both compounds were approximated using squared polynomials in the temperature ranges from 293 to 673 K (η - Mo_4O_{11}) and from 293 to 1023 K ($\text{Mo}_2\text{Ta}_2\text{O}_{11}$). The calculated thermal expansion coefficients at some specific temperatures are given in Table 4.

Fig. 10: The X-ray diffraction patterns of η - Mo_4O_{11} (left) and $\text{Mo}_2\text{Ta}_2\text{O}_{11}$ (right) given at different temperatures.

Fig. 11: The temperature dependencies of the unit cell parameters for $\eta\text{-Mo}_4\text{O}_{11}$ (top) and $\text{Mo}_2\text{Ta}_2\text{O}_{11}$ (bottom).

Tab. 4: The eigenvalues of the thermal expansion tensors of $\eta\text{-Mo}_4\text{O}_{11}$ and $\text{Mo}_2\text{Ta}_2\text{O}_{11}$ at given temperatures.

α (10^6 K^{-1})	Temperature/K		
	293	473	673
$\eta\text{-Mo}_4\text{O}_{11}$			
α_{11}	7.11(1)	8.12(3)	9.31(5)
$\alpha_{22}=\alpha_b$	7.31(1)	4.83(2)	2.13(4)
α_{33}	2.12(3)	1.66(7)	1.14(2)
α_a	4.27(7)	4.51(2)	4.76(6)
α_c	4.56(8)	4.81(2)	5.11(7)
$\mu_{c3}=\alpha_{33}\wedge c$ ($^\circ$)	44.5	44.2	44
α_β	-3.1(3)	-3.9(6)	-4.9(2)
α_v	16.5(2)	14.6(6)	12.5(2)
$\text{Mo}_2\text{Ta}_2\text{O}_{11}$			
$\alpha_a=\alpha_b$	-4.93(1)	-3.21(3)	-1.57(1)
α_c	12.44(6)	12.98(2)	13.48(6)
α_v	2.6(3)	6.6(6)	10.3(3)

The monoclinic oxide $\eta\text{-Mo}_4\text{O}_{11}$ expands anisotropically and the degree of the anisotropy increases as the temperature increases (Figure 12a). A mixed-anion framework is composed of the MoO_4 tetrahedra and MoO_6 octahedra, which are connected to each other through common vertices. The maximum thermal expansion α_{11} is along the direction that is close to the short diagonal of the ac parallelogram (Figure 12a; top), which is consistent with the theory of hinges deformation in monoclinic and triclinic crystals [51, 52].

The layered trigonal $\text{Mo}_2\text{Ta}_2\text{O}_{11}$ expands highly anisotropically and the negative expansion (contraction) is observed within the layers. The Mo atoms are in the tetrahedral coordination of the oxygen atoms and the tantalum atoms are in an octahedral coordination environment. The polyhedra are connected to each other through common vertices forming the thick layers. The maximum expansion is along the c axis ($\alpha_c=12.44(6) \cdot 10^{-6} \text{ K}^{-1}$ at 293 K) (Figure 12b). The expansion can also be described in terms of hinges deformation. The hinge cell is Ta1–O3–Mo1–O3–Ta1–O2–Ta1. The O2 atoms are on special positions and the Ta1–O2–Ta1 angle equals 180° (Figure 12c), whilst the Ta1–O3–Mo1 angle is 166.4° at room temperature [25] and could increase up to 180° under heating. If the Ta1–O3–Mo1 angle increases, the Mo1 atom could shift in the direction of the O1 atom while two Ta1 atoms come closer to each other. The angles between the polyhedra can vary more than the interior polyhedral angles. Thus, the layer expands along the c -axis and contracts along the a -axis.

Fig. 12: The η - Mo_4O_{11} (a) and $\text{Mo}_2\text{Ta}_2\text{O}_{11}$ (b) crystal structure projection and the figures of thermal expansion coefficients (the solid/green line – 293 K, the dashed/red line – the highest temperature), and a structural fragment (two hinge cells) of the $\text{Mo}_2\text{Ta}_2\text{O}_{11}$ layer (c).

Fig. 13: Temperature dependence of the magnetic susceptibilities χ of η - Mo_4O_{11} (red), γ - Mo_4O_{11} (black), and $\text{Mo}_2\text{Ta}_2\text{O}_{11}$ (green) measured with a magnetic field strength of 10 kOe.

