Molybdenum Oxides MoO_x: Spark-Plasma Synthesis and Thermoelectric Properties at Elevated Temperature.

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Elemental analysis of starting materials

The results of elemental analysis results of the starting materials are summarized in **Table S1**.

	Mo	MoO ₂	a-MoO3
Element		Concentration / w%	
Mo	-	74.21 ± 0.20	66.38 ± 0.60
0	1.11 ± 0.01	24.76 ± 0.81	32.59 ± 0.25
С	0.015 ± 0.004	0.022 ± 0.001	≈ 0.02
Ν	n.d. < 0.02	0.34 ± 0.01	0.30 ± 0.01
S	n.d. < 0.01	<i>n.d.</i> < 0.01	n.d. < 0.01
Та	0.092 ± 0.006	0.070 ± 0.004	0.061 ± 0.001
W	0.013 ± 0.003	0.011 ± 0.003	n.d. < 0.01
Nb	n.d. < 0.01	<i>n.d.</i> < 0.01	n.d. < 0.01
Na	0.223 ± 0.003	0.176 ± 0.003	0.154 ± 0.006

Table S1. Chemical compositions of the starting materials. For non-detectable (n.d.) concentration the sensitivity constraints are given.

Decomposition of α -MoO₃ during SPS

When heating α -MoO₃ in SPS with 10 K min⁻¹ we find the decomposition temperature T_{dec} beeing increased according to the detection of the SPS chamber pressure (**Figure S1**, blue lines) and *z*-shift of the punches (**Figure S2**, black lines).

The large range of T_{dec} lead to the assumption that varying denseness of the graphite lining may be responsible for this effect. Thus, one experiment was performed with an intentionally introduced 2 mm gap in the lining. The expected lowering of the sublimation onset did not happen.

A comparison of one exemplary SPS chamber pressure curve during heating α -MoO₃ with the relative mass during thermogravimetric (TG) analysis under similar conditions (10 Kmin⁻¹, vacuum) emphasizes the increase of T_{dec} during SPS (**Figure S2**).



Figure S1. Compaction of α -MoO₃ powder *via* SPS with a heating rate of 10 Kmin⁻¹. *In-situ* indicators for the starting decomposition are the moving position of the SPS punches (black lines) with a simultaneous decrease of the vacuum quality, *i.e.* an increase of the chamber pressure (blue lines). No onset decrease is found when a gap in the graphite lining of the SPS die is introduced (dash-dotted lines)



Contamination of samples during the successive SPS cycles

For all multi-step SPS experiments, the compacted samples were polished and crushed to powders for phase analysis by PXRD. During this repetitive procedure, contaminations may occur from improperly removed lining of the SPS dies (graphitic carbon) as well as from the polishing paper (silicon carbide).

In order to study this issue, we exemplarily traced composition changes for the synthesis of $MoO_{2.889}$ ($Mo_{18}O_{52}$, **Table S2**) using ICP-OES. Since no increase of the carbon concentration was detected, we rather safely excluded contamination due to the repeated polishing process.

	1 st step	2 nd step	3 rd step
C / w%	n.d. ≤ 0.05	n.d. ≤ 0.05	n.d. ≤ 0.05
N / w%	n.d. ≤ 0.05	n.d. ≤ 0.05	n.d. ≤ 0.05
O / w%	32.68 ± 0.26	33.2 ± 0.57	33.38 ± 0.24
S / w%	n.d. ≤ 0.01	n.d. ≤ 0.01	n.d. ≤ 0.01
Ta / w%	n.d. ≤ 0.005	n.d. ≤ 0.005	n.d. ≤ 0.005
Na / w%	0.140 ± 0.001	0.133 ± 0.002	0.145 ± 0.004

Table S2: Chemical compositions of a $MoO_{2.889}$ sample after three successive SPS steps. For non-detectable (n.d.) concentration the sensitivity constraints of the used ICP-OES are given. No changes are observed for the most likely affected carbon content.

