

Supplemental Material: High-Entropy Design of Transition Metal Oxide Semiconductors with Ultra-Low Thermal Conductivity

Robert A. Robinson^{I1}, Tara Karimzadeh Sabet^{I2}, Francisco Marques dos Santos Vieira^{I3},
Saeed S. I. Almishal^{I3}, Sai Venkata Gayathri Ayyagari³, Rowan Katzbaer⁴,
Gabriele Di Gianluca⁵, Saugata Sarker³, Pedro R. Trinidad-Perez⁴, John P. Barber⁶,
Simon Gelin², Seng Huat Lee⁷, James Hodges⁴, Raymond E. Schaak⁴,
Venkatraman Gopalan³, Nasim Alem³, Christina M. Rost⁶, Vincent H. Crespi^{1*},
Jon-Paul Maria^{3*}, Ismaila Dabo^{2*}, Zhiqiang Mao^{1,3,4,7*}

¹Department of Physics, Pennsylvania State University, University Park, 16802, Pennsylvania, USA.

²Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, 15213, Pennsylvania, USA.

³Department of Materials Science and Engineering, Pennsylvania State University, University Park, 16802, Pennsylvania, USA.

⁴Department of Chemistry, Pennsylvania State University, University Park, 16802, Pennsylvania, USA.

⁵Department of Physics, University of Florida, Gainesville, 32611, Florida, USA.

⁶Department of Materials Science and Engineering, Virginia Polytechnic Institute and State Univ., Blacksburg 24061, Virginia, USA.

⁷2D Crystal Consortium, Materials Research Institute, Pennsylvania State University, University Park, 16802, Pennsylvania, USA.

*Corresponding author(s). E-mail(s): vhc2@psu.edu; jpm133@psu.edu; idabo@andrew.cmu.edu; zim1@psu.edu;

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S1 X-ray Absorption Near Edge Structure (XANES)

Fig. S1 shows the spectra of wolframite parent structures along with the respective edge of the A^6WO_4 sample. In the Mn, Co, and Ni edges, there are no significant differences between the standard and the disordered sample. The parent compositions have octahedral coordination on the A-site as depicted in models of wolframite and confirmed by H. Weitzel [1]. Based on chemistry, the A-site will be 2+ due to WO_4 being 2-. The pre-edge peak seen in Fig. S1a indicates that Mn is in the octahedral coordination that we expect [2]. Fig. ?? shows fingerprinting done for the oxidation state of Fe against $\text{Fe}^{2+,3+}$ standards for both the disordered sample and the standard [3]. This analysis shows that Fe has a mixed valence in both samples, with it shifting more towards 3+ in the disordered sample. Work done by Bretesche et al. saw mixed Fe^{2+} and Fe^{3+} in FeWO_4 with alternating cathodic and anodic scans, indicating that FeWO_4 is capable of hosting both Fe oxidation states [4].

^IThese authors contributed equally to this work.

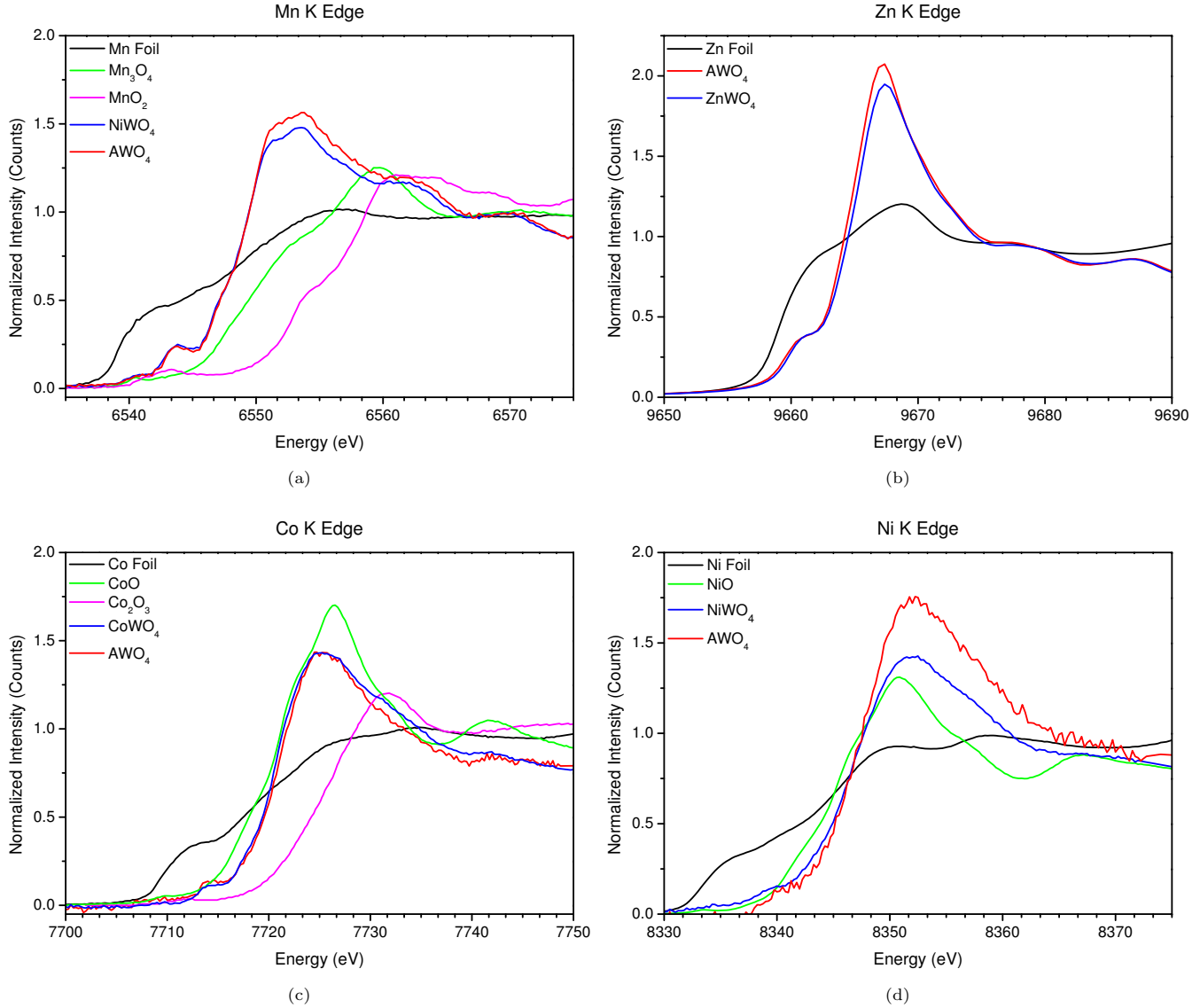


Fig. S1 **a:** Mn K edge XANES for A^6WO_4 , MnWO_4 , and reference samples. **b:** Zn K edge XANES for A^6WO_4 , ZnWO_4 , and Zn foil. **c:** Co K edge XANES for A^6WO_4 , CoWO_4 , and reference samples. **d:** Ni K edge XANES for A^6WO_4 , NiWO_4 , and reference samples.

S2 X-ray Photoelectron Spectroscopy

XPS measurement has been conducted on the uniaxially compressed A^6WO_4 powder samples to identify the oxidation state of the constituent elements (W, O, Mn, Zn, Ni, Co, Cu, and Fe). A series of high throughput scans for each element was chosen to minimize the interference. Fig. S2a showcase the the experimental and fitted data for $4f_{5/2}$, $4f_{7/2}$, and $5p_{3/2}$ spectrum of W. The peak maxima for the $4f_{5/2}$ and $4f_{7/2}$ spectrum is at the binding energy of 37.43 and 35.29 eV, which is consistent with the reported literature showcasing a 6+ oxidation state [5–7]. Fig. S2b illustrated the experimental and fitted data for the O 1s spectrum. The lack of broadening and a peak maximum at a binding energy of 530.27 eV is consistent with similar metal oxides [8–10]. Similarly, the Mn 2p spectrum has been demonstrated in Fig. S2c. The peak shape and the maxima at the binding energy of 641.04 eV have excellent congruence with the 2+ oxidation state [11, 12]. The Zn LMM spectra (Fig. S2e) in XPS show two Auger peaks centered at 496.94 and 493.42 eV, respectively. The higher energy peak can be attributed to the metal oxide with a 2+ oxidation state. The lower energy peak has been reported as an interstitial isolated metallic species [12, 13]. However, the presence of this isolated Zn has been identified to be surpassed under high oxygen concentrations [14]. For the synthesis of A^6WO_4 elemental Zn has not been utilized, indicating a necessity for strong reduction potential

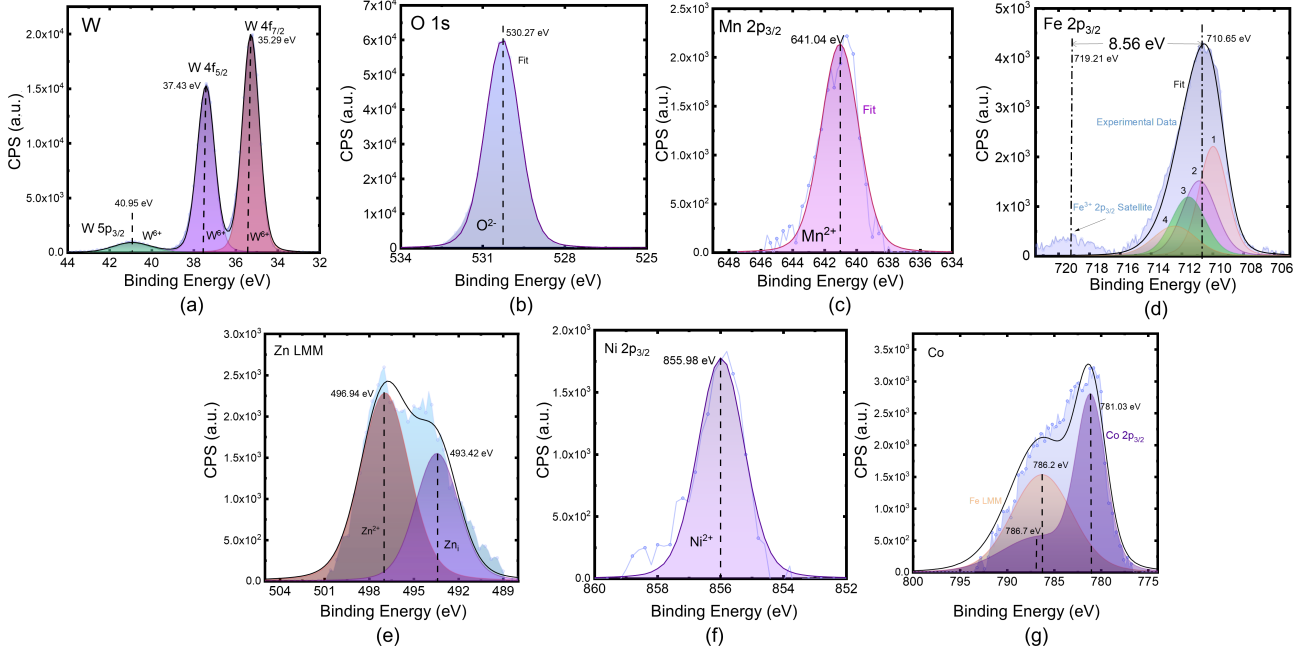


Fig. S2 XPS spectrum of A^6WO_4 around the binding energy resembling the following state: a. Tungsten 4f and 5p, b. Oxygen 1s, c. Manganese 2p, d. Iron 2p, e. Zinc LMM, f. Nickel 2p and g. Cobalt 2p.

