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Studies on Molybdenum Oxides *

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The MoO_2—MoO_3 region of the molybdenum-oxygen system has been investigated within the temperature range 500°—870°C, by means of X-ray diffraction techniques. Temperature regions are given for the formation of the seven intermediate phases found, among which are two previously undescribed oxides designated ϑ- and $\varkappa$-oxides.

Unit cell dimensions and X-ray diffraction data are given and formulae are suggested for the ζ-oxide (Mo_9O_{26}, triclinic), the $\varkappa$-oxide ($Mo_{17}O_{47}$, orthorhombic) and the η-oxide (Mo_4O_{11}, monoclinic). The unit cell dimensions have also been determined for the ϑ-oxide ($MoO_{\sim 2.80}$, tetragonal), which is probably metastable.

The electrical resistivity at room temperature has been determined for the various intermediate phases excluding the ϑ-phase.

The oxidation of the oxides in air at 230°—350°C has been studied. An intermediate stage, called λ-oxide, has been observed in the oxidation of the two Mo_4O_{11} phases to MoO_3.

The first phase analysis by means of X-ray methods on the molybdenum-oxygen system was published in 1944 by Hägg and Magnéli [1]. They reported the existence of four oxides with compositions between MoO_2 and MoO_3, called β-, β'-, γ- and ε-oxide. By determination of the crystal structures Magnéli was later able to establish the exact formula Mo_8O_{23} (monoclinic) for the β-oxide [2], Mo_9O_{26} (monoclinic) for the β'-oxide [2] and Mo_4O_{11} (orthorhombic) for the γ-oxide [3]. These and other structural studies are reviewed and further discussed in Ref.[4].

In 1950 Glemser and Lutz published a paper on molybdenum oxides studied by X-ray powder methods, electrical resistivity measurements and chemical and microscopical techniques [5]. Their phase analysis in general confirmed the results of Hägg and Magnéli, but as has already been pointed out [6], the notations of the phases used in the two articles are inconsistent (*v. infra*).

In connection with studies of the thermal decomposition of MoO_3 *in vacuo*, two other oxide phases were observed, which were provisionally called ζ- and

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η-oxide[7]. There were indications that the composition of ζ-oxide is near $MoO_{2.88}$, but at that time nothing could be said about the composition of the η-oxide.

A review of the structural investigations of oxygen compounds of molybdenum and tungsten carried out at this Institute up to 1954 is given in Ref.[8]

As the investigations by Hägg and Magnéli were limited mainly to a restricted region of temperature around 650—750°C, it was thought desirable to extend the phase analysis studies to a wider range of temperature and to try to establish the formulae of the new oxides.

The results obtained to date are presented in this article. Crystal structure determinations of several of the new oxides are in progress.

EXPERIMENTAL

The starting materials for the preparations were molybdenum trioxide ("Baker's Analyzed", 99.9 % dried at 200°C), and molybdenum dioxide prepared by reducing the trioxide in a stream of dry hydrogen gas at 500°C, the degree of reduction being controlled by weighing. In a few cases molybdenum powder ("Kahlbaum", heated *in vacuo* at about 400°C) was used instead of the dioxide.

The samples, prepared by thoroughly mixing weighed amounts of MoO_2 (or Mo) and MoO_3, were heated in evacuated, sealed silica tubes, which had been cleaned and preheated in air at about 800°C. As had been observed previously by Hägg and Magnéli, MoO_3 attacks the silica to some extent, especially above 700°C, giving a white, crystalline coating inside the tubes. This coating showed the powder lines of low-cristobalite, often together with those of MoO_3. To avoid contamination, those samples which did not contain molybdenum metal were often packed into platinum foil when heated at the higher temperatures.

The high volatility of MoO_3 made it necessary to minimize any temperature gradient within the tubes which were therefore kept in appropriate borings in heavy steel cylinders placed in vertical electrical furnaces[6]. In spite of these precautions a slight escape of MoO_3 from the main sample could not be avoided, especially during the heat treatments above 700°C. This gave rise to a small drift of the composition towards lower oxygen content ($\Delta x < 0.02$ in MoO_x) which had to be taken into account.