Grain growth in α -MoO₃ during SPS

During compaction, α -MoO₃ shows enormous inhomogeneous grain growth from 6-15 µm in the as-received powder (manufacturer information) to the order of millimeters, as depicted exemplary for 1 × 923 K / t_{dwell} with varying t_{dwell} = {10 min, 40 min, 120 min} (**Figure S3**).



Figure S3: Light microscopic images of roughly polished α -MoO₃ after SPS compaction at 923 K with varying dwell time t_{dwell} show remarkable rapid grain growth with proceeding heating time. During LFA measurement, the thermal diffusivity of samples compacted with $t_{dwell} < 120$ min shows significant deviation between heating and cooling.

Specific heat of MoO₂, Mo₄O₁₁, Mo₁₇O₄₇, Mo₁₈O₅₂ and MoO₃

The SPS preparation of MoO_x samples with $x = \{2, 2.760, 2.750, 2.889, 3\}$ yielded single phase material of MoO₂, Mo₁₇O₄₇, γ -Mo₄O₁₁, Mo₁₈O₅₂, and MoO₃, respectively, whose specific heat $c_p(T)$ was measured by differential scanning calorimetry (**Figure S4**). For x = 2 and $x = \{2.760, 2.889, 3\}$ the values do not differ from the theoretical c_p data of MoO₂ and MoO₃, respectively, with respect to the experimental error of 5% **[1,2]**.

For γ -Mo₄O₁₁ (x = 2.750) there is found (1) an c_p increase at 650 K which was confirmed to result from the decomposition γ -Mo₄O₁₁ \rightarrow Mo₁₇O₄₇ + MoO₂ *via* high-temperature synchrotron diffraction (will be published elsewhere) and (2) an delta-shaped c_p increase at 450 K which is presumed to origin from a hitherto unknown phase transition.



Figure S4. Specific heat c_p of MoO_x samples from two cycles of DSC measurements (coloured lines). Theoretical data from NIST Shomate equations is given for MoO₂ and MoO₃ with 5% error bars (black dashed lines) **[1,2]**. Arrows mark effects in the MoO_{2.750} (γ -Mo₄O₁₁) sample (red lines): The reversible delta shaped deviation from theoretic c_p at ~450 K is interpreted as a transition. Transient ranges between the four measurement regions are excluded (grey areas).

Reproducibility of thermoelectric property measurements

Temperature-dependent measurements of the electrical conductivity $\sigma(T)$ and Seebeck coefficient $\alpha(T)$ were performed for at least two heating and cooling cycles to verify reproducibility. In general, both $\sigma(T)$ and $\alpha(T)$ remain reproducible. However, we find also find minor deviation which shall be explained in the following.

In Mo₁₈O₅₂ (MoO_{2.889}) a subtle reproducible hysteresis in $\sigma(T)$ occurs, but with respect to the device error we cannot claim the difference between heating and cooling to be significant (**Figure S5**).



Figure S5. Electrical conductivity during two heating and cooling cycles of $Mo_{18}O_{52}$ (MoO_{2.889}).

For $Mo_{17}O_{47}$ (MoO_{2.650}) in the first heating cycle the electrical conductivity is slightly decreased below 500 K, but again consideration of the errors does not allow for the interpretation of a real effect (**Figure S6**).

During the first heating, the $\alpha(T)$ measurement for γ -Mo₄O₁₁ (MoO_{2.750}) showed some random deviation from the linear temperature dependence, but two further cycles were perfectly stable (**Figure S7**).

These subtle effects demand more detailed study with higher precession.



Figure S6. Electrical conductivity during two heating and cooling cycles of $\rm Mo_{17}O_{47}$ (MoO_ $\rm 2.765$).



Figure S7. Seebeck coefficient during three heating and cooling cycles of γ -Mo₄O₁₁ (MoO_{2.750}). Deviation from the near-linear temperature dependence occurred in the first cycle.

Quantification of secondary phase content in MoO2.889 samples

A quantification of the γ -Mo₄O₁₁ amount in practically single-phase MoO_{2.889} samples from SEM (BSE contrast) and EDX fails due the very small composition differences of the phases γ -Mo₄O₁₁ and Mo₁₈O₅₂. The expected subtle contrast is overridden by the orientation-dependent contrast of the different grains.

