Molybdenum Oxides MoO$_x$: Spark-Plasma Synthesis and Thermoelectric Properties at Elevated Temperature

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ABSTRACT: Molybdenum oxides MoO$_x$ in the composition range 2 ≤ $x$ ≤ 3 were synthesized and compacted by the solid-state reaction of powdered $\alpha$-MoO$_3$ with Mo in the spark-plasma synthesis (SPS) process at temperatures up to 973 K. From six known compounds in the Mo–O system, Mo$_9$O$_{26}$ ($x = 2.889$), Mo$_{10}$O$_{47}$ ($x = 2.760$), and $\gamma$-Mo$_5$O$_{11}$ ($x = 2.750$) were synthesized as practically single-phase products despite their narrow composition ranges (≈0.1 at %) with a yield (0.5–1 g per synthesis) sufficient for thermoelectric property measurements on the polycrystalline bulk material from room temperature to 763 K. For Mo$_{18}$O$_{52}$, which appears to be an intrinsic narrow-gap semiconductor (activation energy ≈ 0.3 eV), exceptionally low thermal conductivity over the full temperature range (0.5–0.9 W m$^{-1}$ K$^{-1}$), high $p$-type Seebeck coefficient at room temperature (+140 μV K$^{-1}$), and a $p$$\to$$n$ transition at 440 K were found. The phases Mo$_{17}$O$_{47}$, $\gamma$-Mo$_5$O$_{11}$, and Mo$_7$O$_{27}$ show poor metallic conductivity. The highest power factor is achieved by Mo$_9$O$_{26}$ (30 W m$^{-1}$ K$^{-2}$ for 440 K ≤ $T$ ≤ 610 K). In $\gamma$-Mo$_5$O$_{11}$, a hitherto unknown reversible transition is found at 450 K from specific heat measurements.

INTRODUCTION

Being versatile structures with a wide range of physical and chemical properties, molybdenum oxides gain ongoing attention for the implementation into optical, electronic, catalytic, bio, and energy systems. Most interesting for thermoelectric (TE) application is the variation of the electric and thermal transport properties of MoO$_3$ (2 ≤ $x$ ≤ 3), which may be similarly tunable as those of WO$_3$ compounds. The transition metal oxide’s (TMO’s) adaptive structures are presumed to reduce the lattice thermal conductivity due to enhanced phonon scattering caused by structural and bonding inhomogeneities.

For $x = 3$, the stable modification is the layered wide-band $n$-type semiconductor $\alpha$-MoO$_3$ with an indirect band gap in the range 2.81–3.03 eV. Herein, edge-sharing [MoO$_6$] octahedra are condensed in zig-zag chains, which are interconnected via corners and form slabs with AB stacking in the [100] direction, which are bonded by van der Waals interactions (Figure 1a).

The removal of oxygen and accompanied partial reduction of Mo(VI) introduce crystallographic shear (CS) while the layer structure is maintained, resulting in triclinic Mo$_{18}$O$_{52}$ ($x = 2.889$, Figure 1b). Based on the crystal structure, Mo$_{18}$O$_{52}$ is presumed to be a pseudo-1D conductor but, except from a note by Kihlborg on its existing electrical conductivity, no evidence is known. For the same composition, a monoclinic high-temperature modification Mo$_{17}$O$_{47}$ (Figure 1d) is reported. This phase is structurally derived from the metastable ReO$_2$-type modification $\beta$-MoO$_3$ (Figure 1c) by introduction of CS as originally described by Magnéli, resulting in a representative of the homologous series Mo$_{14}$O$_{53}$ with $n = 9$. From calculations of the enthalpy of formation, the monoclinic modification should be thermodynamically stable.

Another member of the same series with $n = 8$ is the monoclinic Mo$_{17}$O$_{47}$ ($x = 2.875$), which differs from Mo$_9$O$_{26}$ in the distance between the CS planes (Figure 1e).

Further reduction ($x = 2.765$) yields the pentagonal column (PC) phase Mo$_{12}$O$_{47}$ (Figure 1f) wherein the PC structural motif (orange) exhibits an unusual terminating oxygen atom within the tunnels.

Another reported PC phase Mo$_{13}$O$_{47}$ ($x = 2.800$) is presumed to be a metastable intermediate during the formation of Mo$_7$O$_{27}$. It might not be thermodynamically stable in the binary Mo–O system but is stabilized by Mo substitution with V, Ti, Nb, or Ta, whereas W does not seem to influence the stability range.
Interconnected by \([\text{MoO}_4]\) tetrahedra, ReO\(_3\)-type slabs are oriented in alternating fashion in the orthorhombic \(\gamma\) (Figure 1g) and in parallel fashion in the monoclinic \(\eta\) modification (Figure 1h) of \(\text{MoO}_4\) \((x = 2.750)\). Both are known for their low-temperature transitions around 100 K, which are interpreted as charge density wave (CDW) formations in these pseudo-2D conductors.\(^{15,16}\) The structural \(\gamma \rightarrow \eta\) transition was reported to be sluggish in the solid state, and the transition temperature remains indefinite at around 873 K\(^{10}\) (Figure 2a).