A calibrated platinum-platinum rhodium thermocouple was used, inserted into a boring of the steel cylinder. The cold junction was kept at 0°C. The temperature was measured with a potentiometer bridge at the beginning and the end of each heat treatment, and was kept constant by a Wheelco regulator which controlled only about 5 % of the stabilized voltage of the furnace[6]. In this way the short-time variations of the temperature were reduced to within ± 2°C, but a long-time drift of the temperature level was sometimes observed. The total variations were, however, always within ± 4°C.

The studies have been concerned with the temperature interval 500°—870°C, the lower limit being set by the rapidly decreasing reaction rate. At the lower temperatures heating times of several weeks and repeated powdering of the samples were necessary in order to obtain equilibrium. At the higher temperatures heating for some days was usually sufficient.

The silica tubes were quenched in water from the reaction temperatures. No chemical analysis of the products was considered necessary.

The samples were examined microscopically and X-ray powder photographs were taken in Guinier focusing cameras of 80 mm diameter using monochromatized Cu$K\alpha$ or Cr$K\alpha$ radiation. These cameras, covering the angular region $1.5° < \Theta < 45°$, give a high resolution and very low background which greatly facilitated the identification of the patterns and the detection of phases present in small amounts. The powder patterns were evaluated according to the method given by Hägg, which introduces an automatic correction for film shrinkage[9]. Potassium chloride (Analar, BDH, ground and recrystallized) was added to the powder specimens as an internal standard, and its lattice parameter was taken to be $a = 6.29215$ Å (21°C) according to Hambling[10]. The use of Guinier

Table 1. X-Ray diffraction patterns of molybdenum oxides; Cu*Ka* radiation, $\lambda = 1.5418$ Å.

a Triclinic Mo_9O_{26} (ζ-molybdenum oxide)

I	$\sin^2\Theta_{obs}$	*hkl*	$\sin^2\Theta_{calc}$
w	0.01139	$10\bar{1}$	0.01138
vw−	0.01565	$10\bar{2}$	0.01571
w	0.03657	113	0.03647
vw−	0.04187	$20\bar{1}$ $\bar{1}31$	0.04152 0.04197
vw−	0.04551	$20\bar{2}$	0.04552
st	0.04641	015	0.04653
vw	0.04802	$\bar{1}32$ 114	0.04800 0.04827
st	0.05235	$03\bar{3}$	0.05218
vw−	0.05254	$20\bar{3}$	0.05262
vw	0.05498	$\bar{2}30$	0.05510
m	0.05549	$2\bar{3}1$	0.05561
vw	0.06135	$03\bar{4}$	0.06136
vw	0.06373	212	0.06374
vw	0.07732	$2\bar{2}5$	0.07718
vw	0.08082	041	0.08080
w	0.08749	$\bar{1}43$ 042	0.08772 0.08774
vw	0.09029	$1\bar{2}7$	0.09036
vw+	0.09355	$\bar{3}31$ $2\bar{2}6$	0.09368 0.09381
vw−	0.09671	$13\bar{5}$	0.09656
vw−	0.10602	$3\bar{2}4$ 140	0.10616 0.10635
vw	0.11007	$02\bar{8}$ $\bar{2}44$	0.10968 0.11047
vw+	0.11234	$30\bar{4}$	0.11230
vw	0.11372	311	0.11376
w	0.15029	128	0.15028
vw	0.15494	$23\bar{6}$ $24\bar{1}$ $\bar{4}32$	0.15452 0.15469 0.15512
m	0.17009	$2\bar{6}4$	0.17008

b $Mo_{17}O_{47}$ ($\varkappa$-molybdenum oxide)

I	$\sin^2\Theta_{obs}$	*hkl*	$\sin^2\Theta_{calc}$
m	0.00280	110	0.00281
w	0.00507	200	0.00509
w	0.00616	020	0.00616
w	0.00661	210	0.00663
w	0.00742	120	0.00744
w	0.01124	220	0.01126
w−	0.01893	230	0.01897
w−	0.02979	240	0.02976
m	0.03331	510	0.03334
w	0.03612	340	0.03612
st	0.03804	520 001	0.03797 0.03806
st	0.04507	440	0.04502
w+	0.05199	031 620	0.05194 0.05196
vw	0.05553	060	0.05551
vw	0.05648	540	0.05647
w−	0.05686	160	0.05678
w−	0.05699	231	0.05703
m	0.05843	401	0.05841
st	0.05966	630	0.05967
m	0.06272	041	0.06273
vw	0.06388	710	0.06387
vw	0.07032	550	0.07035
w	0.07139	511	0.07140
w	0.07587	460	0.07586
m	0.07683	170	0.07683
w	0.08063	270	0.08065
m	0.08138	800	0.08141
vst	0.08307	441	0.08308
w−	0.08754	820	0.08758
vw	0.09353	061	0.09357
vw	0.09459	541	0.09453
m	0.09764	631	0.09773

