Supplementary information

Theoretical densities of the single phase materials

Theoretical densities of the single phase materials ρ_{theo} are calculated to

$$\delta_{theo} = [\, Z\, M\,]\, /\, [\, A\, V\,] \tag{S1}$$

(A – Avogadro's constant, M – molar mass, V – unit cell volume, Z – formula units per unit cell). For the compositions $x = \{2, 2.72, 2.90, 3\}$ the unit cell volume V is gained from the lattice parameter refinements in this work, otherwise from literature data (Table 1, main text).

For $x = 2.90$ we find a discrepancy: The density $\rho_{theo} = 7.16$ g cm^{-3} is based on *Magnéli*'s model with perfectly undistorted [WO$_6$] octahedra between the CS planes [35]. This represents the least dense packing of the octahedra. Thus, every real structure wherein tilting and distortion occur must yield a density $\rho_{theo} > 7.16$ g cm^{-3} as observed in previous experimental work [11, 21]. However, we gain a ρ_{theo} from the PXRD data which is considerably lower than predicted by *Magnéli*'s model. Also none of the published values clearly exceeds the density of the room temperature phases γ-WO$_3$ (7.19 g cm^{-3}) and δ-WO$_3$ (7.29 g cm^{-3}) although the CS planes in WO$_{2.90}$ are supposed to result in a distinct compression of the WO$_3$ parent structure [42].

Table S1. Mass density ρ_{theo} of tungsten oxides calculated from their molar mass M and unit cell volume V (see **Table 1** in main text). The relative mass density ρ_{rel} is obtained by measuring the density ρ_m.

X	M g mol^{-1}	Phase	Z	ρ_{theo} g cm^{-3}	ρ_m g cm^{-3}	ρ_{rel} %	Ref.
2	215.84	WO$_2$	4	10.77	-	-	[30]
			4	10.78	9.64	89.42	this work
2.72	4093.12	W$_{18}$O$_{49}$	1	7.69	n.a.	n.a.	[31]
			1	7.71	n.a.	n.a.	[32]
			1	7.73	n.a.	n.a.	[33]
			1	-	7.70	100	[11]
			1	7.72	7.49	97.02	this work
2.90	4604.80	W$_{20}$O$_{58}$	1	7.17	-	-	[21]
			1	7.16	-	-	[35]
			1	7.20	6.95	98	[11]
			1	7.11	7.05	99.12	this work
2.92	5580.16	W$_{25}$O$_{73}$	2	6.88	-	-	[14]
3	231.84	ε-WO$_3$	4	7.39	-	-	[43]
		δ-WO$_3$	8	7.29	-	-	[44]
		δ- & γ –WO$_3$	-	-	7.19	-	this work
		γ –WO$_3$	8		-	-	this work
		γ-WO$_3$	8	7.19	-	-	[36]
		β-WO$_3$	8	7.12	-	-	[36]
		α-WO$_3$	8	7.03	-	-	[36]

Thermoelectric properties

In **Figure S1a** the electrical conductivities of the known compositions $x = 2, 2.72$ and 2.90 are compared. WO$_{2.90}$ shows $\sigma(T) = 77(4) \cdot 10^3$ S m^{-1} over the whole temperature range and a local maximum at 635 K. WO$_2$ and WO$_{2.72}$ reveal a metallic behaviour with the typical dependency $\sigma(T) \propto 1/T$ over a wide temperature range (**Figure S1b**).
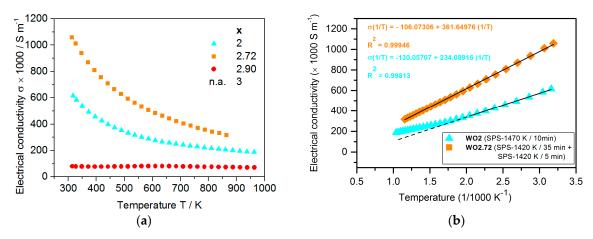
Figure S1. (**a**) Electrical conductivity $\sigma(T)$ of the reference materials WO_2, $WO_{2.72}$ and $WO_{2.90}$. No measurement was possible for WO_3 due to its insulating character. (**b**) A linear interpolation (black line) shows the metallic behaviour of WO_2 and $WO_{2.72}$ with $\sigma(T) \propto 1/T$ dependency. An extrapolation (dashed lines) reveals a deviation from this behaviour for WO_2 at high temperatures $T > 500$ K.