to justify the presence of elemental metallic species. The exact mechanism of this formation might require further investigation. The Ni 2p spectrum from XPS has been showcased in Fig. S2f. The spectrum shows one predominant peak centered at 855.98 eV binding energy, congruent with the reported literature [15]. The Co spectrum has been showcased in Fig. S2g, and the interference between the auger LMM peak of Fe and the Co 2p spectrum is strong, which makes it difficult to analyze this element reliably. Irrespective of these limitations, the Co spectrum can be defined through two distinct peaks centered around 781.03 and 786.7 eV, consistent with the metallic oxide references [16]. The fitting parameters for each of these elements have been listed in Table 1.

XPS has been further utilized to identify the oxidation state of Cu and Fe. The Fe spectrum (Fig. S2d) has been fitted with four multiples, and the energy difference between the central peak and satellite has been measured to be 8.56 eV. The reported surface peak at high binding energy has not been considered to avoid convolution in the fitting. The energy difference between the main peak and the satellite can be utilized to identify the oxidation state of Fe [17]. For the 3+ oxidation state, the energy difference is usually in the range of 8-8.8 eV, while for the 2+ oxidation state, the energy difference varies from 4.8 to 5.9 eV. The experimentally measured energy difference between the main peak and the satellite is 8.56 eV, which indicates that the predominant oxidation state of Fe in A^6WO_4 is 3+. Notably, as the satellites, due to the 2+ oxidation state forming at a relatively 2-3 eV lower in energy, it is difficult to differentiate that from the spread of the main $2p_{3/2}$ peak. Moreover, the XPS spectrum for the Cu has been demonstrated in Fig. ?? in the main text. The spectrum demonstrates the coexistence of both 2+ and 1+ oxidation states in Cu, which is in agreement with the literature [18].

Table 1 XPS fitting parameters of different elements present in $A^6\text{WO}_4$ sample

Element	Spectrum	Position	FWHM	% Area
W $4f_{7/2}$	3	35.29	0.95	36.07
W $4f_{5/2}$	2	37.43	0.99	36.28
W $5p_{3/2}$	1	40.95	2.15	27.66
O $1s$	1	530.27	1.46	100
Mn $2p_{3/2}$	1	641.04	2.72	100
Ni $2p_{3/2}$	1	855.98	1.73	100
Zn LMM	2	493.42	3.42	37.51
Zn LMM	1	496.94	3.87	62.49
Co $2p_{3/2}$	2	786.7	9.24	33.33
Co $2p_{3/2}$	1	781.03	3.74	66.67

S3 Electronic Structure Calculations

The generalized gradient approximation (GGA) to density functional theory (DFT) tends to underestimate the band gap energies of semiconductors. Of the six parent phases, only ZnWO_4 has its band gap reasonably described at the GGA level. For the remaining five parent phases, a Hubbard U correction was applied to the $3d$ orbitals of the corresponding A -site cation to reproduce the experimental bandgap energy. In the case of CuWO_4 , shown in figure S4, the magnitude of the Hubbard correction principally shifts the energy range in which the vacant $3d$ band is found, restoring agreement with experiment.

The calculated bandgaps at the GGA and GGA+ U levels are shown on the parity plot in Fig. S3 highlighting the improvement provided by the Hubbard U correction. Application of the Hubbard U correction to Zn was not found to improve accuracy; this is unsurprising given Zn's fully occupied $3d$ shell. As such, subsequent calculations forwent applying a Hubbard correction to Zn. The band structure diagrams and projected density of states (PDOS) of the six parent phases are shown in Fig. S5. For the first three phases (MnWO_4 , FeWO_4 , and CoWO_4), the PDOS exhibits a splitting-off of the top levels of the valence band which narrows the band gap vis-à-vis the parent phases that host later transition metals.

From the binary mixtures of each pair of parent phases, three compositions were studied, namely, $(A_{1-x}A'_x)\text{WO}_4$, where $x \in \{0.25, 0.5, 0.75\}$. Fig. S6 shows the crystal structure of the three compositions. From the 15 pairs of A -site

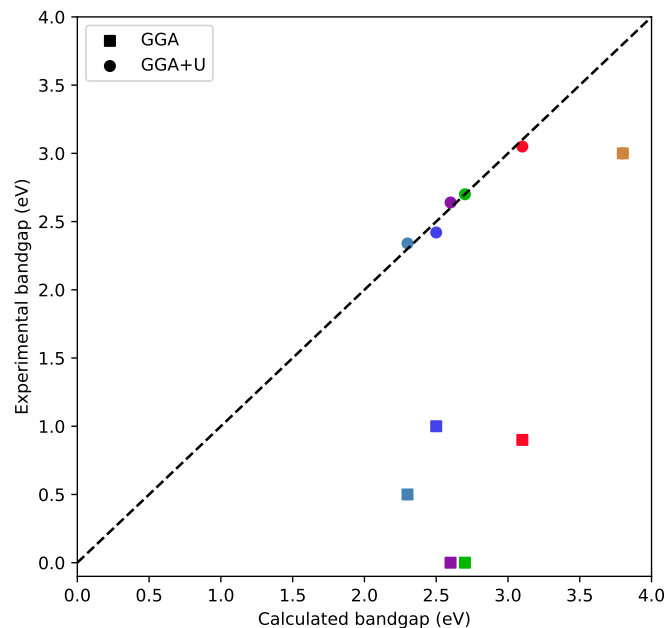


Fig. S3 Parity plot of band gap of the six parent phases at the GGA and GGA+ U levels of theory.

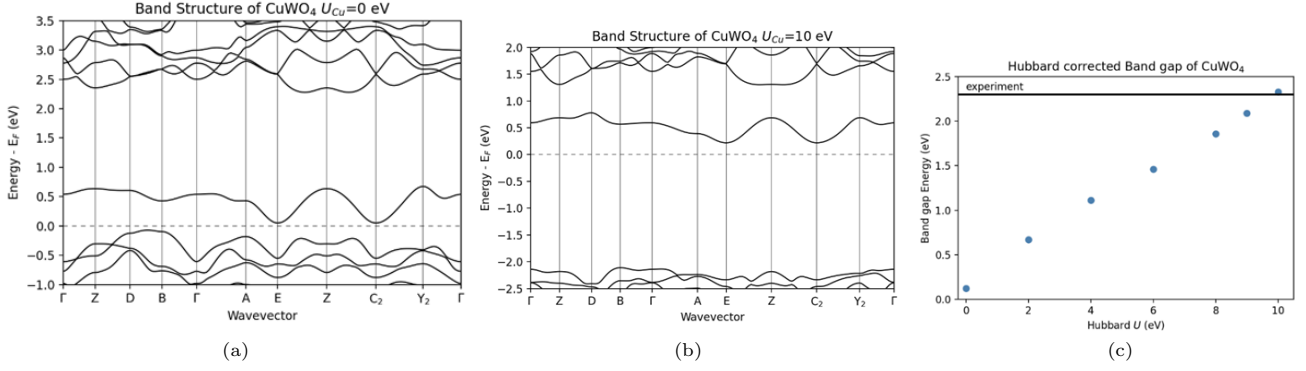


Fig. S4 Band structure diagram of CuWO₄ **a:** without and **b:** with Hubbard U correction. **c:** Plot of band gap energy of CuWO₄ with respect to Hubbard U parameter.

cations, 45 structures were constructed. Following the optimization of their geometry, their band gap energies were determined. The relative narrowing of the band gap of each composition was computed as

$$narrowing = \frac{E_g(A_{1-x}A'_x)WO_4}{(1-x)E_g(AWO_4) + xE_g(A'WO_4)}. \quad (1)$$

In Fig. S7, the solid lines represent the average narrowing over all relevant binary compositions, while the shaded regions represent the 95% confidence interval. A' representing the element with a higher atomic number in each binary. As the green line shows, the mixing of binaries narrows the band gap only modestly. Also plotted in Fig. S7 is the data for the compositions in which Cu is present, and those from which it is absent highlighting the key role of Cu in the narrowing of band gap. When Cu is paired with Fe, the latter donates an electron to the former producing the d^5 cation Fe^{3+} and the d^{10} cation Cu^+ . This transfer leaves the vacant electron levels of Fe^{3+} in the bandgap narrowing it, as shown in Fig. S9d. When Cu is paired with any other cation, such as Mn shown in Fig. S8a, no charge transfer occurs and the vacant Cu^{2+} level resides in the band gap narrowing it. Also shown in these panels is the preservation of the split-off levels in the binary compositions.