Magnetic investigations

For all compounds, the magnetic susceptibility was investigated in zero-field-cooled mode (ZFC) with an applied external field of 10 kOe in the temperature range of 3–300 K (Figure 13). All curves show almost temperature independent behaviour with small upturns below 25 K, which can be linked to traces of paramagnetic impurities. The susceptibilities at 300 K are: $\chi(\gamma\text{-Mo}_4\text{O}_{11}) = +9(1) \times 10^{-6}$ emu mol $^{-1}$, $\chi(\eta\text{-Mo}_4\text{O}_{11}) = +429(1) \times 10^{-6}$ emu mol $^{-1}$ and $\chi(\text{Mo}_2\text{Ta}_2\text{O}_{11}) = -155(1) \times 10^{-6}$ emu mol $^{-1}$, indicating the expected diamagnetism for the latter compound, since all atoms exhibit close shell electron configurations according to $(\text{Mo}^{6+})_2(\text{Ta}^{5+})_2(\text{O}^{2-})_{11}$. The observed value is in line with the calculated diamagnetic increment of $\chi(\text{Mo}_2\text{Ta}_2\text{O}_{11}) = -172(1) \times 10^{-6}$ emu mol $^{-1}$ using the

tabulated values of the respective ions ($\chi(\text{Ta}^{5+}) = -14 \times 10^{-6}$, $\chi(\text{Mo}^{6+}) = -7 \times 10^{-6}$, $\chi(\text{O}^{2-}) = -12 \times 10^{-6}$ emu mol $^{-1}$) [53].

The binary molybdenum oxides in contrast, exhibit a very different magnetic behaviour. A weak positive but also temperature independent susceptibility is observed, contradicting a potentially expected paramagnetism caused by the Mo^{5+} ($4d^1$) cations according to $(\text{Mo}^{5+})_2(\text{Mo}^{6+})_2(\text{O}^{2-})_{11}$. The present magnetism is more in line with band-paramagnetism, caused by a metallic-like behaviour of the material. This, however, implies that no ordering of the $\text{Mo}^{5+}/\text{Mo}^{6+}$ cations but rather a delocalization is present. Studies of the electrical resistivity and the band structures of γ - and η - Mo_4O_{11} confirm this assumption. The Mo 4d states are filled and therefore lower in energy, the Fermi level therefore is found in the conduction band leading to the metallic character [54–56]. The absence of charge ordering has been already predicted in structural studies [28].

XPS measurements

The relevant Mo 3d spectra of the phases η - and γ - Mo_4O_{11} are shown in the panels a and b of Figure 14, respectively. The extended region between 230 and 290 eV binding energy features the C 1s region (mainly adventitious carbon and surface-adsorbed oxygenate species in agreement with the deconvoluted O 1s spectra) and a Mo 3d peak region with at least three different oxidation states of Mo in surface-near regions. Each Mo component (corresponding to Mo(IV), Mo(V), and Mo(VI)) has been accordingly fitted with a spin-orbit split component. For η - Mo_4O_{11} , the Mo $3d_{5/2}$ component of Mo(IV) is measured at 230.5 eV, the Mo $3d_{5/2}$ component of Mo(V) at 231.8 eV and the one of Mo(VI) at 233.1 eV. The assignment is corroborated by literature-reported values of Mo in different oxidation states [54, 57, 58].

Fig. 14: XPS analysis of η - Mo_4O_{11} (Panel a), γ - Mo_4O_{11} (Panel b), and $\text{Mo}_2\text{Ta}_2\text{O}_{11}$ (Panels c and d). The relevant regions (C 1s, O 1s, Mo 3d, and Ta 4f) have been deconvoluted into different components wherever applicable. The O 1s spectra are shown in Panels e (η - Mo_4O_{11}) and f ($\text{Mo}_2\text{Ta}_2\text{O}_{11}$), respectively.

The O 1s region (Panel e), besides organic residues and lattice oxygen, shows a well-developed OH species at 531.9 eV, indicative of protonated Mo_4O_{11} . Mo(VI) is the majority species, followed by Mo(V) and Mo(IV). The respective at.-% Mo(VI):Mo(V) ratio is 6:1, the one for Mo(VI):Mo(IV) is 15:1. Transferring the analysis to γ - Mo_4O_{11} , the relevant XP spectra of the phase Mo_4O_{11} shows strikingly similar features, both in the Mo 3d and O1 region, as well as in the qualitative and quantitative distribution of the existing Mo species.

