Supporting Information

Computational and experimental investigation of TmAgTe₂ and *XYZ*₂ compounds, a new group of thermoelectric materials identified by first principles high-throughput screening

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Area	$\mu_e(eV)$	Carrier concentration (cm ⁻³)
1	-0.2201	5.2×10^{20}
2	0.1374	1.35×10^{17}
3	-0.1243	2.29×10^{20}
4	0.5268	-8.77×10^{17}



Figure S1. The volume of $P\overline{3}m1$ and $P\overline{4}2_1m$ *XYZ*₂ per unit formula (Å³). The red line indicates equal volumes for the two structures.



Figure S2. Band structure of trigonal TmAgTe₂ with no spin orbit coupling (NSOC) and with spin orbit coupling (SOC) effects.



Figure S3. Band structure of tetragonal TmAgTe₂ with no spin orbit coupling (NSOC) and with spin orbit coupling (SOC) effects.



Figure S4. Band structure of trigonal PrAgSe₂ with no spin orbit coupling (NSOC) and with spin orbit coupling (SOC) effects.



Figure S5. Band structure of trigonal YAgS₂ with no spin orbit coupling (NSOC) and with spin orbit coupling (SOC) effects.



Figure S6. Phase diagrams of the Y-Ag-Te systems from the Materials Project Database. Different growth areas of the XYZ_2 compounds are denoted by numbers.



Figure S7. Calculated defect formation enthalpies $\Delta H_{d,q}$ in tetragonal YAgTe₂ as a function of Fermi level, μ_e plotted for chemical potentials corresponding to the different 3-phase regions with area numbers corresponding to those labeled in Figure S6. Vertical dashed lines represent the calculated band gap of YAgTe₂.



Figure S8. Predicted zT at 600 K versus decomposition energy (E_{decomp}) per atom for n-type XYZ₂ candidates. Sulfides, selenides and tellurides are shown in blue, red and green, respectively. The compositions of best candidates with zT > 1.5 are indicated

in the figure. For clarity, we only show a small window of E_{decomp} (< 0.05 eV per atom). κ_{lat} is assumed to be 0.5 W m⁻¹ K⁻¹.



Figure S9. The distribution of energy above hull for XYZ_2 in the P $\overline{3}$ m1 structure with Y = Ag, Au, Cu and Z = S, Se and Te. The mean values are indicated and represented by red vertical lines.



Figure S10: PXRD patterns of $TmAgTe_2$ samples after quenching from 600 °C to room temperature (bottom), after annealing at 400 °C for 1 d (middle) and 4 d (top). The sample crystallize in trigonal symmetry after quenching from 600 °C. A partial transformation from HT-Trigonal to LT-Tetragonal phase takes place after annealing the sample at 400 for 1 d. Phase transformation is complete after annealing at 400 °C for 4 d.



Figure 11: DSC analysis of TmAgTe₂ starting from the tetragonal phase. While two endothermic peaks ($T_{\text{onset},1} = 725$ K and $T_{\text{onset},2} = 735$ K) were recorded on the first heating, only one endothermic peak ($T_{\text{onset},2} = 735$ K) appeared on the second and third heating cycle. On the cooling cycle the trigonal phase partially transforms back to the tetragonal as determined by XRD.



Figure S12: XRD patterns of TmAgTe₂ samples after synthesis, after hot-press and after transport measurements. After synthesis, an almost pure trigonal phase of TmAgTe₂ is obtained. After hot-press, the sample contained a very small amount of the tetragonal phase. XRD pattern after all the measurements points to formation of virtually negligible amounts of tetragonal phase, signifying metastability of the trigonal phase at low temperatures.



Figure S13: Room temperature optical absorption edge spectrum (F(R)=(1-R)²/2R, Kubelka Munk function) for TmAgTe₂ trigonal phase sample. The large absorption near 0.4 eV is likely due to surface hydroxide. The absorption edge onset is observed above 0.54 eV.



Figure S14: Specific heat of the trigonal phase of $TmAgTe_2$. At high temperature the experimental specific heat extrapolates to a constant (~ 0.2 J g⁻¹ K⁻¹).



Figure S15: The computed power factor, thermal conductivity and zT for trigonal TmAgTe₂ at 600 K, assuming the electron relaxation time is 10^{-14} s and the lattice thermal conductivity is 0.5 W m⁻¹ K⁻¹.



Figure S16: XPS spectrum of the trigonal phase of TmAgTe₂. The four XPS peaks at the valence band are in agreement with the DFT calculations. The dashed line above the VBM indicates the DFT predicted unoccupied Tm state, which should not affect transport properties.