![Crystal structures of molybdenum oxides MoO\(_2\) represented as assemblies of Mo–O polyhedra: (a) Layered \(\alpha\)-MoO\(_3\) (three unit cells shown) with AB stacking and zig-zag chains of edge-sharing \([\text{MoO}_6]\) octahedra (purple) along b direction; (b) triclinic \(\text{Mo}_2\text{O}_5\) \((x = 2.889, \text{low temperature})\) with crystallographic shear planes (blue), which contain \([\text{MoO}_4]\) tetrahedra (red); (c) metastable ReO\(_3\)-type \(\beta\)-MoO\(_3\); (d) MoO\(_{26}\) \((x = 2.889, \text{high temperature})\) with crystallographic shear planes (green); (e) \(\gamma\)-Mo\(_x\)O\(_{11}\) \((x = 2.750, \text{high temperature})\); (f) \(\eta\)-Mo\(_x\)O\(_{11}\) \((x = 2.750, \text{low temperature})\); (g) edge-sharing \([\text{MoO}_6]\) octahedra (cyan) along a direction. Corner-sharing octahedra are shown in gray. Black boxes mark unit cell marks.

**Figure 1.** Crystal structures of molybdenum oxides MoO\(_2\) represented as assemblies of Mo–O polyhedra: (a) Layered \(\alpha\)-MoO\(_3\) (three unit cells shown) with AB stacking and zig-zag chains of edge-sharing \([\text{MoO}_6]\) octahedra (purple) along b direction; (b) triclinic \(\text{Mo}_2\text{O}_5\) \((x = 2.889, \text{low temperature})\) with crystallographic shear planes (blue), which contain \([\text{MoO}_4]\) tetrahedra (red); (c) metastable ReO\(_3\)-type \(\beta\)-MoO\(_3\); (d) MoO\(_{26}\) \((x = 2.889, \text{high temperature})\) with crystallographic shear planes (green); (e) \(\gamma\)-Mo\(_x\)O\(_{11}\) \((x = 2.750, \text{high temperature})\); (f) \(\eta\)-Mo\(_x\)O\(_{11}\) \((x = 2.750, \text{low temperature})\); (g) edge-sharing \([\text{MoO}_6]\) octahedra (cyan) along a direction. Corner-sharing octahedra are shown in gray. Black boxes mark unit cell marks.

**EXPERIMENTAL SECTION**

**Starting Materials.** Mixtures of MoO\(_2\) for solid-state reduction in the composition range \(2 < x < 3\) were prepared according to the general redox reaction

\[
\frac{x}{3}\text{Mo}^{\alpha+}\text{O}^{-2} + (1 - \frac{x}{3})\text{Mo}^{0} \rightarrow \text{Mo}^{\text{12+}}\text{O}^{-2}
\]

from \(\alpha\)-MoO\(_3\) (ChemPur, 99.9%) and Mo (ChemPur, 99.95%) in powder form by mixing them for 15 min in an inert atmosphere. Samples of MoO\(_2\), and MoO\(_2\) (Alfa Aesar, 99.9%) were directly compacted from the starting material. Prior to mixing, powder X-ray diffraction (PXRD) showed all three starting materials to be free from crystalline contaminations. Optical emission spectrometry with inductively coupled plasma (ICP-OES) expectably yields minor amounts of nitrogen in both oxides, and common impurities in all starting materials are Na \((<0.223 \text{ wt \%})\), Ta \((<0.1 \text{ wt \%})\), C \((≈0.1 \text{ wt \%})\), and W \((<0.013 \text{ wt \%})\) (for details, see Table S1, Supporting Information).

**Spark-Plasma Synthesis.** The spark plasma synthesis (SPS) was used to perform the redox reaction (eq 1) in the MoO\(_x\) + Mo powder mixtures, as well as for compaction of the polycrystalline products into solid pellets for physical property measurements (Figure 2b). Details on the SPS process were published elsewhere.\(^{27}\) Graphite dies with diameters of 10 mm and a graphite lining were filled with \(\sim 1.5 \text{ g}\) of starting mixture in an inert atmosphere and processed with an SPS-515 ET Sinter Lab apparatus (Fuji Electronic Industrial Co. Ltd., Tsurugashima, Japan).\(^{27}\) Fast linear heating \((50 \text{ K min}^{-1})\) was performed in vacuum \((<0.4 \text{ mbar})\) under uniaxial pressure \((80 \text{ MPa})\), followed by a dwell time \(T_{\text{dwell}}\) at the maximum temperature \(T_{\text{max}}\) and free cooling (Figure 2c). The maximum temperature for all syntheses was constrained to \(T_{\text{max}} \geq 973 \text{ K}\) to avoid deviation from the nominal compositions (see section Synthesis of MoO\(_x\) Compounds). After every experiment, the sample pellet was polished and crushed to

![Phase regions in the \(x-T\) diagram of the binary system Mo–O (redrawn from ref 10). (b) Evolution of the sample morphology from the starting powder to a bar for physical property measurement. (c) Principled setup of the spark-plasma synthesis.

**Figure 2.** (a) Phase regions in the \(x-T\) diagram of the binary system Mo–O (redrawn from ref 10). (b) Evolution of the sample morphology from the starting powder to a bar for physical property measurement. (c) Principled setup of the spark-plasma synthesis.
Table 1. SPS Regimes Yielding Single-Phase Material and Measured Densities of the Compacted Samples

| x   | phase       | process | n | T_max (K) | t_final (min) | \( \rho_{\text{meas}} \) (g cm\(^{-3}\)) | \( \rho_{\text{theor}} \) (g cm\(^{-3}\)) | \( \rho_{\text{rel}} \) (%) |
|-----|-------------|---------|---|-----------|---------------|------------------------------------------|------------------------------------------|------------------|
| 2   | MoO\(_3\)   | C       | 1 | 973       | 10            | 6.46                                     | 6.20                                      | 96.0             |
| 2.750 | \( \gamma \)-MoO\(_3\) | S       | 5 | 973       | 60            | 4.12                                     | 4.13                                      | >100'            |
| 2.765 | Mo\(_3\)O\(_7\) | C       | 1 | 973       | 5             | 4.72                                     | 4.65                                      | 98.4             |
| 2.889 | Mo\(_{10}\)O\(_{31}\) | C       | 1 | 973       | 10            | 4.78                                     | 4.76                                      | 99.6             |
| 3   | \( \alpha \)-MoO\(_4\) | C       | 1 | 923       | 120           | 4.71                                     | 4.62                                      | 98.1             |