c ϑ-molybdenum oxide

I	$\sin^2\Theta_{obs}$	*hkl*	$\sin^2\Theta_{calc}$
w	0.00448	400	0.00449
w	0.00563	420	0.00562
w	0.01126	620	0.01124
vw−	0.01460	640	0.01461
vw	0.01800	800	0.01798
w	0.02028	660	0.02023
vw−	0.02248	840	0.02247
vw−	0.03262	10,4,0	0.03259
st	0.03829	001	0.03834
m	0.04045	12,0,0	0.04045
w	0.04156	12,2,0	0.04158
vw	0.04494	12,4,0	0.04495
m	0.04607	10,8,0	0.04607
w	0.05619	10,10,0	0.05618
w	0.05845	12,8,0	0.05843
w	0.05954	14,4,0	0.05956
vw−	0.07086	10,4,1	0.07093
vw	0.07192	16,0,0	0.07192
m	0.07305	14,8,0 16,2,0	0.07304

d Monoclinic Mo_4O_{11} (η-molybdenum oxide)

I	$\sin^2\Theta_{obs}$	*hkl*	$\sin^2\Theta_{calc}$
w	0.00393	200	0.00397
w	0.01332	001	0.01331
w	0.01618	$20\bar{1}$	0.01619
vw	0.01836	201	0.01836
w+	0.02697	$40\bar{1}$	0.02702
m−	0.03336	011	0.03340
vw	0.03629	$21\bar{1}$	0.03628
vst+	0.03844	211	0.03845
vw	0.04393	311	0.04396

vst	0.04571	60$\bar{1}$	0.04578
st	0.05145	411	0.05145
vw	0.05574	610	0.05582
vw	0.07235	611 80$\bar{1}$	0.07238 0.07248
vw+	0.07352	012 402	0.07333 0.07346
m	0.07522	21$\bar{2}$ 112	0.07513 0.07541
m	0.08031	020	0.08036
m	0.08345	502 810	0.08348 0.08360
m	0.08490	41$\bar{2}$	0.08487
w+	0.09927	10,0,0	0.09924
vw	0.10262	61$\bar{2}$	0.10254
vw	0.10805	80$\bar{2}$	0.10807
w−	0.11911	10$\bar{3}$ 10,1,0	0.11915 0.11933
w	0.12008	003	0.11979
w	0.12606	62$\bar{1}$	0.12614
vw	0.13975	222 013	0.13974 0.13988
w−	0.14148	10,0,$\bar{2}$	0.14163
w	0.15381	313 422	0.15370 0.15382
vw	0.16245	413 12,0,1	0.16227 0.16273
vw	0.16383	522	0.16384
m	0.17590	622	0.17584
w	0.18282	12,1,1	0.18282
m	0.19051	813	0.19037

e λ-molybdenum oxide

I	$\sin^2\Theta_{obs}$
st	0.0398
w	0.0437
m	0.0469
vw	0.0527
vw	0.0865
vw	0.0890
vw	0.0907
vw	0.1594
vw	0.1689
vw	0.1878

vst = very strong
st = strong
m = medium
w = weak
vw = very weak

cameras for accurate determination of lattice dimensions has recently been demonstrated in this journal[11]. The powder patterns of several of the molybdenum oxide phases are given in Table 1.

Single crystal photographs were taken in Weissenberg and precession cameras using Cu*K* and Mo*K* radiation.

The electrical resistivity of the oxides was determined in a simple cell, permitting the measurements to be carried out on a powder specimen under considerable pressure, applied by means of a screw press. The data thus obtained are given in Table 2.