Six multi-component compositions were studied assuming the experimentally measured lattice parameters of A^6WO_4 . The first considered all six A -site species, the second excluded Fe and Zn; the third excluded Cu and Zn. The fourth fifth and sixth excluded Ni and Zn varying the ratio of Fe to Cu. Fig. S9 shows the band structure diagrams and PDOS of each composition near the band gap. Zn was found to make small contributions to the density of states near the valence band maximum (VBM) and conduction band minimum (CBM). For this reason it was omitted from all but the first composition. Exclusion of Fe in the second composition preserved Cu^{2+} and the associated in-gap vacant electron states above the Fermi level quite close to the split-off levels contributed by Mn and Co. Exclusion of Cu in the third composition ensures there are no in-gap states contributing to the narrowing of the band gap. The last three compositions include both Fe and Cu, excluding Ni and Zn. In the first of these compositions Fe outnumbers Cu; in the third Cu outnumbers Fe; the middle composition is equimolar. In the equimolar system, each Fe donates an electron to Cu as seen in the binary studies. When the mole fraction of the two differ, the minority cation fully engages in charge transfer while the majority cation is present in two valence states. Presence of unoccupied in gap states associated with Fe^{3+} and Cu^{2+} can each narrow the band gap. The electronic structure of the last composition was computed before and after optimizing the geometry of the structure. The optimization involves increased distortion of the AO_6 octahedra, and the narrowing of the band gap from 1.1 to 0.5 eV. This results from the introduction into the gap of unoccupied states originating from $3d$ orbitals of Mn. Mn is not predicted to engage in charge transfer with

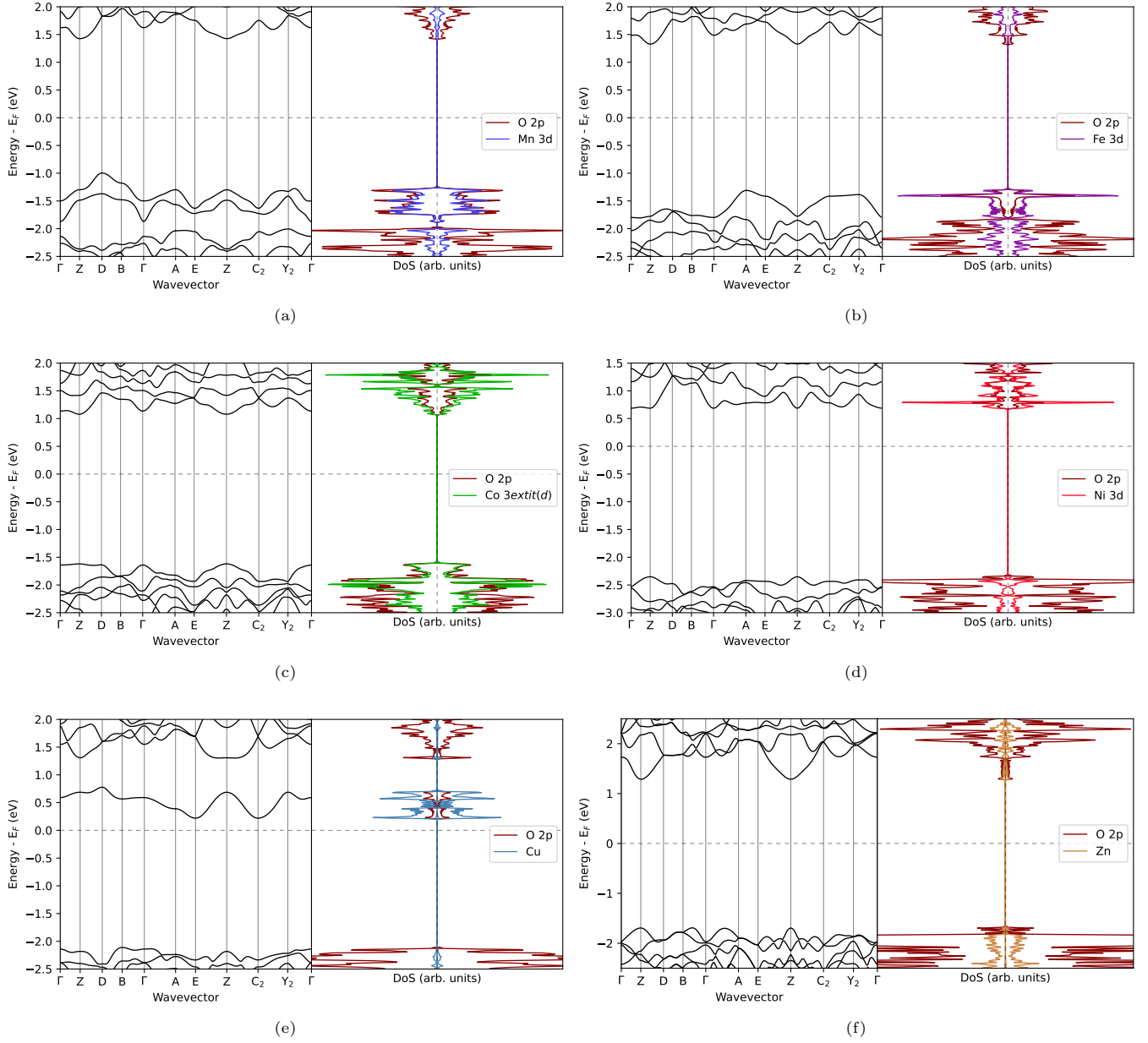


Fig. S5 Band structure diagrams and PDOS plots of **a:** MnWO_4 , **b:** FeWO_4 , **c:** CoWO_4 , **d:** NiWO_4 , **e:** CuWO_4 , **f:** ZnWO_4 .

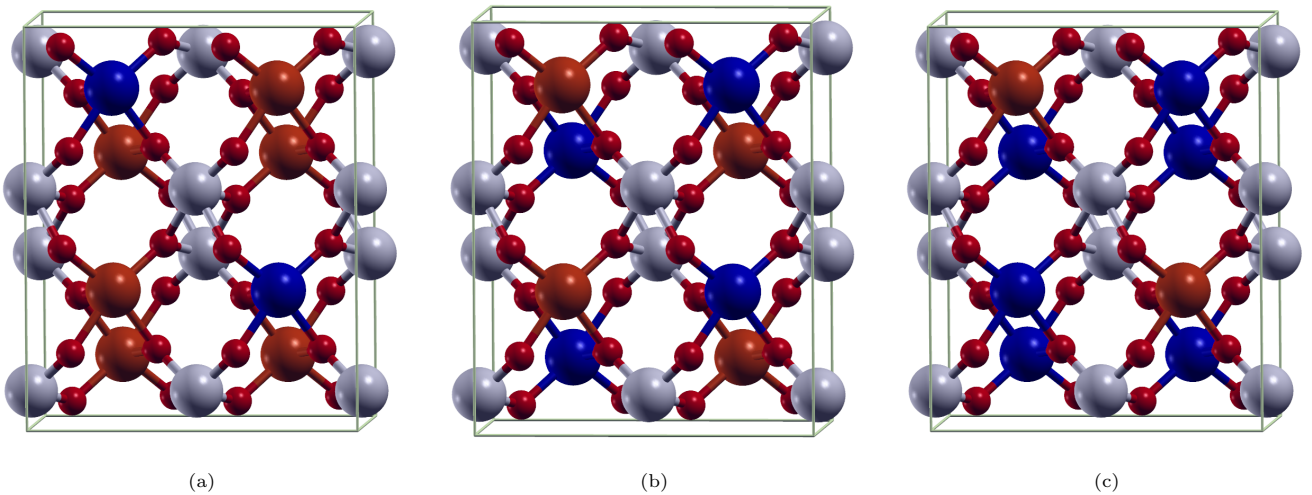


Fig. S6 Crystal cells of the three binary stoichiometries tested for each pair of parent phases. **a:** $(A_{0.75}A'_{0.25})\text{WO}_4$, **b:** $(A_{0.5}A'_{0.5})\text{WO}_4$, **c:** $(A_{0.25}A'_{0.75})\text{WO}_4$ Orange and blue spheres represent A and A' cations, gray represent W and dark red represent O.

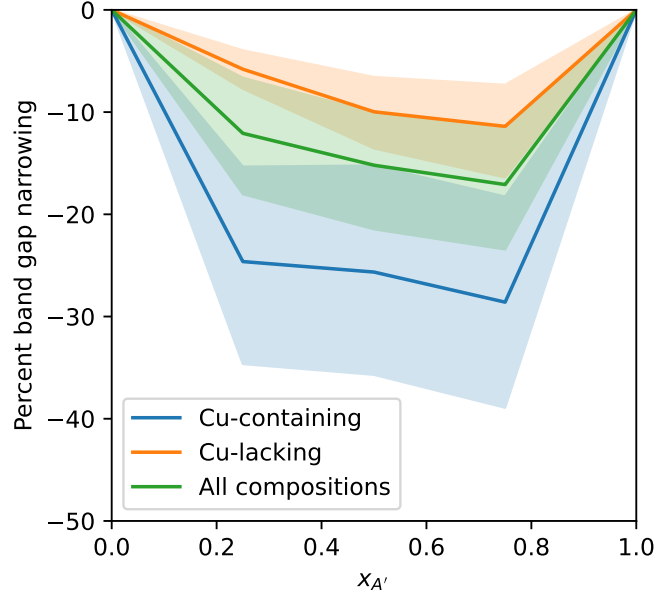


Fig. S7 Plot of the relative narrowing of the band gap as a function of composition.

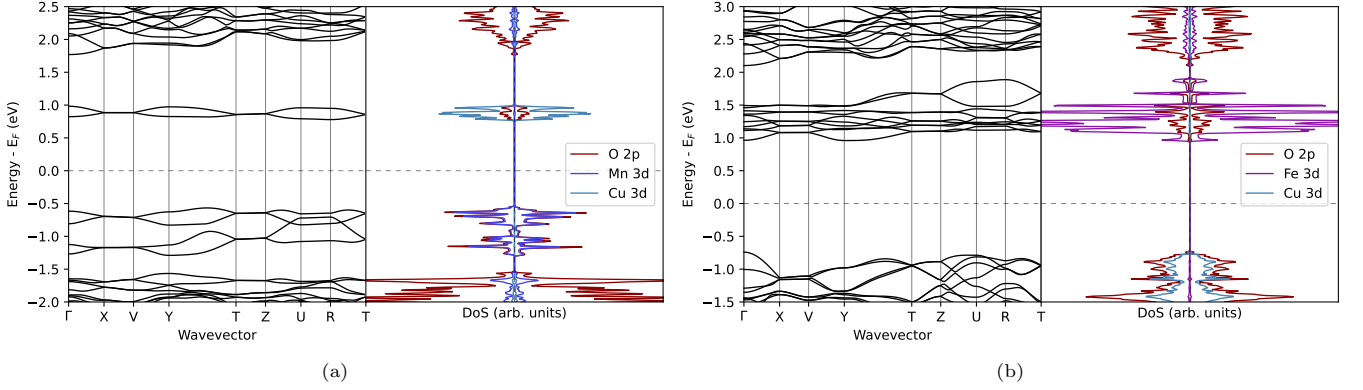


Fig. S8 Band structure diagram and PDOS of **a:** $(\text{Mn}_{0.5}\text{Cu}_{0.5})\text{WO}_4$, **b:** $(\text{Fe}_{0.5}\text{Cu}_{0.5})\text{WO}_4$.

Cu, and is not observed doing so in experiment. The Mn unoccupied state in the band gap emerges from the lifting of orbital degeneracy caused by asymmetry of the MnO_6 coordination octahedron. While we observed this only in the case of Mn, other cations may undergo similar phenomena.