\( n \) number of cycles; \( S \) synthesis; \( C \) compaction. \( \rho_{\text{rel}} = (\rho_{\text{theor}}/\rho_{\text{meas}}) \times 100\% \) (\( \rho_{\text{theor}} \): Archimedean density; \( \rho_{\text{meas}} \): theoretical density from X-ray diffraction results (Table 2)). \( \rho_{\text{rel}} \) overestimation due to residues of secondary phase MoO\(_4\) (Figure 3).

The electronic contribution \( \kappa_a \) to the total thermal conductivity and consequently the lattice contribution \( \kappa_l \) were calculated with the Wiedemann–Franz (WF) equation

\[
\kappa_l = \kappa_{\text{tot}} - \kappa_a = \kappa_{\text{tot}} - L \cdot \sigma \cdot T
\]

For the calculation, \( \kappa_{\text{tot}} \) values were fitted with fourth order polynomials. Since for semiconductors the Lorenz number \( L \) can strongly deviate from the table value, the approximation

\[
L(T) = L_0 + \frac{\alpha(T)}{T}
\]

was used, which is based on the single parabolic band model of acoustic phonon scattering.\(^1\)\(^3\) Comparative results obtained with constant \( L = 2.4453 \times 10^{-8} \) \( \text{W m}^{-1} \text{K}^{-2} \) show negligible deviations, and all trends remain the same.

For a comparison with other TE materials, the power factor was calculated according to

\[
P_F = \sigma \cdot \alpha^2
\]

with a maximum error for \( \alpha \) of +1%/-13.2% earlier established for the used setup.\(^1\)^\(^4\)

Measurements of \( \sigma(T) \) and \( \alpha(T) \) were performed for at least two heating and cooling cycles to verify reproducibility. Since \( \alpha(T) \) of MoO\(_{2.750}\) showed some unsystematic aberration during the first heating cycle from the following cycles (Figure S7, Supporting Information), we present here the data of all second heating cycles for consistency.

**RESULTS AND DISCUSSION**

**Synthesis of MoO\(_x\) Compounds.** From six MoO\(_x\) phases known in the composition range 2 \( < x < 3 \), \( \gamma \)-MoO\(_{11}\) (\( x = 2.750\)), Mo\(_{17}\)O\(_{47}\) (\( x = 2.765\)), and Mo\(_{18}\)O\(_{47}\) (\( x = 2.750\)) were synthesized via SPS as single-phase samples according to PXRD (Figure 3).

The phase MoO\(_{14}\) was not obtained via SPS because by now, this phase has been prepared only with Mo substitution by V, Tl, Nb, or Ta and might not be stable in the binary system.\(^1\)^\(^3\)^\(^4\) Obtained single-phase specimens confirm the SPS technique to be suitable for the preparation of MoO\(_x\) phases despite small composition differences between them (\( \geq 0.1 \) at % oxygen, see also section Phase Homogeneity Ranges and Composition Control). Reduction due to the usage of graphite-lined dies at high temperatures (\( T \leq 973 \) K) in an evacuated chamber (\( < 0.4 \) mbar) is visible at the sample surface in graphite contact but does not proceed into the bulk within the applied dwell times (\( \leq 1 \) h per cycle). For maintaining the target stoichiometry during multiple-step synthesis, polishing of the compacted samples is inevitable. Thus, the product yield with respect to the starting mass of the educt mixture is reduced to a minimum of 25% in the case of Mo\(_{47}\)O\(_{97}\), whose
low formation temperature (<550 K) necessitates seven synthesis cycles.

As-received α-MoO₃ powder was compacted directly in one-step SPS treatment. Unlike in WO₃, no reduction of the sample bulk to lower oxides is observed according to PXRD due to the much lower applied temperatures: an increase of the sample bulk to lower oxides is observed according to PXRD (Figure 4 and Figure S1/S2, Supporting Information). The suppressed decomposition during SPS treatment. Unlike in WO₃, a considerably lower decomposition onset at 932 K is found (Figure 4 and Figure S1/S2, Supporting Information). The suppressed decomposition during SPS may be caused by the formation of less volatile species on the α-MoO₃–graphite interface within the die. TG of MoO₃ samples (2 < x ≤ 3) in vacuum shows the decomposition temperature of MoO₂₋x (Mo₁₉O₄₅, Mo₂₋xO₇₆₅ (Mo₁₀₂O₁₇), and MoO₂₋x.7₅₆ (γ-Mo₄O₁₁)) increased by ~30 K with respect to that of α-MoO₃. Also, the lower quality of the SPS vacuum (<0.4 mbar) must cause a higher oxygen vapor pressure above the oxide surface and may be a further explanation for the increased decomposition temperature compared with that in TG vacuum (4 × 10⁻³ mbar). It is worth mentioning that the grain size of the as-received powder changed by three orders of magnitude within only 120 min of SPS (Figure S3, Supporting Information).