The sum formula for Mo_4O_{11} allows for different oxidation states of molybdenum in the structure. With the mean oxidation state being +5.5, Mo_4O_{11} is at first expected to incorporate an equal amount of Mo(V) and Mo(VI), as indicated by Inzani et al. [54]. Taking into account the crystallographic data provided by Knorr and Müller [28], Mo_4O_{11} seems to consist of Mo(VI) inside the tetrahedra and Mo(V) and Mo(VI) in a ratio of 2:1 inside the octahedra, resulting in an overall ratio of 2:2. XPS measurements have previously been undertaken, indicating the presence of Mo(IV), Mo(V), and Mo(VI). However, as described in [59, 60], the distribution of Mo(VI), Mo(V), and Mo(IV) depends on the specific temperature, at which the samples were synthesized.

For $\text{Mo}_2\text{Ta}_2\text{O}_{11}$ (Panels c, d and f of Figure 14), deconvolution of the Mo 3d region is not possible due to strong overlap with the Ta 4d region. The qualitative peak shape

(intensity profiles, as well as the low binding energy shoulder) is, by direct comparison to Panels a and b, very similar, inferring an at least qualitatively similar distribution of Mo species. The Ta 4f region shows the presence of three Ta oxidation states between Ta(V) and Ta(III). Ta(V) and Ta(IV) are present in an almost 1:1 ratio, whereas Ta(III) is clearly the minority component (approximately half of the at.-% amount compared to Ta(V) or Ta(IV)). The Ta 4f_{7/2} components of Ta(V), Ta(IV), and Ta(III) were measured at binding energies of 29.5, 28.8, and 25.2 eV. Due to charging issues on that particular sample, the Ta 4f binding energies are shifted to too high binding energies with respect to literature data [61]. A protonated OH species is also present at 531.5 eV.

Raman spectroscopic measurements

The Raman spectrum of $\text{Mo}_2\text{Ta}_2\text{O}_{11}$ with the band positions marked is shown in Figure 15. To the best of our knowledge, no Raman spectrum of $\text{Mo}_2\text{Ta}_2\text{O}_{11}$ is available in the literature. Therefore, this spectrum was mainly recorded to serve as a future reference for the identification of $\text{Mo}_2\text{Ta}_2\text{O}_{11}$.

In contrast, Raman spectra of both η - Mo_4O_{11} [5, 62, 63] and γ - Mo_4O_{11} [37, 63] have been reported in the literature. All of these reports have found little to no difference

Fig. 15: Raman spectrum of a powder sample of $\text{Mo}_2\text{Ta}_2\text{O}_{11}$ with the band positions marked.

Fig. 16: Raman spectra of η - Mo_4O_{11} (top) and γ - Mo_4O_{11} (bottom) with different orientations of the laser polarisation relative to the crystal (same colour indicates the same orientation).

between the band position, but vast differences in relative band intensities even between the same phase of η/γ - Mo_4O_{11} [5, 62, 63]. This can in part be explained due to the use of different laser excitations. Also little to no difference was found between the Raman spectra of η - Mo_4O_{11} and γ - Mo_4O_{11} , especially by Olson [63], which is the only report we are aware of that has measured both phases thus far. The Raman spectra measured of η/γ - Mo_4O_{11} in this study are shown in Figure 16. The band positions are consistent with the literature and there is little difference between η - Mo_4O_{11} and γ - Mo_4O_{11} . However, interestingly a strong dependence of the relative band intensities on the orientation of the sample relative to the laser polarization was found. The relative band intensities for the orientation

referred to as “pol x” are consistent with what was found by Blume [5] and Borovška et al. [62], whereas the orientation “pol z” is consistent with the relative intensities in [37] and [63]. Thus, orientation effects seem to be a dominated factor in the measurement of Mo_4O_{11} Raman spectra and need to be considered.

Conclusion

Stability up to high temperatures was observed for η - Mo_4O_{11} and $\text{Mo}_2\text{Ta}_2\text{O}_{11}$. The phase γ - Mo_4O_{11} on the other hand is only stable to around 443 K, where a phase transition is indicated by DSC and dilatometry measurements. Heat capacity was measured for all three compounds, with the highest value observed in γ - Mo_4O_{11} . As expected, $\text{Mo}_2\text{Ta}_2\text{O}_{11}$ displays diamagnetism, whereas the binary oxides show a very different magnetic behaviour that is more in line with band-paramagnetism. The vast difference in band intensities found in Raman spectra of η/γ - Mo_4O_{11} are attributed to orientation effects dominating the Raman measurements of η/γ - Mo_4O_{11} . In contrast, no orientation effects are found with the Raman measurements of $\text{Mo}_2\text{Ta}_2\text{O}_{11}$.

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