The presence of multiple transition metal species on the A-site sublattice induces significant local lattice distortions suppressing thermal conductivity, and influencing the electronic structure. We estimated the local distortion of AO_6 octahedra from the A–O bond lengths of each A-site cation. The average of A–O bond lengths over the six multi-component compositions simulated was used as the reference point for the analysis. For each cation, the mean absolute percent deviation (MAPD) of its A–O bondlengths from the average was used as a proxy for the distortion of its coordination octahedron. Likewise, the mean percent deviation (MPD) of its A–O bond lengths from the average was used as a proxy for the size of its coordination octahedron, and consequently the cation size. The Mn^{2+} cation from which emerged the in gap states in the last composition is represented by the solitary blue triangle in Fig. S10a. It's coordination octahedron is severely distorted due to sharing an edge with that of the similarly distorted Cu^{2+} represented by the isolated blue-gray triangle. In Fig. S10b, the opaque right-side up triangle exhibits the low bandgap enabled by the significant local distortion. The transparent black triangle represents the same composition before geometry optimization. The lower distortion of this structure produces a band gap energy of 1.1 eV, shown in Fig. S11. However, it is evident that local distortion of octahedra is not responsible for the unexpectedly low band gap of the

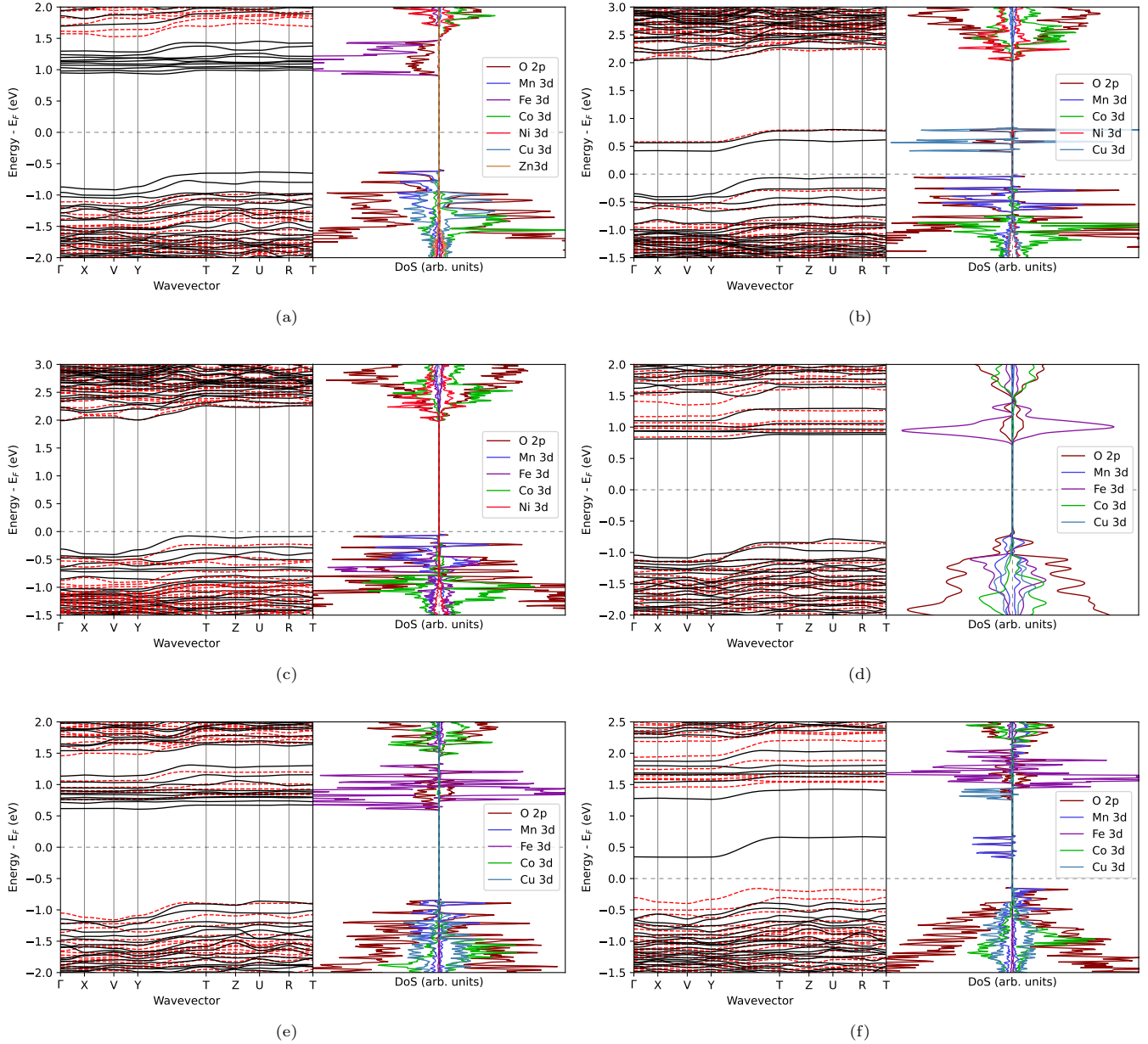


Fig. S9 Band structure diagrams and PDOS plots of **a:** $A^6\text{WO}_4$, **b:** $(\text{Mn Co Ni Cu})\text{WO}_4$, **c:** $(\text{Mn Fe Co Ni})\text{WO}_4$, **d:** $(\text{Mn}_{0.25} \text{Fe}_{0.33} \text{Co}_{0.25} \text{Cu}_{0.17})\text{WO}_4$, **e:** $\text{Mn Fe Co Cu})\text{WO}_4$, and **f:** $\text{Mn}_{0.25} \text{Fe}_{0.17} \text{Co}_{0.25} \text{Cu}_{0.33})\text{WO}_4$.

second composition $(\text{Mn Co Ni Cu})\text{WO}_4$ which rather emerges from the large split-off of valence states stemming from Mn and Co 3d-orbitals, as shown in S9b.

The simulations performed for various 4- and 6-component compositions identified several mechanisms synergistically contributing to the narrowing of the band gap of the synthesized material. Some of these mechanisms emerge directly from chemical complexity: variability of electronegativity contributes to states associated with A-site 3d orbitals spreading over a wider energy range which is compounded by the tendency of Mn^{2+} , Fe^{2+} , and Co^{2+} to exhibit occupied split-off at the top of the valence band. Another factor limiting the band gap is the presence of unoccupied states of 3d character. Among the parent phases only CuWO_4 exhibits these stemming from the vacant 3d orbital of Cu^{2+} . In a multicomponent composition, the coexistence of Fe and Cu results in charge exchange producing Cu^+ and Fe^{3+} . Like Mn^{2+} , Fe^{2+} , and Co^{2+} , Cu^+ exhibits split-off states toward the top of the valence band. Like Cu^{2+} , Fe^{3+} contributes vacant states at the bottom of the conduction band.

Lastly, the presence of Cu^+ significantly distorts coordination octahedra lifting the degeneracy of A-site 3d states which can further narrow the band gap. This last mechanism ensures that the presence of Cu^+ amplifies the narrowing

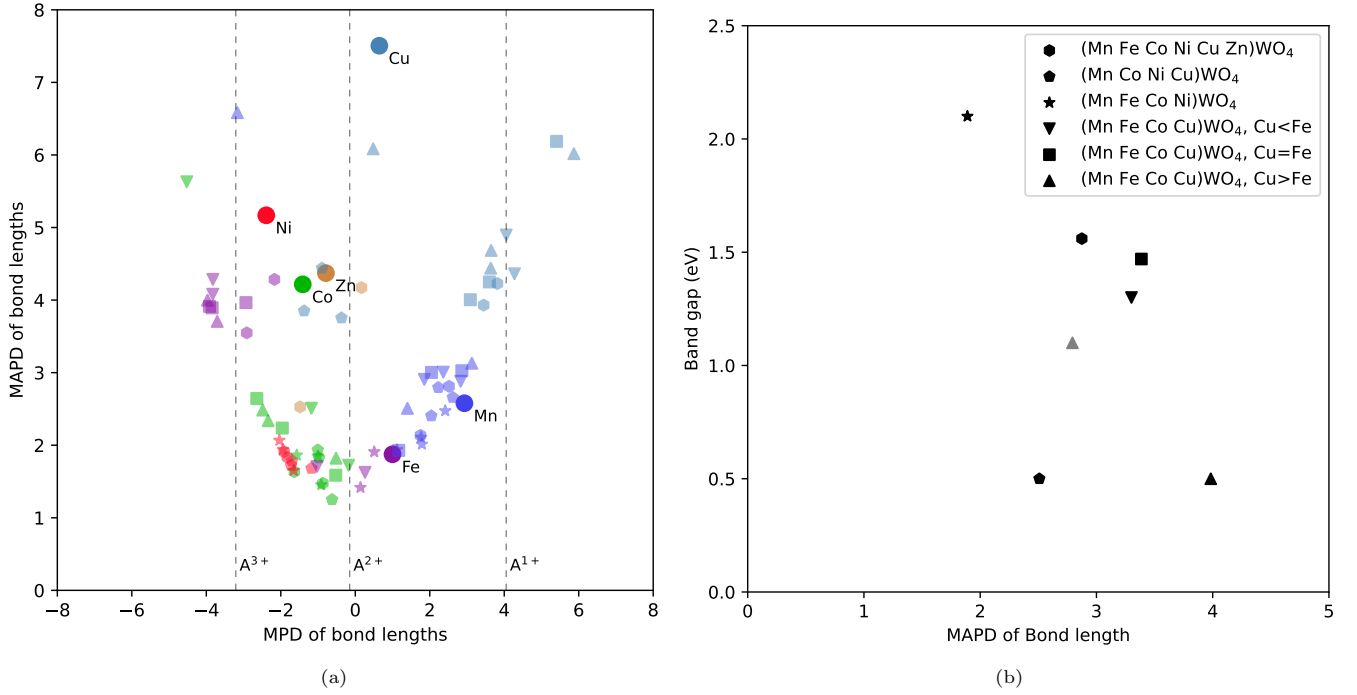


Fig. S10 **a:** Plot of MAPD vs MPD of A–O bond lengths for each cation in each multi-component compositions studied. Large circles represent octahedra in end members, small symbols represent individual multi-component compositions. **b:** Plot of band gap energy vs average MAPD of A–O bond lengths for each multi-component compositions studied

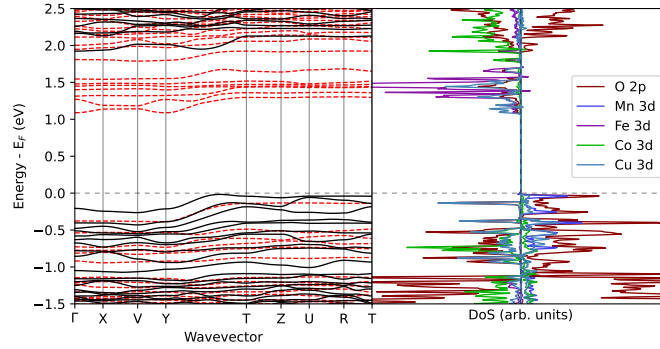


Fig. S11 Band structure diagram and PDOS plot of Mn_{0.25}Fe_{0.17}Co_{0.25}Cu_{0.33})WO₄ prior to geometry optimization.

effect of split-off states associated with Mn²⁺, Fe²⁺, and Co²⁺ 3d orbitals (non-linear synergy). We confirmed the band gap narrowing effect of local distortions by calculating the band gap of Cu-rich (Mn Fe Co Cu)WO₄ before and after geometry optimization. We found that proximity to Cu⁺ distorted the coordination octahedra of Mn²⁺ sufficiently to introduce vacant Mn²⁺ states at the bottom of the band gap narrowing the bandgap by over 0.5 eV, as shown in figure S12.