A two-phase Rietveld refinement of the full X-ray diffraction profile fails because of the very low intensity of the two detected γ -Mo₄O₁₁ reflections which are both overlapped by Mo₁₈O₅₂ reflections and not easily deconvoluted. Also, the low symmetry of Mo₁₈O₅₂ (space group: *P*-1) introduces a large number of free variables. From the obtained diffraction data a valid quantification of the phase contents appears impossible.

A very rough estimation of the phase content can be performed from the intensity relation of the most intense reflections of both phases (conditions: $\Delta\theta$ of both reflections must be small; the elements in both phases should have similar scattering factors, which is the case for two MoO_x phases). Due to the complicated deconvolution we compared only the (unintegrated) maximum intensity. From this, an average phase content $\langle c_{Mo4O11} \rangle = 6.3$ vol% is calculated (**Figure S8**). Both γ -Mo₄O₁₁ reflection intensities must be overrated due to the missing deconvolution and therefore neglected contribution of the Mo₁₈O₅₂ reflection intensity. Thus, the approximated 6.3 vol% represent an upper limit and the real phase content is expected to be $\langle 5 \text{ vol}\%$.



Reflection pair 211/015: (4399-3433) / (18083-3017) * 100% = **6.4** % Reflection pair 311/0-33: (4112-3209) / (17269-2775) * 100% = **6.2** % Figure S8. X-ray diffraction pattern of practically single-phase MoO_{2.889}. The linearly fitted background intensity (blue) is substracted from the overall intensity. Then a rough estimation of the phase content can be calculated from the relation of maximum intensities of the most intense reflection pairs of Mo₁₈O₅₂ (black) and γ -Mo₄O₁₁ (red).

In all three compositions the unit cell parameters of γ -Mo₄O₁₁ were refined in the space group *P*na2₁ using 31 identical non-overlapping reflections which are listed (**Tables S2-S4**).

h	k	1	$2\theta / \circ (exp)$	2 heta / ° (theo)	FWHM
2	0	0	7.209	7.218	0.2169(5)
4	1	0	19.565	19.565	0.1016(3)
0	1	1	20.900	20.916	0.1278(3)
2	1	1	22.150	22.153	0.0972(1)
5	1	0	22.410	22.417	0.0925(1)
3	1	1	23.607	23.613	0.0924(1)
6	1	0	25.486	25.493	0.1043(1)
2	2	1	31.997	31.997	0.1075(2)
5	2	0	32.177	32.185	0.1166(3)
0	0	2	32.799	32.801	0.1099(2)
3	2	1	33.050	33.053	0.1018(1)
8	0	1	33.555	33.557	0.0962(1)
6	2	0	34.461	34.459	0.1050(2)
6	1	2	41.994	41.995	0.1000(1)
5	2	2	46.626	46.616	0.0865(1)
6	2	2	48.310	48.310	0.0951(2)
7	2	2	50.256	50.258	0.1062(3)
7	3	1	51.035	51.042	0.1014(3)
2	1	3	52.610	52.606	0.0936(1)
1	3	2	52.825	52.824	0.1030(1)
13	1	1	53.186	53.183	0.1018(2)
3	1	3	53.312	53.317	0.1095(2)
11	1	2	54.912	54.915	0.1007(1)
9	3	1	55.575	55.574	0.0923(1)
14	1	1	56.921	56.923	0.0991(1)
12	1	2	58.049	58.047	0.0960(1)
3	2	3	58.719	58.716	0.0971(1)
8	0	3	59.041	59.039	0.1001(1)
4	4	1	59.215	59.211	0.1014(1)
11	2	2	60.220	60.219	0.1000(1)
16	0	2	70.544	70.528	0.1050(2)

Table S3: Reflections used for the lattice parameter refinement of γ -Mo₄O₁₁ in the two-phase MoO_{2.740} sample (Cu-K_{α 1}, room temperature).