RESULTS OF THE PHASE ANALYSIS

The results of the phase analysis within the 500°—800°C region are summarized in Fig. 1, where the formation temperatures *versus* composition are indicated for the intermediate phases found. As far as can be determined from the powder photographs, none of the phases has an extended homogeneity range. It must be emphasized that the temperature ranges indicated do not necessarily represent the true stability regions. These may be very difficult to establish because of an observed disposition of several phases to remain for a long time in a metastable state.

Preparations — the starting mixtures as well as the pure oxides prepared — heated above 800°C and quenched in water always contained at least three phases, *viz.* MoO_2, MoO_3 and orthorhombic Mo_4O_{11} (γ-oxide), and thus did not represent a state of equilibrium. When the cooling rate was slower, the lines of MoO_2 generally disappeared. This seems to indicate that MoO_2 and MoO_3 are the only phases stable above 800°C, but that orthorhombic Mo_4O_{11}

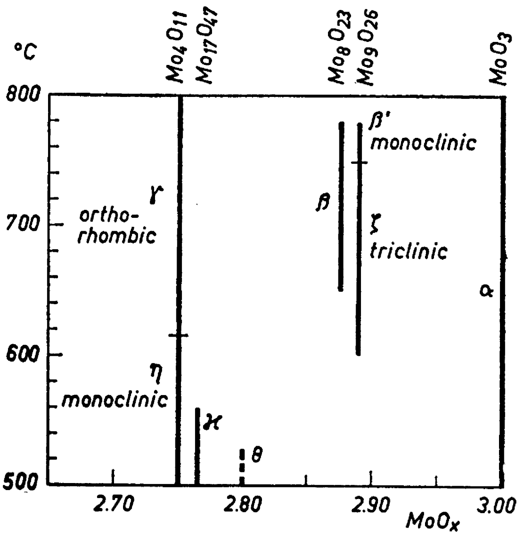

Fig. 1. Formation temperature *v.* composition diagram for molybdenum oxides.

forms fairly rapidly when the temperature is lowered. The triclinic Mo_9O_{26} (ζ-oxide) likewise was sometimes found in samples slowly cooled from above 800°C. According to Fig. 1, the formation of this phase should occur below 750°C.

Hägg and Magnéli reported that the β'-oxide (monoclinic Mo_9O_{26}) and the γ-oxide (orthorhombic Mo_4O_{11}) decompose when heated to 850°C, giving MoO_2, MoO_3 and a new phase which they designated ε-oxide[1]. Upon reexamination of samples prepared by these authors and reported to contain ε-oxide, it became evident that this phase was identical with the ζ-oxide (triclinic Mo_9O_{26}). The cooling rate was, however, not very high in these early experiments and may explain the occurrence of this phase.

Description of the phases observed

Triclinic Mo_9O_{26} (ζ-oxide). The ζ-phase has been obtained between 600° and 750°C [*], and is the purest in samples of compositions close to $MoO_{2.89}$. It is transformed into monoclinic Mo_9O_{26} (β'-oxide) when heated at 760°—780°C (within 2 h at 780°C), and is slowly decomposed into MoO_3 and monoclinic Mo_4O_{11} (η-oxide) at 550°C. It forms almost-black, irregular, but rather flaky crystals, readily distinguishable from the other molybdenum oxides. With the aid of single crystal data, its powder pattern (see Table 1a) has been indexed and the following triclinic unit cell has been derived by least squares refinement

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[*] The accuracy of the formation temperature limits given in the following are, in general, about ± 10°C.

$a = 8.145$ Å $b = 11.89$ Å $c = 19.66$ Å $V = 1779.5$ Å^3
$\alpha = 95.47°$ $\beta = 90.39°$ $\gamma = 109.97°$

As is the case with all the oxides below MoO_3 the electrical conductivity makes impossible the use of piezo-electrical methods for detection of any non-centrosymmetry.

The density was found to be 4.74, which corresponds to 35.7 $MoO_{2.89}$ per unit cell and suggests a cell content of 4 formula units Mo_9O_{26}.

Mo_8O_{23} (β-oxide) and monoclinic Mo_9O_{26} (β'-oxide). These two phases, first described by Hägg and Magnéli [1], have been obtained within the temperature ranges 650°—780°C for Mo_8O_{23} (by decomposition of $Mo_{17}O_{47}$ even at 630°C; see below) and 750°—780° for monoclinic Mo_9O_{26}. Both decompose into MoO_3 and orthorhombic Mo_4O_{11} when heated at 785° and 800°C. At temperatures below their formation regions they are, however, markedly stable; no change was actually observed after tempering Mo_8O_{23} for three days at 643°C or three weeks at 550°C and monoclinic Mo_9O_{26} three days at 700°C or one week at 648°C.