Significantly larger simulation cells are necessary to quantify the effect of Fe³⁺-Cu⁺ separation on band gap narrowing. However, we suspect that here too there is a non-linear synergistic effect because we expect the coordination octahedra of the relatively small Fe³⁺ cation to be significantly distorted to accommodate a nearest neighbor Cu⁺ cation. The significant distortions of these two neighboring octahedra are expected to lift the degeneracy of states associated with vacant Fe³⁺ 3d orbitals potentially lowering the relative energy of these states, and thereby further narrowing the band gap.

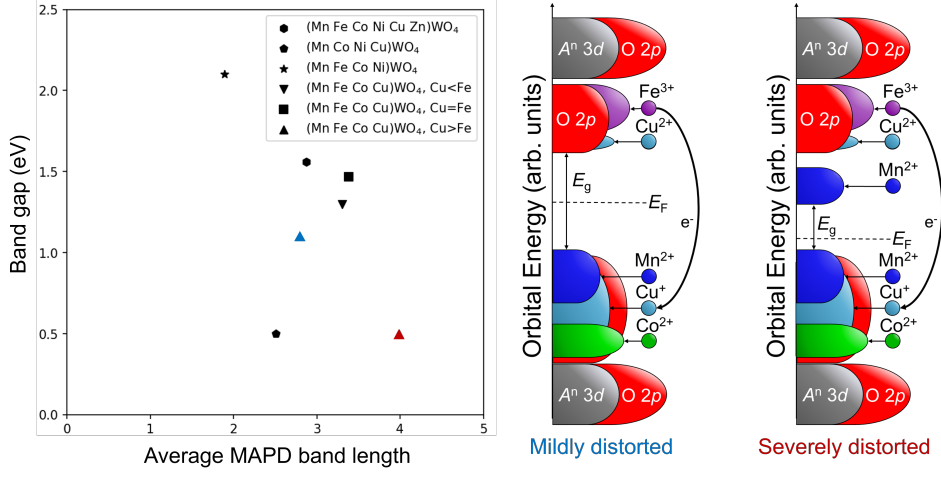


Fig. S12 Average MAPD band length vs Band gap highlighting difference between mild (blue) and severe (red) local lattice distortions.

S4 High-Entropy Stabilization

In order to better understand how configurational entropy contributes to the phase stabilization of A⁶WO₄, six wolframites with 2 elements occupying the *A* site were grown and checked for phase purity via XRD (Fig. S13). If some the binaries do not form, then this would indicate that A⁶WO₄ may not be conventionally stable, and thus likely relies on configurational entropy for stabilization. The mechanism by which entropy can stabilize a system is given by:

$$G = H - TS \quad (2)$$

where G is the Gibbs free energy, H is the enthalpy, T is the temperature, and S is the configurational entropy [19]. As S increases, a lower T is required for $G < 0$, the condition for formation of a stable chemical phase, so by introducing more elements at the *A* site in A⁶WO₄ the system can be stabilized even if the binaries cannot. Results indicate that while some binary phases do form the *P2/c* structure with little to no impurity, others show significant impurity phases despite identical synthesis processes for all samples. Binaries containing Cu are especially prone to forming impurity phases as CuWO₄ has a different structure phase at ambient pressure [20]. These results suggest that configurational entropy is necessary in order to stabilize A⁶WO₄.

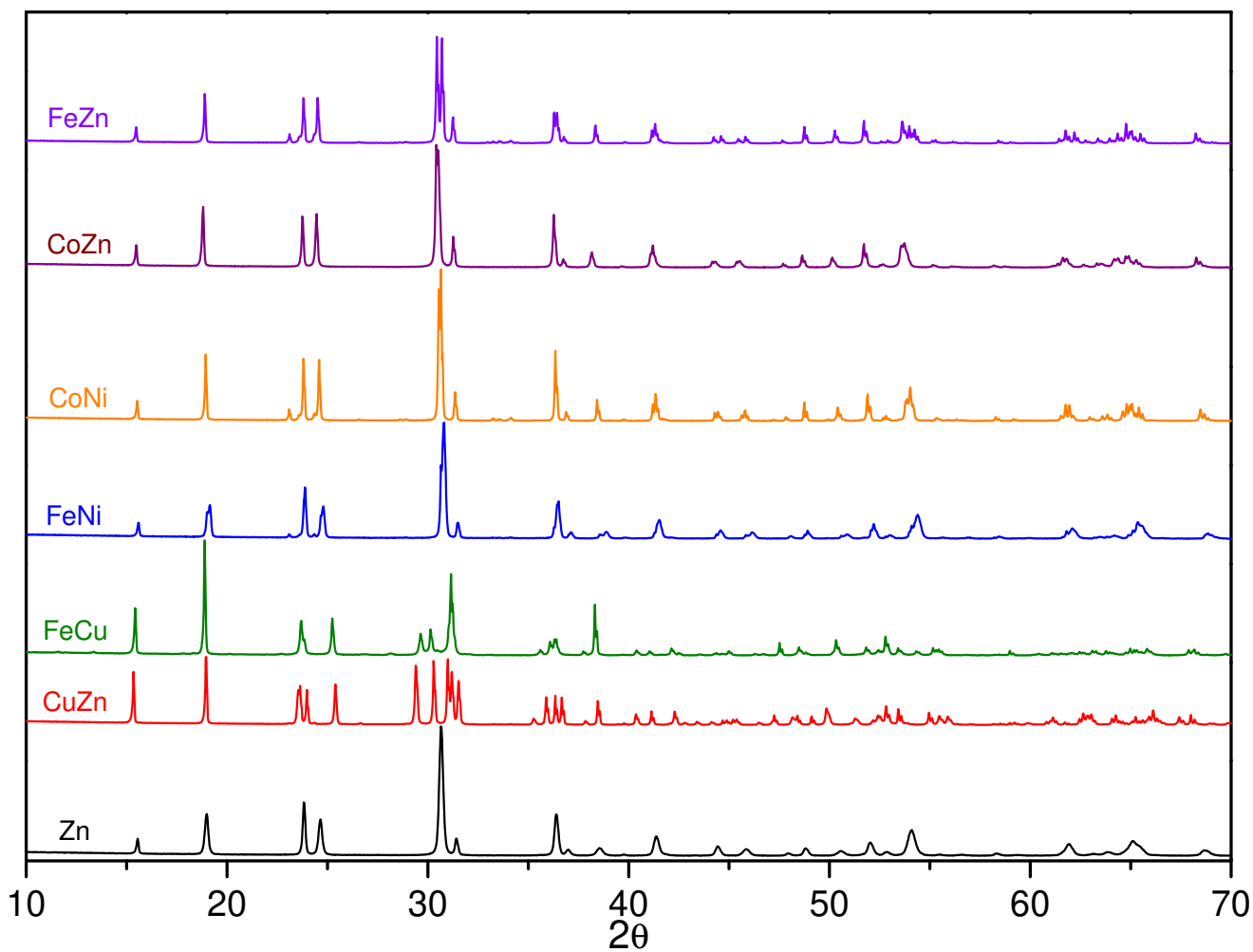


Fig. S13 X-ray diffraction patterns of grown binary wolframite phases with pattern for ZnWO_4 (black) for comparison. Most binaries show generally good agreement with prediction except for those containing copper which show substantial deviation.

S5 Thermal Calculations

The initial primitive cells for *ab initio* calculations were sourced from the Materials Project [21] database (Fig. S14).

Choice of supercell size: Selecting an appropriate supercell size was essential to balance computational efficiency and precision. An 8-fold increase in cell size, from $1 \times 1 \times 1$ to $2 \times 2 \times 2$, led to intractable computational time and memory usage, making larger supercells ($\geq 3 \times 3 \times 3$) impractical for extensive phonon calculations. This was particularly critical for the calculation of third-order interatomic force constants, which required numerous finite-displacement calculations. Hence, a supercell size of $2 \times 2 \times 2$ was selected to perform the simulations effectively.

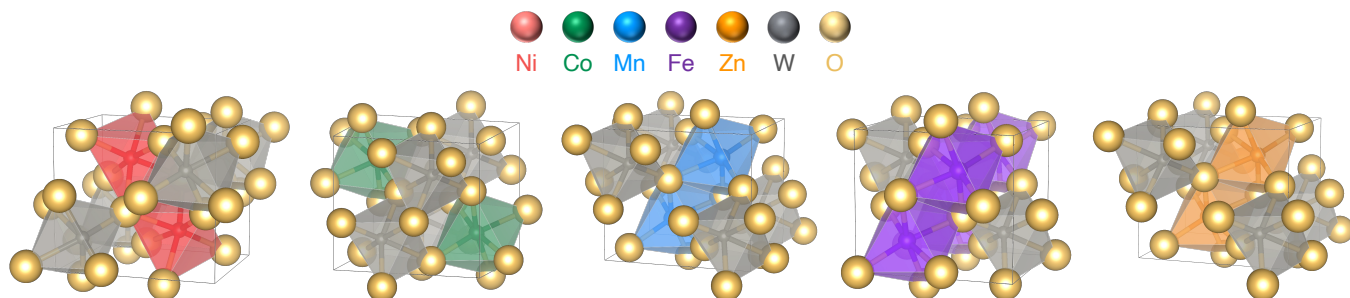


Fig. S14 Visualization of conventional cells for $(\text{Co,Ni,Mn,Fe,Zn})\text{WO}_4$ parent phases. The space group symbol of these monoclinic transition metal oxide structures is $P2_1/c$, with the M^{2+} cations having a VI-fold oxygen coordination in distorted M^{2+}WO_4 octahedra.