Samples with 2 < x < 3 required multiple SPS cycles (n in Table 1) with intermediate crushing to increase concentration gradients between grains, homogenize grain sizes and thus reach phase equilibrium faster. ICP-OES measurements on MoO₂₋₅₈₅ powder after three successive SPS steps reveal no change of the contamination concentrations due to the polishing and crushing (Table S2, Supporting Information).

In all synthesis experiments, according to eq 1, the triclinic Mo₁₉O₅₂ (x = 2.889) is observed after the initial heating cycle, although from calculations of the enthalpy of formation, the monoclinic Mo₉O₄₆ is predicted to be the more stable modification.12 However, due to the constrained T max = 973 K, the suggested formation temperature of MoO₂₋₅₈₅ (1033–1055 K) is never reached in our experiments. Practically, single-phase material MoO₂₋₅₈₅ obtained by [3 × 973 K/1 h] synthesis contains traces of γ-Mo₆O₁₁ (Figure 3, blue; see also Figure S8, Supporting Information, for an estimation of the secondary phase content). Refinement shows the unit cell parameters of the SPS-synthesized Mo₁₉O₅₂ close to those previously published (Table 2).

In contrast, all MoO₂₋₅₇₅ specimens that were prepared in the suggested stability range of MoO₂₋₅₃ (x = 2.875) contained Mo₉O₄₂ and γ-Mo₆O₁₁ only. Thus, the high-temperature phase Mo₉O₂₃ is either not formed during SPS or decomposes during relatively slow SPS cooling.

The synthesis of MoO₂₋₅₇₅ with [7 × 823 K/2 h] yielded straightforward Mo₁₂O₄₇ (x = 2.765, Figure 3, orange) with unit cell parameters in perfect agreement with available literature data (Table 2). The low formation temperature <833 K and the accompanied diminished diffusion require an overall dwell time of as long as 14 h. Preparation of MoO₂₋₅₇₅ at 973 K, which is above the proposed upper formation limit of Mo₁₂O₄₇, resulted in γ-Mo₆O₁₁ and Mo₉O₄₂ (see section Phase Homogeneity Ranges and Composition Control), that is, the cooling rate in SPS is sufficient to suppress Mo₁₂O₄₇ formation.

Preparation of MoO₂₋₅₇₅ samples with [5 × 973 K/1 h] yielded the high-temperature phase γ-Mo₆O₁₁ with traces of MoO₂₋₅₇₅ (Figure 3, red). The low-temperature η-modification, which should exist at temperatures <873 K, was never observed, as discussed more detailed in the section Phase Formation.

Abundant crystallographic data is available for γ-Mo₆O₁₁ (Table 2). The obtained lattice parameters b and c (space group: Pna₂₁) agree well with both, single-crystal (sc) and powder (p) data. The a parameter is significantly shorter in the polycrystalline samples of our work (24.4760(10) Å) and by Fun et al. (24.4756 Å) in comparison to single-crystals by Kihlborg et al. (≈24.49 Å) and a single crystal, which we synthesized (24.501(2) Å, details will be published elsewhere). Since single-crystal data is generally not standardized, it
Table 2. Lattice Parameters of the SPS-Prepared Single-Phase Oxides MoO_3 (Cu Kα_1 Radiation, λ = 1.54056 Å, LaB_6 Standard) in Comparison With Literature Values

| n   | x phase     | space group | a [Å] | b [Å] | c [Å] | α [°] | β [°] | γ [°] | V [Å³] | preparation | reference |
|-----|-------------|-------------|-------|-------|-------|-------|-------|-------|--------|-------------|-----------|
| 2   | MoO_3       | Pnma        | 5.61(3) | 4.85(3) | 5.62(3) | 90    | 90    | 90    | 120.9(4) | 1821        | this work |
| 1.750 | γ-MoO_11  | Pnma        | 5.67(3) | 4.87(3) | 5.62(3) | 90    | 90    | 90    | 120.9(4) | 1821        | this work |
| 2.750 | η-MoO_11  | Pna_2       | 6.70(4) | 6.59(3) | 4.55(2) | 90    | 90    | 90    | 120.9(4) | 1821        | this work |
| 2.750 | η-MoO_11  | Pnma        | 6.75(4) | 6.56(3) | 4.55(2) | 90    | 90    | 90    | 120.9(4) | 1821        | this work |
| 2.750 | η-MoO_11  | Pnma        | 6.76(4) | 6.57(3) | 4.55(2) | 90    | 90    | 90    | 120.9(4) | 1821        | this work |
| 2.765 | MoO_2      | Pnma        | 6.78(4) | 6.58(3) | 4.56(2) | 90    | 90    | 90    | 120.9(4) | 1821        | this work |
| 2.889 | MoO_2      | Pnma        | 6.80(4) | 6.59(3) | 4.57(2) | 90    | 90    | 90    | 120.9(4) | 1821        | this work |
| 3   | α-MoO_3    | Pnma        | 6.83(4) | 6.60(3) | 4.58(2) | 90    | 90    | 90    | 120.9(4) | 1821        | this work |

"Most recent literature data is quoted for MoO_3 and α-MoO_3. Diffraction data was obtained from single-crystals (sc) or powder (p) in the as-received state (AR) or after preparation via SPS, solid-state reaction of MoO_3 and Mo or MoO_2 in vacuo (SSR), chemical vapor transport (CVT), electrocrystallization (EC), and sublimation growth (SG). Powder from SPS was annealed (-a) for 1 week at 573 K. Originally published setting changed for better comparison of the axis lengths. Secondary phase MoO_2.5. I_2 was used as a transport agent. TeCl_4 was used as a transport agent. ZnI_2 was used as a transport agent. TeCl_4 was used as a transport agent.