The structures of the two oxides have been determined by Magnéli [2]. They constitute the first two members of a series of structurally interrelated oxides of the general formula Me_nO_{3n-1} [12]. By substituting tungsten for part of the molybdenum, higher homologues in this series have been prepared, *e.g.* $(Mo, W)_{10}O_{29}$ and $(Mo, W)_{12}O_{35}$ [6]. The introduction of a small proportion of tungsten has furthermore been found to extend the formation range for the β'-phase down to 650°C [6].

The *d*-values of the powder patterns of Mo_8O_{23} and monoclinic Mo_9O_{26} are listed in Ref.[13], and the unit cell dimensions are given in Table 2 of Ref.[6]

It has been pointed out earlier [6] that, in view of its chemical properties, the "β-molybdenum oxide" of Glemser and Lutz [5] is probably identical with the triclinic Mo_9O_{26} (ζ-oxide), while their "β'-oxide" is Mo_8O_{23}, monoclinic Mo_9O_{26} or a mixture of these two phases. The resistivity measurements made (*cf.* Table 2) strongly support this view: the triclinic Mo_9O_{26} is seen to have by far the highest resistivity of all the intermediate phases, as has the "β-oxide" according to Glemser and Lutz.

$Mo_{17}O_{47}$ (κ-oxide). In samples heated below about 560°C, a new phase appeared with a composition close to $MoO_{2.78}$. It decomposes into orthorhombic Mo_4O_{11} (γ-oxide) and Mo_8O_{23} (β-oxide) at 630°C, but does not change when kept at 590°C for one week.

Table 2. Specific electrical resistivity of molybdenum oxides (at room temperature).

Phase	Resistivity ohm . cm
Mo_9O_{26} triclinic	~ 250
Mo_9O_{26} monoclinic	~ 3.7
Mo_8O_{23}	~ 1.2
$Mo_{17}O_{47}$	< 0.05
Mo_4O_{11} orthorhombic	~ 0.25
Mo_4O_{11} monoclinic	~ 0.2

The $\varkappa$-oxide forms long, flat, extremely thin, black needles and looks dark grey when powdered. Its powder pattern, given in Table 1b has revealed an orthorhombic unit cell with the dimensions

$$a = 21.61_5 \text{ Å} \qquad b = 19.63_2 \text{ Å}, \qquad c = 3.951_5 \text{ Å}.$$

The reflection absences found in the single crystal photographs are in accordance with the space groups No. 32, *Pba*2 and No. 55, *Pbam.*

The density was measured to be 4.72, which corresponds to 34.0 $MoO_{2.78}$ units per cell and suggests the formula $Mo_{17}O_{47}$, with 2 formula units per cell.

The low electrical resistivity of this phase is noteworthy (see Table 2).

ϑ-Oxide. A second phase not previously reported has been observed in preparations heated for a relatively short time below 530°C. The composition of this phase, called ϑ-oxide, seems to be in the neighbourhood of $MoO_{2.80}$, but it has not been possible to obtain it in a very pure state. With prolonged heating, it slowly decomposes into $Mo_{17}O_{47}$ ($\varkappa$-oxide) and MoO_3. It seems, therefore, probable that the ϑ-oxide is not stable within the temperature region investigated, but is formed in a metastable state.

Its powder pattern is given in Table 1c. The unit cell is tetragonal with the dimensions

$$a = 45.99 \text{ Å}, \qquad c = 3.937 \text{ Å}.$$

The reflections *hkl* with *h* or *k* odd are absent for $l = 0$; they are revealed in the layer line $l = 1$ as very weak, diffuse spots growing stronger in the higher layer lines. This phenomenon evidently indicates the presence of a subcell of the dimensions

$$a' = \tfrac{1}{2}a = 23.00 \text{ Å}, \qquad c' = c = 3.937 \text{ Å}.$$

The most probable space-group of the large cell is No. 129, *P4/nmm.*

As it has not been possible to prepare the oxide in an amount sufficient for density determinations, no proposal of its formula can be given at present.