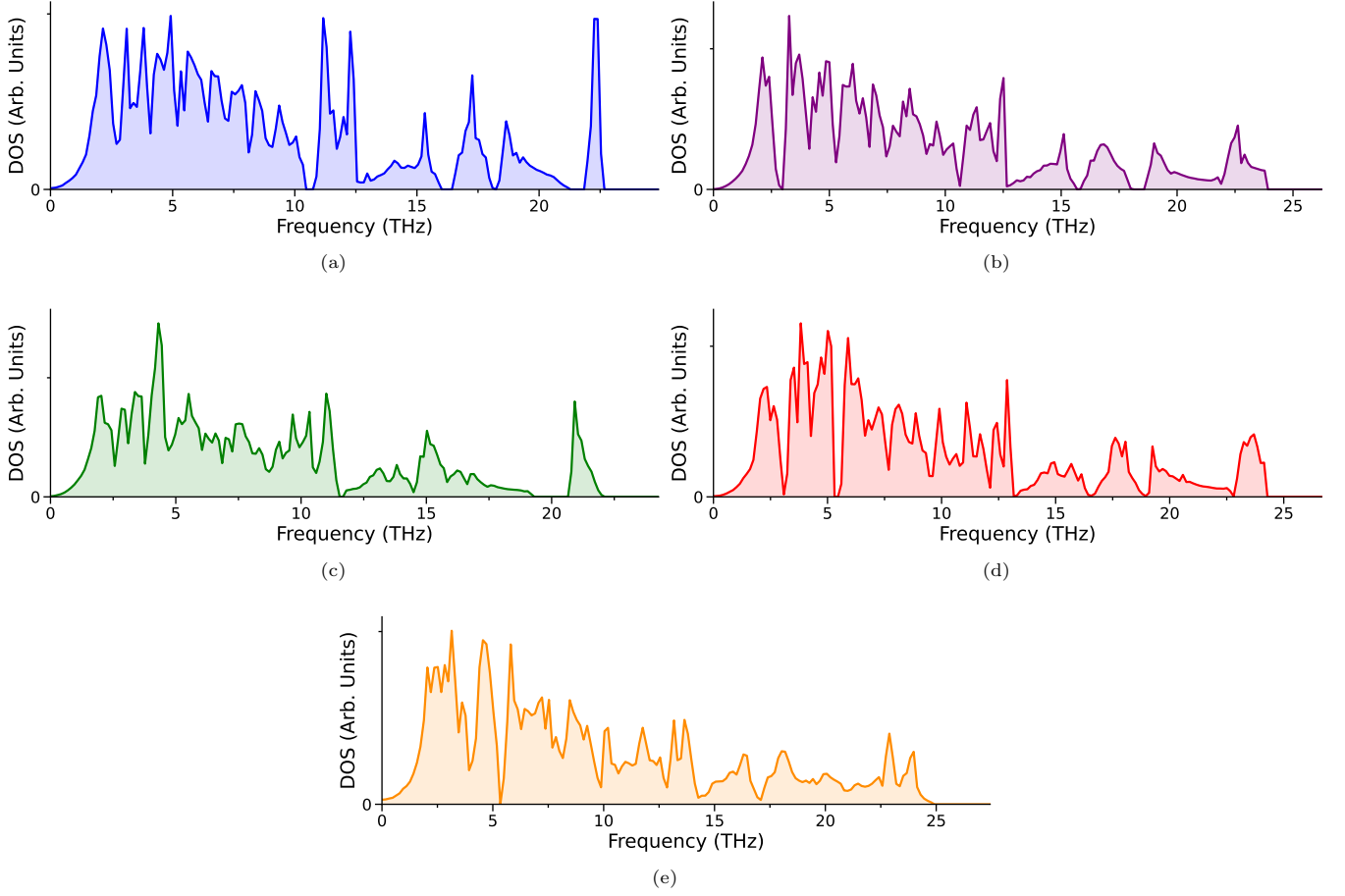


Fig. S15 Vibrational density of states (VDOS) plotted against frequency (THz) for **a**: MnWO₄, **b**: FeWO₄, **c**: CoWO₄, **d**: NiWO₄, and **e**: ZnWO₄, computed via first principles.

Second-order force constants: The vibrational density of states (VDOS) for the five parent phases MnWO₄, FeWO₄, CoWO₄, NiWO₄, and ZnWO₄ are shown in Fig. S15 as a function of the phonon frequencies. The corresponding phonon dispersion relations along high-symmetry directions of the Brillouin zone are presented in Fig. S16. Both the VDOS and the dispersion relations were calculated via density functional theory (DFT) using the finite-displacement method within the harmonic approximation (second-order interatomic force constants).

Third-order force constants: In bulk solids, heat is conducted through lattice vibrations known as phonons. The Boltzmann transport equation under the single-mode relaxation time approximation [22, 23], the macroscopic lattice thermal conductivity tensor of the material κ_{latt} is calculated as a sum of the contributions of individual phonon modes λ and can be expressed as a tensor product of the phonon group velocities, the specific heat capacities, and the phonon lifetimes, which are computed via the finite-displacement method within the anharmonic approximation (third-order interatomic force constants).

$$\kappa_{\text{latt}} = \frac{1}{NV} \sum_{\lambda} \kappa_{\lambda} = \sum_{\lambda} C_{\lambda} v_{\lambda} \otimes v_{\lambda} \tau_{\lambda}^{\text{SMRT}} \quad (3)$$

where V is the volume of the unit cell, N is the number of phonon wavevectors $\mathbf{q}$, C_{λ} is the volumetric specific heat capacity, v_{λ} is phonon group velocity, $\tau_{\lambda}^{\text{SMRT}}$ is the single-mode relaxation time (SMRT), and $\lambda = (\mathbf{q}, i)$ represents an individual phonon mode as a pair of phonon wavevector $\mathbf{q}$ and branch i . Within the relaxation-time approximation, the phonon scattering rate τ_{λ}^{-1} quantifies how long it takes for the phonon λ to return to its equilibrium state. In the

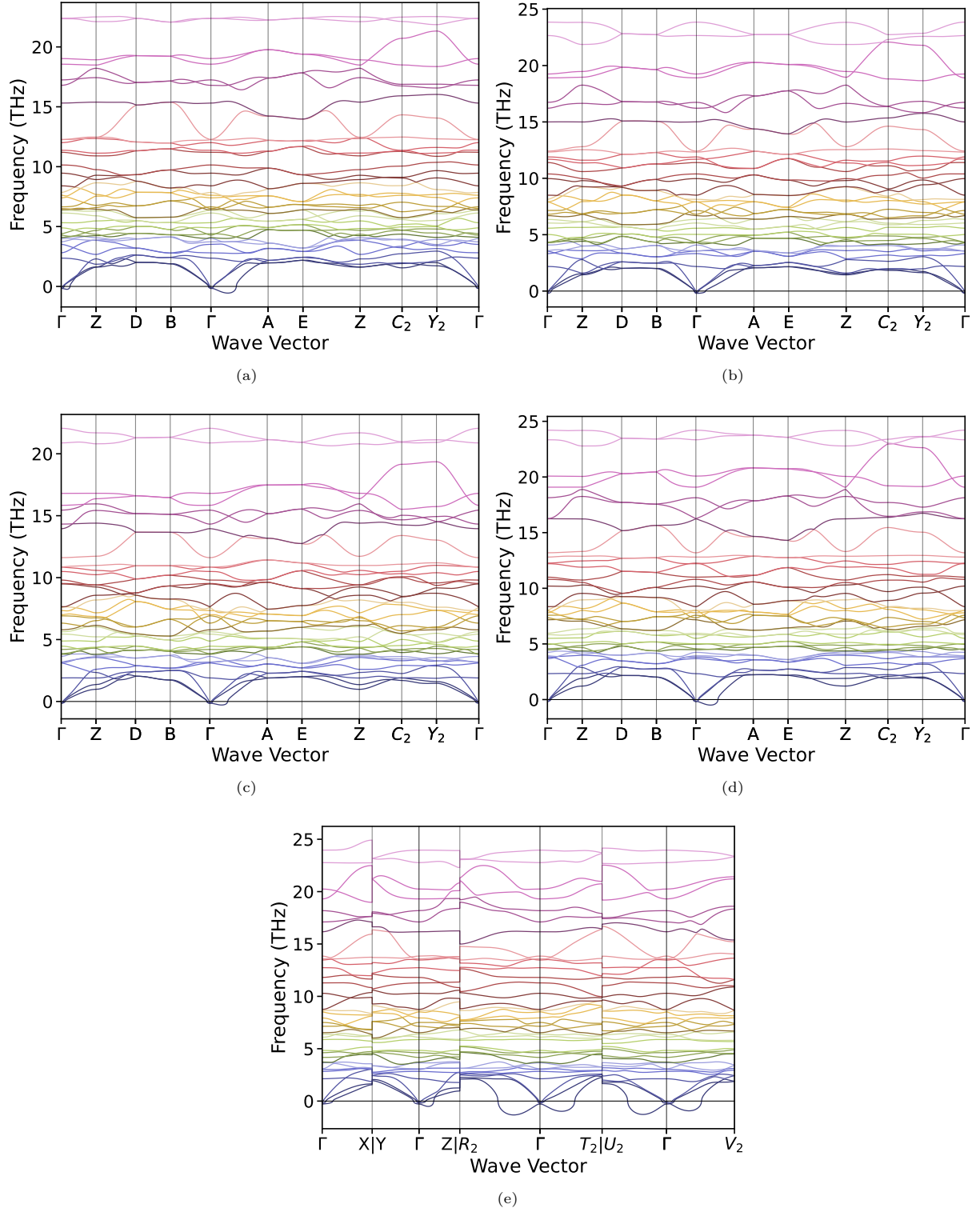


Fig. S16 Phonon dispersion relations in **a**: MnWO₄, **b**: FeWO₄, **c**: CoWO₄, **d**: NiWO₄, and **e**: ZnWO₄, computed via first principles.

above equation, C_λ and v_λ are computed within the harmonic approximation. τ_λ is computed as the inverse of the anharmonic phonon linewidths Γ_λ .

$$\tau_\lambda = \frac{1}{2\Gamma_\lambda} \quad (4)$$

Phonon linewidths, due to phonon–phonon interactions, are computed as the cumulative contribution of three-phonon scattering processes, including collision and decay events. The probability of each process is determined by the product of the three-phonon interaction strength, denoted $\Phi_{\lambda\lambda'\lambda''}$, and a set of terms that enforce energy conservation.

$$\Gamma_\lambda = \frac{18\pi}{\hbar^2} \sum_{\lambda'\lambda''} |\Phi_{\lambda\lambda'\lambda''}|^2 \times \{ (n_{\lambda'} + n_{\lambda''} + 1) \delta(\omega_\lambda - \omega_{\lambda'} - \omega_{\lambda''}) + (n_{\lambda'} - n_{\lambda''}) [\delta(\omega_\lambda + \omega_{\lambda'} - \omega_{\lambda''}) + \delta(\omega_\lambda - \omega_{\lambda'} + \omega_{\lambda''})] \} \quad (5)$$

where ω_λ are the phonon frequencies and n_λ are the mode occupation numbers.