As expected due to its semiconducting behaviour $WO_{2.90}$ exhibits the highest negative Seebeck coefficient among the known compositions (**Figure S2a**). Therefore $WO_{2.90}$ also shows the highest figure of merit ZT for temperatures > 535 K whilst for $T < 535$ K the low electrical conductivity is disadvantageous and $WO_{2.72}$ exhibits the higher ZT (**Figure S2b**).
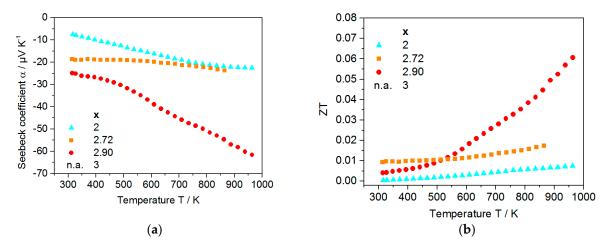

Figure S2. (**a**) Seebeck coefficient $\alpha(T)$ and (**b**) the resulting figures of merit ZT of the reference materials WO_2, $WO_{2.72}$ and $WO_{2.90}$. No measurement was possible for WO_3 due to its insulating character.

Reference sample $WO_{2.90}$

In the samples WO_x prepared with SPS-1420 K / 10 min we find the phase "$WO_{2.82}$" for $2.72 \leq x \leq 2.90$ which might be $W_{12}O_{34}$. This phase cannot be formed due to SPS-specific effects since it is also observed in $WO_{2.90}$ material which was synthesized in an evacuated silica tube for 72 h at 1370 K (**Figure S3a**).
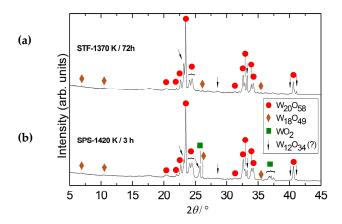
Figure S3. PXRD patterns of WO$_{2.90}$ obtained **(a)** from heating in an evacuated silica tube at 1370 K for 72 h and **(b)** from SPS synthesis at similar temperature for 3 h. Reflections of the new phase "WO$_{2.82}$" which might be W$_{12}$O$_{34}$ appear for both routines. Radiation was Cu-K$_{\alpha1}$.

c_P measurements of WO$_x$ materials from differential scanning calorimetry (DSC)

Preliminary $c_P(T)$ measurements were performed for WO$_x$ materials which were synthesized with SPS-1320 K / 10 min. Differences between the measured $c_P(T)$ values were non-systematic and smaller than the 10 % error of the *DSC 404 C Pegasus* (Netzsch, Selb, Germany) device (**Figure S4**, error bars). Thus, for calculations of the thermoelectric properties of WO$_x$ and WO$_2$ theoretical values of WO$_3$ and WO$_2$ from the *NIST-JANAF* database were used respectively (**Figure S4**, dotted lines).
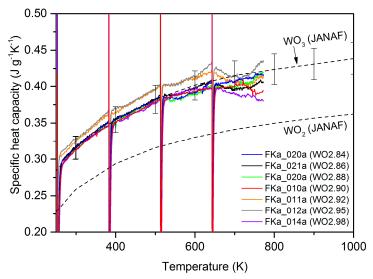

Figure S4. Specific heat capacity $c_P(T)$ of WO$_x$ materials show values close to calculations from the NIST-JANAF database (dotted lines) and differed by less than 10 % (error bars).