remains questionable if this is a real effect. Mechanical stress implied during grinding can be ruled out by subsequent annealing for 1 week at 573 K in an argon atmosphere (200 mbar). The cell parameters of the annealed γ-MoO_11 show a subtle decrease of c while a and b remain unchanged (Table 2, SPS-p-a). Minor amounts of MoO_3 and MoO_2.5 observed in the annealed sample indicate a decomposition and confirm the instability of both MoO_11 polymorphs below 888 K as analyzed by Kihlborg but also suggest that MoO_11 is stable below a proposed lower limit of 873 K (Figure 2a).10

Phase Formation. The stepwise SPS process allows a time-dependent observation of the phase formation by PXRD. This is shown for two MoO_2.750 mixtures prepared in the previously suggested formation ranges of γ-MoO_11 (973 K, Figure 5a) and of η-MoO_11 (873 K, Figure 6a). The given dwell times of t_{well} = (1, 2, 3, 4, and 5 h) and (1, 2, 3, 4, 6, and 11 h) refer to the sums of isoeithermic heating durations in SPS, excluding heating-up and cooling-down. From a comparison of the change of relative reflection intensities, one can qualitatively estimate the phase volume fractions in the samples (Figures 5b and 6b).

At 973 K, after 1 h, all stable oxides except MoO_2.5 appear as intermediates in the diffusion zone between α-MoO_3 (purple) and MoO_3, namely, γ-MoO_11 (red), MoO_2.5 (blue), and MoO_2 (cyan) (Figure 5). The latter vanish with longer dwell time in favor of γ-MoO_11, which is the main phase after 5 h with only traces of MoO_2 as expected10 (Figure 2a).

At 873 K, the phase formation looks essentially identical after 1 h (α-MoO_3, MoO_2, γ-MoO_11, MoO_2.5) but even after 3 h still α-MoO_3 remains due to limited diffusion (Figure 6). The expected η-MoO_11 formation is not observed. Instead, although the synthesis temperature exceeds its suggested upper formation temperature (863 K), TeCl_4 is formed (Figure 2a, orange). After 6 h, γ-MoO_11 and MoO_2.5 are further reduced, and only MoO_2 and MoO_2.5 are found. Since no
change is observed even after a dwell time as long as 11 h, we assume this state to be the equilibrium under the applied SPS conditions. Heating the obtained sample again to 973 K yields the formation of \( \gamma\)-Mo\(_{17}\)O\(_{47} \), according to

\[
\text{MoO}_2 + 3 \text{Mo}_{17}\text{O}_{47} \xrightarrow{\text{973 K}} 13 \gamma\text{Mo}_{4}\text{O}_{11}
\]

within only 5 min (not shown).

The synthesis of the \( \eta \) polymorph is usually performed directly at temperatures below the \( \gamma \) stability range, which excludes the possible necessity of supercooling \( \gamma \) to reach a \( \gamma \to \eta \) transition.\(^{10,13,22,25,26,39} \) Thus, under SPS conditions, the equilibrium may be influenced by the applied electric field, which introduces a driving force additional to the concentration gradient and therefore affects the diffusion paths of mobile charged species, that is, Mo cations and O anions. For comparison, reports on SPS processed hyperstoichiometric UO\(_{2+\delta} \) show the uranium oxidation state to gradually increase with the anode (+) due to directional migration of oxygen defects.\(^{40} \) Based on this, an increase of the Mo oxidation state is expected at the anode (+) leading to the formation of \( \text{Mo}_{4}\text{O}_{11} \) (\( x = 2.765 \)), whereas \( \text{MoO}_2 \) should be formed at the cathode (–). This was not observed on a macroscopic scale, but on a microscopic scale, within single grains, a decomposition \( \text{MoO}_{11} \xrightarrow{11 \text{h}} \text{MoO}_2 + \text{Mo}_{17}\text{O}_{47} \) driven by the electric field cannot be excluded.

More extensive studies on the still not understood \( \gamma \to \eta \) transition kinetics during both SPS and classical solid-state reaction are ongoing.

**Phase Homogeneity Ranges and Composition Control.** The complex structures in the Mo\(_x\)O\(_{2x+\delta} \) compounds form within a narrow composition range (2 \( \leq x \leq 3 \)) with composition differences as low as \( \Delta x \approx 0.015 \) (\( \pm 0.1 \text{ at } \% \) oxygen) between the \( \text{Mo}_{11}\text{O}_{11} \) polymorphs (\( x = 2.750 \)) and \( \text{Mo}_{17}\text{O}_{47} \) (\( x = 2.765 \)). Thus, it is reasonable to ask if the small stoichiometric differences of the starting mixtures can be maintained during the SPS process.

To study this issue, two mixtures with \( x = \{2.740, 2.760\} \) were SPS-treated additionally to the aforementioned \( x = 2.750 \) (compare Figure 3, red) with identical the parameters [5 \( \times \) 973 K/1 h]. The resulting PXRD patterns differ in the presence of secondary phase reflections next to primary \( \gamma\)-Mo\(_{17}\)O\(_{47} \) (Figure 7a): for Mo\(_{2.740}\), additional Mo\(_2\)O\(_3\) reflections occur in accordance with ref \( ^{10} \), and for Mo\(_{2.760}\), there is found additionally Mo\(_{18}\)O\(_{52}\) (\( x = 2.875 \)) but not Mo\(_{2}\)O\(_3\) (\( x = 2.765 \)). Thus, the uncontrolled cooling appears to suppress the formation of \( \eta\)-Mo\(_{17}\)O\(_{47} \) and \( \text{Mo}_{18}\text{O}_{52} \), which are expected to be in equilibrium below 823 K. Both results show the synthesis routine to be capable of composition adjustments by at least \( \Delta x \approx 0.010 \) (\( \pm 0.07 \text{ at } \% \) oxygen).