The Debye–Klemens–Callaway model for thermal conductivity: The temperature dependence of the thermal conductivity tensors κ_{xx} , κ_{yy} and κ_{zz} , as well as their isotropic average $\bar{\kappa} = (\kappa_{xx} + \kappa_{yy} + \kappa_{zz})/3$ is presented with a logarithmic scale in Fig. S17. Before fitting the computed data to align with the experimental results, it is evident that the relative differences in peak values of the average thermal conductivity among the parent phases exhibit a trend similar to the experimental observations. However, this underscores the crucial importance of understanding the intrinsic phonon scattering mechanisms that govern the thermal conductivity (Fig. 4a), particularly within the 50–100 K temperature range. The Debye model [24, 25], formulated for mono- and polycrystal samples, describes an expression for thermal conductivity. To further investigate the individual contributions of various phonon scattering mechanisms, the Debye–Klemens–Callaway (DKC) model [26] has been used. The simplified dependencies of the phonon–boundary, phonon–defect, and phonon–phonon scattering lifetimes on frequency and temperature, discussed by Klemens [27], are $\tau_b^{-1} = B$, $\tau_d^{-1} = D\omega^4$, and $\tau_p^{-1} = UT^3\omega^2e^{-a/T}$, respectively, where B , D , U , and a are constants. This formulation captures both normal and Umklapp phonon scattering within a single expression τ_p . In first-principles phonon calculations, only the relaxation time of the three-phonon scattering could be directly computed using the harmonic and anharmonic interatomic force constants (Fig. S18), and the calculations do not represent boundary, defect or other scattering mechanisms.

A comparison between the thermal conductivity values obtained through experiments vs. calculations is presented in Fig. S19. Computed properties (three-phonon scattering lifetimes, frequencies, specific heat capacities, and Debye temperatures) were used as model inputs and to align the theoretical fits for thermal conductivity with the experimental values for NiWO_4 , CoWO_4 , MnWO_4 , FeWO_4 , and ZnWO_4 , which allowed the extraction of parameters such as the phonon–defect scattering lifetime; a crucial parameter in capturing the contribution of chemical disorder to the ultra-low thermal conductivity observed in A^6WO_4 . The Debye temperatures Θ_D of the parent phases were determined by fitting the heat capacities C_λ , obtained from phonon calculations, to the Debye model [28]. We employed a multi-method optimization approach to determine the scattering parameters (B , D , P) that minimize the squared difference between the model predictions and experimental measurements:

$$\min_{B,D,N} \sum_i [\kappa_{\text{model}}(T_i; B, D, P) - \kappa_{\text{exp}}(T_i)]^2 \quad (6)$$

subject to physical constraints ($B, D, P > 0$). The computed errors associated with the model along with the Debye temperatures and frequencies and sound velocities are presented in Table 2. The phonon properties of A^6WO_4 were estimated by averaging the corresponding properties of the chemically ordered parent phases. Specifically, phonon frequencies, group velocity tensors, and heat capacities were averaged from parent phases. The thermal conductivity was then computed using the DKC model, summing over all phonon modes and q-points while incorporating the averaged phonon properties. Finally, the total thermal conductivity was weighted by the q-point weights and then normalized to ensure consistency with experimental data.

Table 2 Supplementary information on the thermal conductivity modeling for parent compounds and A^6WO_4 : Debye temperatures (Θ_D), Debye frequencies (ω_D), sound velocities (ν_s), and the corresponding mean absolute error (MAE) and root mean squared error (RMSE) values for the fits.

Material	DKC Parameters			Fitting Errors	
	Θ_D (K)	ω_D (THz)	ν_s (m/s)	MAE (W/K-m)	RMSE (W/K-m)
MnWO ₄	385	8.02	3850	0.32	0.41
FeWO ₄	375	7.81	3800	0.27	0.35
CoWO ₄	365	7.60	3750	0.20	0.24
NiWO ₄	370	7.71	3780	0.17	0.25
ZnWO ₄	310	6.46	3400	0.64	0.81
A^6WO_4	348	7.25	3530	0.01	0.01

Phonon scattering mechanisms: Phonon–phonon scattering generally dominates at high temperatures where more thermal energy results in more transverse phonons and decreases in strength with decreasing temperature, and the phonon–boundary term results in an overall shift in the magnitude of κ_{ph} in the DKC model for all samples without temperature dependence. In the high-entropy phase, the phonon–defect term is affected by the increase in configurational entropy, which leads to increased lattice defects. Lattice defects in high-entropy materials come in a number of forms, including the variance of cation masses and atomic radii, ionic displacements, changes in interatomic force potentials and the variance in length, strength, or angle of interatomic bonds [29, 30]. Such defects cause τ_d to be substantially smaller in A^6WO_4 . This is consistent with the observed thermal conductivity of A^6WO_4 which is 1 – 2 orders of magnitude lower than any parent compound at or above T_{max} even though the high-entropy phases have an additional electronic contribution to κ due to being semiconductors. Beyond the decrease in magnitude, the peak strength and location are substantially different, indicating that the effect of phonon–defect scattering is so strong that it still dominates even at high temperatures where we would usually expect phonon–phonon interactions to have the largest effect. This also raises the question of why certain parent phases exhibit higher three-phonon scattering relaxation times. Given that phonon–phonon scattering lifetimes are intrinsically linked to atomic structure and bonding characteristics, factors such as atomic mass, bond strength, and bond length warrant closer examination to better understand the differences in thermal conductivity in specific temperature ranges. The A –O bond lengths are presented in Fig. S20.

Discussion on defect scattering: By “defects”, we specifically refer to the chemical disorder arising from the presence of multiple cation species occupying a single sublattice in the high-entropy structure. This aligns with the unique characteristics in high-entropy materials, where the coexistence of multiple cations inherently introduces structural complexity. In this context, the configurational entropy leads to significant variations in the local bonding environment, which disrupts the periodicity of the lattice and effectively allows for non-conserving phonon–phonon and phonon–defect scattering. This definition does not correspond to conventional point defects such as vacancies or interstitials but rather to a spatially random arrangement of cations with different sizes, charges, and electronegativities. The resulting fluctuations in masses, bond lengths, and force constants create a complex environment that allows for massive phonon scattering. Thus, the ultra-low thermal conductivity observed in A^6WO_4 is intrinsically tied to the chemical disorder that defines the high-entropy nature.

Looking at Fig. S21a, excluding parent-averaged three-phonon scattering from the DKC model reveals that defect scattering alone could be sufficient to yield ultra-low thermal conductivity in A^6WO_4 , while replacing the parent-averaged Umklapp and normal processes as well as the small correction term with a wavevector non-conserving term $\tau_{\mathcal{N}}^{-1} = \mathcal{N}T^3\omega^2$ (Fig. S21b) helps capture the low-temperature profile. Hence, as the tungstate transitions to a high-entropy phase, phonon scattering shifts from Umklapp-dominated to defect-driven mechanisms and wavevector non-conserving three-phonon channels that are opened up due to disorder, drastically reducing the thermal conductivity. Fig. S21c illustrates the temperature dependence of thermal conductivity in a representative parent phase, ZnWO_4 , highlighting the influence of various scattering mechanisms. The thermal transport behavior of ZnWO_4 can also be substantially influenced by variations in the isotopic composition. The effect of mass variation at atomic sites due to isotopes on the thermal conductivity of ZnWO_4 using Tamura’s second-order perturbation theory for mass-disorder scattering [31] has also been simulated, which is presented here for demonstration purposes only and is not present in the original fit.

$$\frac{1}{\tau_{\lambda}^{\text{iso}}(\omega)} = \frac{\pi\omega_{\lambda}^2}{2N} \sum_{\lambda'} \delta(\omega - \omega_{\lambda'}) \sum_{\kappa} g_{\kappa} \left| \sum_{\alpha} W_{\kappa\alpha}^*(\lambda') W_{\kappa\alpha}(\lambda) \right|^2 \quad (7)$$

The natural isotopic diversity of ZnWO_4 ’s components makes the mass variance parameter g_{κ} especially relevant. With zinc possessing five stable isotopes (^{64}Zn through ^{70}Zn), this parameter is calculated as:

$$g_{\kappa} = \sum_i f_i \left(1 - \frac{m_{i\kappa}}{\sum_j f_j m_{j\kappa}} \right)^2 \quad (8)$$

Here, f_i represents the isotopic mole fraction and $m_{i\kappa}$ denotes the atomic weight at the site κ . The total phonon relaxation time combines intrinsic anharmonic effects with isotope scattering via Matthiessen’s rule.

$$\frac{1}{\tau_{\lambda}^{\text{total}}} = \frac{1}{\tau_{\lambda}} + \frac{1}{\tau_{\lambda}^{\text{iso}}(\omega_{\lambda})} \quad (9)$$

In ZnWO_4 , isotope scattering significantly reduces thermal conductivity in the 50-150 K range compared to isotopically pure crystals. Systematically quantifying phonon–defect scattering processes is crucial to understanding κ_{latt} suppression in high-entropy materials like A^6WO_4 , where cation mass and size variations create strain field fluctuations and multiple phonon scattering pathways. Despite large mass-disorder typically enhancing anharmonic phonon scattering, high-entropy oxides exhibit small thermal expansion coefficients, indicating conventional anharmonicity. Thus, the temperature-independent κ_{latt} reduction, particularly in those with 5- to 6-cation compositions, likely stems from interatomic force constants disorder rather than enhanced anharmonicity [23, 32–35].