h	k	1	2θ / ° (exp)	2 heta / ° (theo)	FWHM
2	0	0	7.226	7.217	0.0734(5)
4	1	0	19.568	19.565	0.0627(7)
0	1	1	20.924	20.917	0.0569(7)
2	1	1	22.135	22.154	0.0696(6)
5	1	0	22.417	22.417	0.0523(5)
3	1	1	23.602	23.613	0.0902(1)
6	1	0	25.512	25.492	0.0685(2)
2	2	1	32.006	32.000	0.0869(1)
5	2	0	32.187	32.188	0.0748(3)
0	0	2	32.807	32.800	0.0766(3)
3	2	1	33.051	33.055	0.0849(1)
8	0	1	33.555	33.554	0.0825(1)
6	2	0	34.473	34.460	0.1297(3)
6	1	2	41.999	41.994	0.0771(2)
5	2	2	46.617	46.617	0.0840(1)
6	2	2	48.315	48.311	0.0916(1)
7	2	2	50.265	50.258	0.0931(3)
7	3	1	51.057	51.046	0.0795(3)
2	1	3	52.615	52.605	0.0910(3)
1	3	2	52.833	52.828	0.1042(2)
13	1	1	53.190	53.178	0.1290(6)
3	1	3	53.319	53.316	0.1013(5)
11	1	2	54.918	54.912	0.1023(4)
9	3	1	55.587	55.576	0.0786(2)
14	1	1	56.926	56.918	0.0898(2)
12	1	2	58.064	58.044	0.0821(2)
3	2	3	58.736	58.716	0.0881(3)
8	0	3	59.051	59.036	0.1021(3)
4	4	1	59.232	59.218	0.0955(2)
11	2	2	60.215	60.218	0.0982(2)
16	0	2	70.539	70.521	0.0895(2)

Table S4: Reflections used for the lattice parameter refinement of γ -Mo₄O₁₁ in the single-phase MoO_{2.750} sample (Cu-K_{α 1}, room temperature).

h	k	1	$2\theta / \circ (exp)$	2 heta / ° (theo)	FWHM
2	0	0	7.205	7.219	0.1878(5)
4	1	0	19.579	19.566	0.1051(3)
0	1	1	20.928	20.917	0.0964(2)
2	1	1	22.144	22.154	0.1156(1)
5	1	0	22.413	22.418	0.0995(1)
3	1	1	23.604	23.614	0.1119(1)
6	1	0	25.491	25.494	0.1145(1)
2	2	1	32.002	31.998	0.0987(1)
5	2	0	32.188	32.187	0.1064(2)
0	0	2	32.793	32.801	0.0974(1)
3	2	1	33.049	33.054	0.1036(1)
8	0	1	33.540	33.559	0.1114(1)
6	2	0	34.462	34.460	0.1110(3)
6	1	2	41.998	41.997	0.0967(2)
5	2	2	46.613	46.617	0.0893(2)
6	2	2	48.310	48.312	0.0895(1)
7	2	2	50.252	50.260	0.0914(2)
7	3	1	51.036	51.045	0.0983(2)
2	1	3	52.606	52.607	0.0866(2)
1	3	2	52.828	52.826	0.0941(1)
13	1	1	53.189	53.186	0.1166(3)
3	1	3	53.318	53.318	0.0940(2)
11	1	2	54.914	54.918	0.1017(2)
9	3	1	55.572	55.577	0.0949(1)
14	1	1	56.929	56.926	0.0878(1)
12	1	2	58.051	58.050	0.0901(1)
3	2	3	58.722	58.717	0.0864(1)
8	0	3	59.041	59.039	0.1001(1)
4	4	1	59.215	59.211	0.1014(1)
11	2	2	60.220	60.219	0.1000(1)
16	0	2	70.544	70.528	0.1050(2)

Table S5: Reflections used for the lattice parameter refinement of γ -Mo₄O₁₁ in the two-phase MoO_{2.760} sample (Cu-K_{α 1}, room temperature).

References

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 [2] NIST Chemistry webbook, SRD 69: "Molybdenum trioxide – Condensed phase thermochemistry data", https://webbook.nist.gov/cgi/cbook.cgi?ID=C1313275&Units=SI&Mask=2#Thermo-Condensed, accessed Mai 2019.