A schematic depiction illustrates why the unit cell parameters of \( \gamma\)-Mo\(_{17}\)O\(_{47} \) in all three samples may yield information on the homogeneity range of the \( \gamma \)-phase (Figure 7b): for \( x = 2.740 \) (A), 2.750 (B), and 2.760 (C), there would be expected unit cell parameters [5 \( \times \) 973 K/1 h] (Cu K\( \alpha \) radiation, \( \lambda = \text{1.54065 Å} \)). Relections from secondary phases next to \( \gamma\)-Mo\(_{17}\)O\(_{47} \) are marked (plus sign, Mo\(_2\)O\(_3\); circle solid, \( \text{Mo}_{18}\text{O}_{52} \)). Calculated reflection positions are shown as ticks at the bottom of the panel. (b) Exaggerated schematic representation of a possible \( \gamma\)-Mo\(_{17}\)O\(_{47} \) homogeneity range.
Table 3. Lattice parameters of γ-MoO₃ (Space Group: Pna₂₁) Found in MoO₃ Samples with x = {2.740, 2.750, and 2.760} after SPS Preparation

| x   | a [Å] | b [Å] | c [Å] | V [Å³] |
|-----|-------|-------|-------|--------|
| 2.740 | 24.4732(9) | 6.7513(3) | 5.4563(2) | 901.52(7) |
| 2.750 | 24.4760(10) | 6.7503(4) | 5.4564(3) | 901.51(9) |
| 2.760 | 24.4720(10) | 6.7511(4) | 5.4561(3) | 901.42(9) |

*Cu Kα1 radiation, λ = 1.54056 Å, LaB₆, standard, 31 identical non-overlapping reflections 2θ < 71° used for each sample. *Second phase MoO₂. *Second phase Mo₉O₃₂.

Figure 8. Electrical conductivity σ of MoO₃ samples in dependence of temperature. Insulating MoO₃ could not be measured.

From x = 2.889 to 2.750, a progressive increase of σ(T) with decreasing oxygen concentration for all temperatures suggests a strong influence of the formed crystal structures (Figure 9a). With proceeding reduction, the weak interlayer van der Waals interactions in α-MoO₃ and MoₙO₃₄ collapse in favor of strong ionic or (polar) covalent interactions. Thus, evolving 3D interactions of molybdenum orbitals give rise to the formation of Mo 4d bands close to the Fermi level as demonstrated for Mo₉O₂₆ *γ-Mo₉O₁₁, and MoO₂ by DFT calculations.¹²

The electrical conductivity (σ = neµ) of MoO₂₈₈₈ shows the temperature dependence of an intrinsic semiconductor (n, carrier concentration; e, elementary charge; µ, carrier mobility). Assuming that µ is temperature independent, the activation energy Eₐ can be extracted from Arrhenius plots due to the proportionality σ(T) ∝ exp[−Eₑ/2k_B𝑇] (k_B, Boltzmann constant) as exemplary shown in Figure 8 (inset). From two heating cycles of two MoO₂₈₈₉ samples each, this yields Eₑ = 0.30(3) eV and indicates Mo₉O₁₂ to be a narrow-gap semiconductor. Since no band structure and theoretic band gap Eₑ are known, Eₑ is not necessarily associated with Eₑ but can also result from an energy difference between impurity states and the valence band. A subtle hysteresis of σ(T) between heating and cooling may be a real effect but is not significant with respect to the error of our measurement (Figure S5, Supporting Information).

Similar, for the bad-metallic MoO₂₇₆ (Mo₇O₂₇), there is found an insignificantly decreased σ(T) below 500 K in the first heating cycle (Figure S6, Supporting Information).

At room temperature, for MoO₂₇₅₀ the electrical conductivity reported for single crystals is strongly anisotropic and varies from 0.23 × 10⁵ S m⁻¹ parallel to the bc plane to 5–13 × 10⁵ S m⁻¹ perpendicular to it.¹⁶,²⁵,⁴¹,⁴² A value of σ = 3.12 × 10⁵ S m⁻¹ measured for our polycrystalline samples ranges in between, which is plausible because of approximately isotropic distribution of crystallite directions and increased scattering at grain boundaries.

The electrical conductivity of MoO₃ at room temperature is close to a value of 5 × 10⁵ S m⁻¹ reported for 298 K.¹⁹ The large variation of published room-temperature conductivities σ = 3.35 × 10⁵ to 11 × 10⁵ S m⁻¹ may be traced back to a neglect of crystallographic directions in these measurements: MoO₃ is expected to be highly anisotropic due to alternating short (2.51 Å) and long (3.11 Å) Mo–Mo distances along the a axis.²⁵ In our polycrystalline samples, an average conductivity is plausible, assuming nonpreferred orientation of the grains.

Figure 9. (a) Electrical conductivity σ and (b) lattice thermal conductivity κₐ of MoO₃ samples in dependence of the O/Mo ratio x. *κₐ was estimated from the WF law.