Orthorhombic Mo_4O_{11} (γ-oxide). The orthorhombic Mo_4O_{11} (γ-oxide) forms between 615° and 800°C approximately. As was mentioned above, it is often found also in samples heated above this upper limit and furthermore sometimes in preparations treated at about 500°C. In these cases equilibrium had, however, never been reached. It is transformed into the monoclinic form, η-oxide (see below), by heating for three weeks at 550° but remains unchanged after one week at 590°C.

The crystal structure has been determined by Magnéli [3] and the X-ray powder pattern is listed in Ref.[13]. The unit cell dimensions are *

$$a = 24.49 \text{ Å}, \qquad b = 5.457 \text{ Å}, \qquad c = 6.752 \text{ Å}, \qquad V = 902.3 \text{ Å}^3.$$

Monoclinic Mo_4O_{11} (η-oxide). Below about 615°C another phase of composition $MoO_{2.75}$ is formed. This phase, η-oxide, has previously been observed

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* The present values are somewhat more exact than those previously given [13].

as a product of thermal decomposition of MoO_3 *in vacuo* at 549° and 608°C [7]. It is probably identical with the phase designated γ' by Glemser and Lutz which was rarely obtained at 600°C [5]. It remains unchanged after heating for two days at 634°, but is transformed into the orthorhombic, high-temperature form (γ-oxide) within two weeks at 655°C.

This phase forms wine-red, rather irregular crystals, which are similar to those of the orthorhombic form (γ-oxide). The powder pattern given in Table 1d has been evaluated with the aid of single crystal photographs, and the following unit cell has been derived

$$a = 24.54 \text{ Å}, \quad b = 5.439 \text{ Å}, \quad c = 6.701 \text{ Å}, \ \beta = 94.28° \quad V = 891.8 \text{ Å}^3.$$

The observed density is 4.17, which is in good agreement with the value 4.168 calculated for Mo_4O_{11} with 4 formula units in the unit cell. The space group in probably No. 14, $P2_1/a$.

The close similarity of the unit cell dimensions of the two Mo_4O_{11}-modifications is striking; the slight monoclinic deformation of the η-oxide is the main difference. In addition there are many common features in the intensity distribution of the diffraction pattern indicating that the structures of the two oxides are probably interrelated. In view of this the sluggishness of the transformation between the two forms is remarkable.

By means of differential thermal analysis no polymorphic transformation has been observed[14], which is not surprising in the light of the sluggishness of the transformation.

OXIDATION IN AIR OF MOLYBDENUM OXIDES

A few experiments have been carried out on the oxidation of molybdenum oxides in air at elevated temperatures. Finely ground specimens of the various oxides (except the ϑ-oxide) were heated in a muffle furnace at a few temperatures within the region 230°—350°C.

It was found that MoO_2 and triclinic Mo_9O_{26} (ζ-oxide) were the phases most resistant to oxidation (hardly affected by heating for two days at about 270°C), while orthorhombic Mo_4O_{11} (γ-oxide) was the most sensitive phase (completely transformed to MoO_3 within 18 h at about 300°C). The high-temperature forms of Mo_4O_{11} and Mo_9O_{26}, in a metastable state at the oxidation temperature, were much more rapidly oxidized than the low-temperature forms.

Indications from the powder photographs of intermediate stages in the course of oxidation were found only in the cases of monoclinic and orthorhombic Mo_4O_{11} heated at about 230° and 270°C, at which temperatures a quite new, somewhat diffuse pattern appeared in the photographs of partially oxidized products. In the samples treated at about 300° and 350°C, this intermediate stage, here designated λ-oxide, was not observed. When a mixture of λ-oxide and MoO_3 (the mixture obtained by oxidizing orthorhombic Mo_4O_{11} for 13 days at about 230°C) was heated *in vacuo* at 390° for 20 h, the lines of the λ-oxide disappeared: the sample consisted of MoO_3 and monoclinic Mo_4O_{11}. It is thus evident that the λ-oxide is unstable, at least at higher temperatures, and that it has a composition lying somewhere within the range

$MoO_{2.75} \leq MoO_x < MoO_3$, but is probably not very close to the latter limit. The main lines of its powder pattern are listed in Table 1e.

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