Over the whole temperature range, the total thermal conductivities κₐ of the phases MoO₂ (15 to 25 W m⁻¹ K⁻¹), γ-Mo₉O₁₁ (x = 2.750, 5 to 7 W m⁻¹ K⁻¹), and Mo₉O₂₄ (x = 2.765, 3 W m⁻¹ K⁻¹) exceed the exceptionally low value of semiconducting Mo₉O₃₂ (x = 2.889, κₐ ≈ κₐ ≈ 0.5–0.9 W m⁻¹ K⁻¹) due to the larger electronic contribution κₑ (eq 4, Figure 10). In the studied temperature range, polycrystalline Mo₉O₃₂ appears to be the only binary compound among known low-κ oxides including, for example, the ternary phases La₂Mo₉O₂₃ (0.7–8 W m⁻¹ K⁻¹), Bi₅Te₃O₁₂ (0.9–1.0 W m⁻¹ K⁻¹), Sr₅Nb₂O₉ (~1.1 W m⁻¹ K⁻¹), the quaternary phases Gd₃Ca₄(SiO₄)₂O (0.9–1.0 W m⁻¹ K⁻¹) or BaNd₃Te₃O₁₀ (0.9–1.3 W m⁻¹ K⁻¹),¹³,⁴⁴ pyrochlore KTaWO₆ (~0.6 W m⁻¹ K⁻¹),¹⁴ and many further thermal barrier coating materials.⁴⁶ A relative density of 99.6% rules out porosity as a major contribution to scattering effects (Table 1). A more
Almost temperature-independent $\kappa_{\text{tot}}$ is observed in Mo$_x$O$_{47}$ ($x = 2.765$). The highest $\kappa_{\text{lat}}$ is found for MoO$_2$ (9–20 Wm$^{-1}$ K$^{-1}$), which is the structure with most condensed [MoO$_4$] octahedra (Figure 11). The general trend of increasing $\kappa_{\text{lat}}$ with decreasing O/Mo ratio $x$ is attributed to the proceeding condensation of [MoO$_6$] octahedra (Figure 9b). Temperature dependence increases for $x \leq 2.750$, but with respect to the approximative character of the calculation from the WF law, these $\kappa_{\text{lat}}$ values should not be overinterpreted.

All MoO$_2$ samples with $2 \leq x \leq 2.765$ exhibit a negative Seebeck coefficient $\alpha$ according to the expected $n$-type conductivity (Figure 11). Seebeck coefficients of MoO$_2$ and Mo$_4$O$_{11}$ are low due to the presumed high charge carrier concentration in these bad-metal-like materials. For MoO$_2$, the values of $\alpha$ range from $-6 \mu$V K$^{-1}$ to a local minimum of $-9 \mu$V K$^{-1}$ at 540 K. Cycling of three independent Mo$_{17}$O$_{47}$ ($x = 2.750$) samples yields values of $-12$ to $-21 \mu$V K$^{-1}$ and a linear temperature dependency $\alpha(T) \propto -0.017(1) \mu$V K$^{-2}$T (exemplary depicted in the inset of Figure 11), which is typical for degenerate semiconductors. Minor unsystematic deviation from this linearity occurred in the first heating cycle (Figure S7, Supporting Information). A calculation of the carrier mobility was not possible yet due to a not yet understood oscillatory behavior of the Hall voltage with temperature observed in Hall-effect measurements. With $-44$ to $-70 \mu$V K$^{-1}$, Mo$_{17}$O$_{47}$ ($x = 2.765$) exhibits the highest negative $\alpha$ values with no maximum in the measured temperature range.

In contrast, a positive and exceptionally high Seebeck coefficient in the range of $+140 \mu$V K$^{-1}$ is found for Mo$_{18}$O$_{52}$ ($x = 2.889$) at room temperature. It decreases toward 440 K where a $p$–$n$ transition occurs, followed by a depressive increase to $-38 \mu$V K$^{-1}$ at 763 K.

The power factors $PF = \sigma \alpha^2$ of MoO$_2$, Mo$_{18}$O$_{52}$ ($x = 2.750$), and Mo$_{18}$O$_{52}$ ($x = 2.889$) are small ($<8 \times 10^{-5}$ W m$^{-1}$ K$^{-2}$, Figure 12) over the whole temperature range due to the low Seebeck coefficients of the first two and the low electrical conductivity of the latter. Highest $PF$ of $30 \times 10^{-3}$ W m$^{-1}$ K$^{-2}$ results for Mo$_{17}$O$_{47}$ ($x = 2.765$) in a range of 440 K $\leq T \leq 610$
The absence of electrical conductivity while conserving the exceptionally low thermal conductivity due to additional introduction of point defects and bonding inhomogeneity: species, which are electron poorer than Mo, should increase the concentration of defect electrons in the p-type conduction range (<450 K), and electron-richer species should increase the performance in the n-type range (>450 K). Similarly, the electric properties of n-type Mo18O52 may be tuned. The bad-metal phases MoO2 and γ-MoO11 are not suitable for thermoelectrics.

**CONCLUSIONS**

Spark-plasma synthesis (SPS) is shown to be a suitable method for single-phase oxide materials with well-defined composition in the system Mo–O. The reducing conditions, which MoO2 samples are exposed to during the high-temperature preparation (T ≤ 973 K) in graphite-lined SPS dies, do not affect the phase formation in the bulk, allowing synthesis of single-phase materials by means of powder X-ray diffraction (PXRD) with composition differences as low as Δα = 0.01 (±0.07 at% of oxygen).

The formation of Mo18O52 (x = 2.889), Mo52O47 (x = 2.760), and γ-MoO11 (x = 2.750) is observed straightforward after successive identical synthesis steps. Due to decomposition of α-MoO3 at elevated temperatures, SPS is constrained to T\text{max} ≈ 973 K to control the stoichiometry. This prevents the formation of high-temperature phases like Mo9O28 (x = 2.760), and γ-MoO11 (x = 2.750), respectively, and ZT = 0.9 \times 10^{-3} for MoO2 at 690 K.

The resulting figure-of-merit ZT is low for all MoO2 phases (2 ≤ x < 3) with the following maxima: ZT = 5 \times 10^{-3}, 39 \times 10^{-3}, and 14 \times 10^{-3} for Mo18O52, Mo17O47, and γ-MoO11, respectively, all at a maximum temperature of 760 K; MoO2 shows a local maximum of ZT = 0.9 \times 10^{-3} at 690 K.

No phase homogeneity range is found for γ-MoO11 from X-ray diffraction data of MoO2.175±0.001. A reversible endothermal effect at 450 K found from thermal conductivity and specific heat measurements is presumed to be a hitherto unknown phase transition.

Figure 12. Power factor (PF) of MoO2 samples in dependence of temperature. Insulating MoO3 could not be measured. The uncertainties of the Seebeck coefficient α and thus of PF = f(α) are asymmetric (see ref 32).

K. Highest ZT values are found to be 5 \times 10^{-3}, 39 \times 10^{-3}, and 14 \times 10^{-3} for Mo18O52, Mo17O47, and γ-MoO11, respectively, all at a maximum temperature of 760 K; MoO2 shows a local maximum of ZT = 0.9 \times 10^{-3} at 690 K.

Figure S1: decomposition of α-MoO3 starting material during SPS; Figure S2: decomposition onsets of α-MoO3 as found from thermogravimetry and from the chamber pressure during SPS; Figure S3: light microscopic images of α-MoO3 after SPS compaction; Figure S4: specific heat of MoO2 samples from DSC measurements; Figure S5: cycling of electrical conductivity measurements on MoO2; Figure S6: cycling of electrical conductivity measurements on MoO2.750; Figure S7: cycling of Seebeck coefficient measurements on MoO2; Figure S8: estimation of the secondary phase content in practically single-phase MoO2.889 from the X-ray diffraction pattern; Table S1: chemical compositions of the starting materials; Table S2: chemical composition of a MoO2.889 sample with proceeding SPS cycling; Table S3–S5: reflections used for the lattice parameter refinement of γ-MoO11 in MoO2.750±0.010 samples (PDF).

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.9b05075.

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No phase homogeneity range is found for γ-MoO11 from X-ray diffraction data of MoO2.175±0.001. A reversible endothermal effect at 450 K found from thermal conductivity and specific heat measurements is presumed to be a hitherto unknown phase transition.

Electrical and thermal transport properties have been determined for bulk polycrystalline samples of MoO2, γ-MoO11, Mo17O47, and Mo18O52 between room temperature and 763 K. From the determined activation energy for electrical conduction of E_g = 0.30(3) eV, the MoO2.175 phase is assumed to be a narrow-gap p-type semiconductor below 440 K, which shows exceptionally low thermal conductivity of k_{tot} ≈ k_{lat} = 0.5–0.9 Wm^{-1} K^{-1} in the whole temperature range. Also, a large positive Seebeck coefficient of +140 μV K^{-1} is observed at room temperature, which however is relativized due to a presumably low charge carrier concentration. For heating above 440 K, a p–n transition occurs and the Seebeck coefficient is distinctly decreased (−38 μV K^{-1} at 763 K).

An encouraging Seebeck coefficient (−70 μV K^{-1} at 763 K) and power factor (≈30 Wm^{-1} K^{-2}) at 440 K ≤ T ≤ 610 K) are found for n-type Mo17O47.

The resulting figure-of-merit ZT is low for all MoO2 phases (2 ≤ x < 3) with the following maxima: ZT = 5 \times 10^{-3}, 39 \times 10^{-3}, and 14 \times 10^{-3} at a maximum temperature of 763 K for Mo18O52 (x = 2.889), Mo52O47 (x = 2.760), and γ-MoO11 (x = 2.750), respectively, and ZT = 0.9 \times 10^{-3} for MoO2 at 690 K.

In the case of Mo18O52, substitution of heavy transition metals on the cationic Mo site might tailor the unfavorable low electrical conductivity while conserving the exceptionally low thermal conductivity due to additional introduction of point defects and bonding inhomogeneity: species, which are electron poorer than Mo, should increase the concentration of defect electrons in the p-type conduction range (<450 K), and electron-richer species should increase the performance in the n-type range (>450 K). Similarly, the electric properties of n-type Mo18O52 may be tuned. The bad-metal phases MoO2 and γ-MoO11 are not suitable for thermoelectrics.
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**Author Contributions**

Synthesis and physical property measurements including data analysis were performed by F.K. M.S. performed specific heat measurements including the data analysis. All authors contributed equally to the data interpretation and discussion. The manuscript was written by F.K. and revised by Y.G., I.V., and M.S. All authors have given approval to the final version of the manuscript.

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**ABBREVIATIONS**

CDW, charge density wave; CS, crystallographic shear; CVT, chemical vapor transport; EC, electrocrystallization; FF, power factor; RT, room temperature; SG, sublimation growth; SPS, spark-plasma Synthesis; SSR, solid-state reaction; TE, thermoelectric; WF, Wiedemann–Franz

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