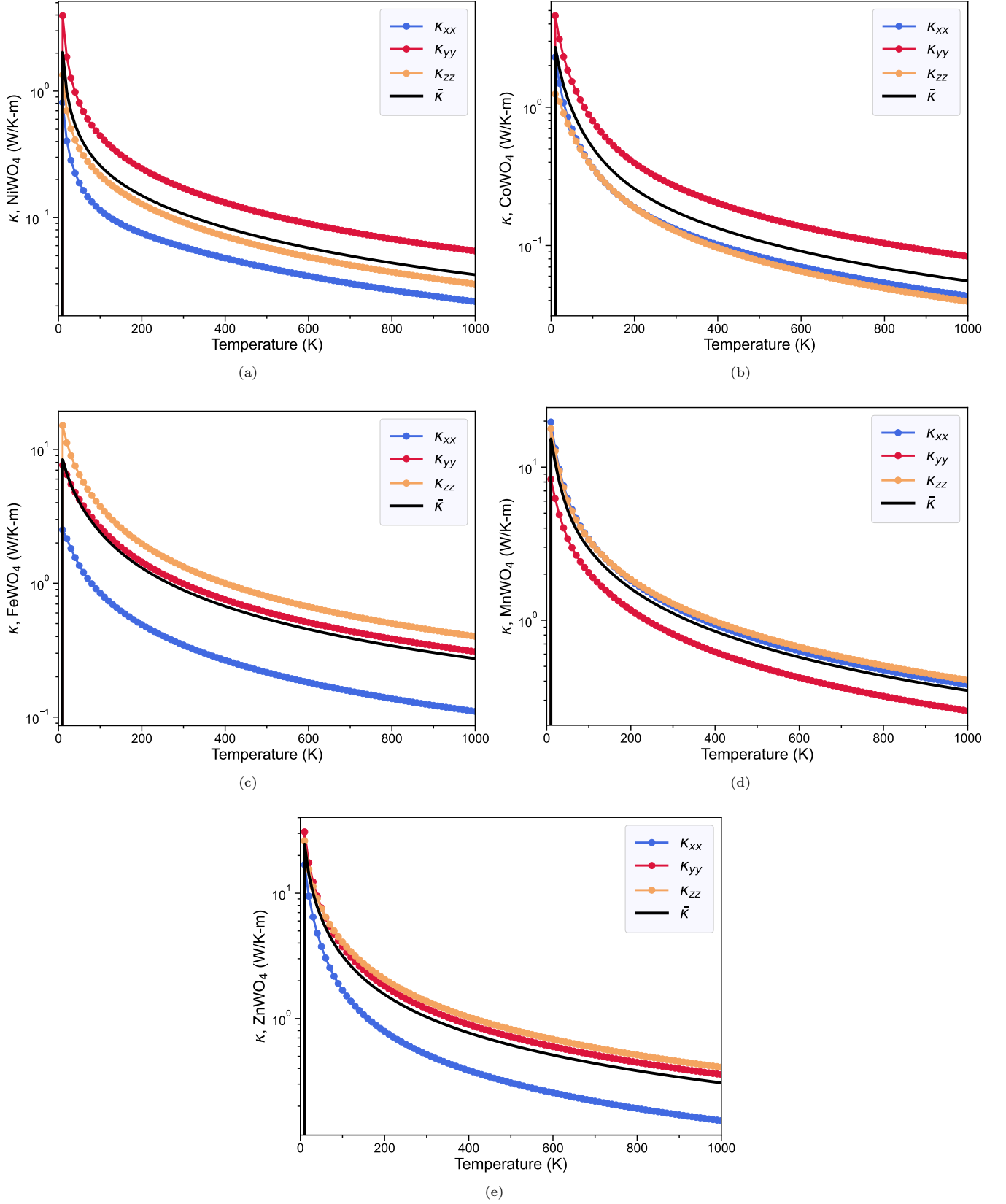


Fig. S17 Log-scaled diagonal κ_{xx} , κ_{yy} and κ_{zz} components of κ_{latt} and the isotropic average $\bar{\kappa}$ plotted against temperature for **a:** NiWO_4 , **b:** CoWO_4 , **c:** FeWO_4 , **d:** MnWO_4 , and **e:** ZnWO_4 . These plots correspond to the computed lattice thermal conductivity tensors only, and are not used in the DKC model fitting.

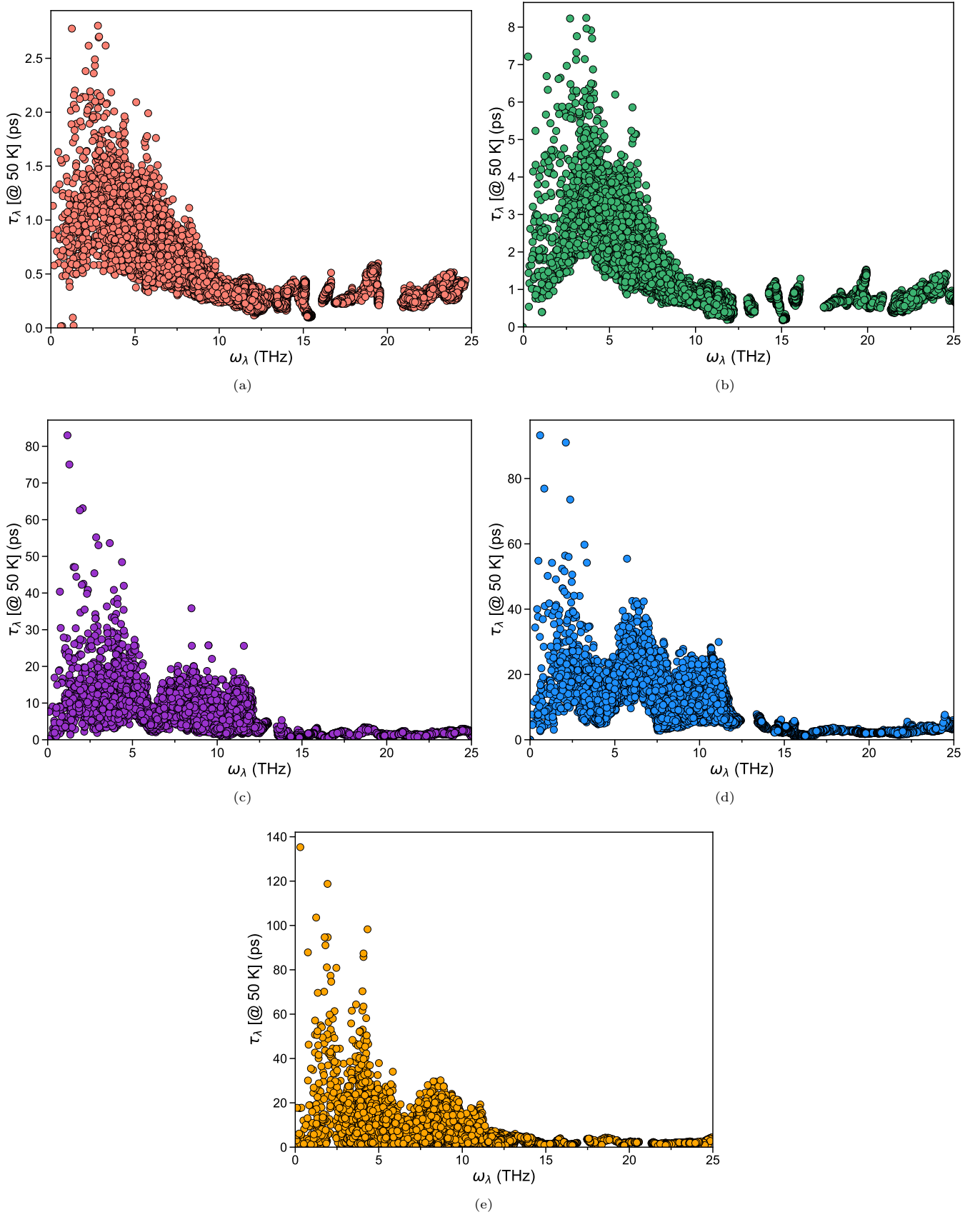


Fig. S18 Frequency-dependent distribution of phonon–phonon scattering lifetimes for parent phases at 50 K computed from first principles, demonstrating a key process that begins to suppress the thermal conductivity in crystalline materials at higher temperatures: **a:** NiWO_4 , **b:** CoWO_4 , **c:** FeWO_4 , **d:** MnWO_4 , and **e:** ZnWO_4 .

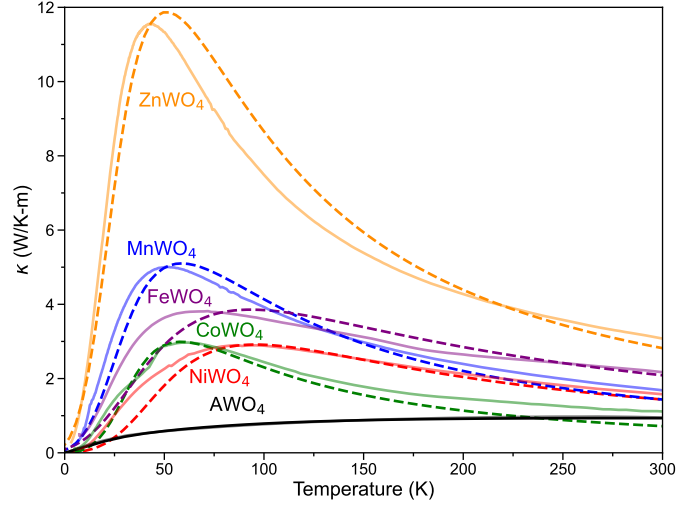


Fig. S19 Temperature-dependent thermal conductivity of $A^6\text{WO}_4$ and its parent compounds ($A = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \& \text{Zn}$): experimental data (solid lines) compared with first-principles calculations (dashed lines) using the Debye–Klemens–Callaway model with anharmonic force constants derived from first principles.

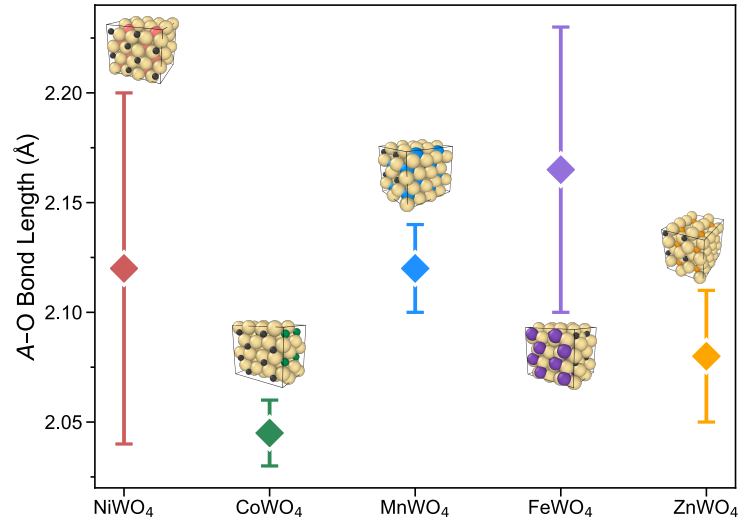


Fig. S20 A–O bond-lengths among $A^6\text{WO}_4$ parent phases ($A = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \& \text{Zn}$).

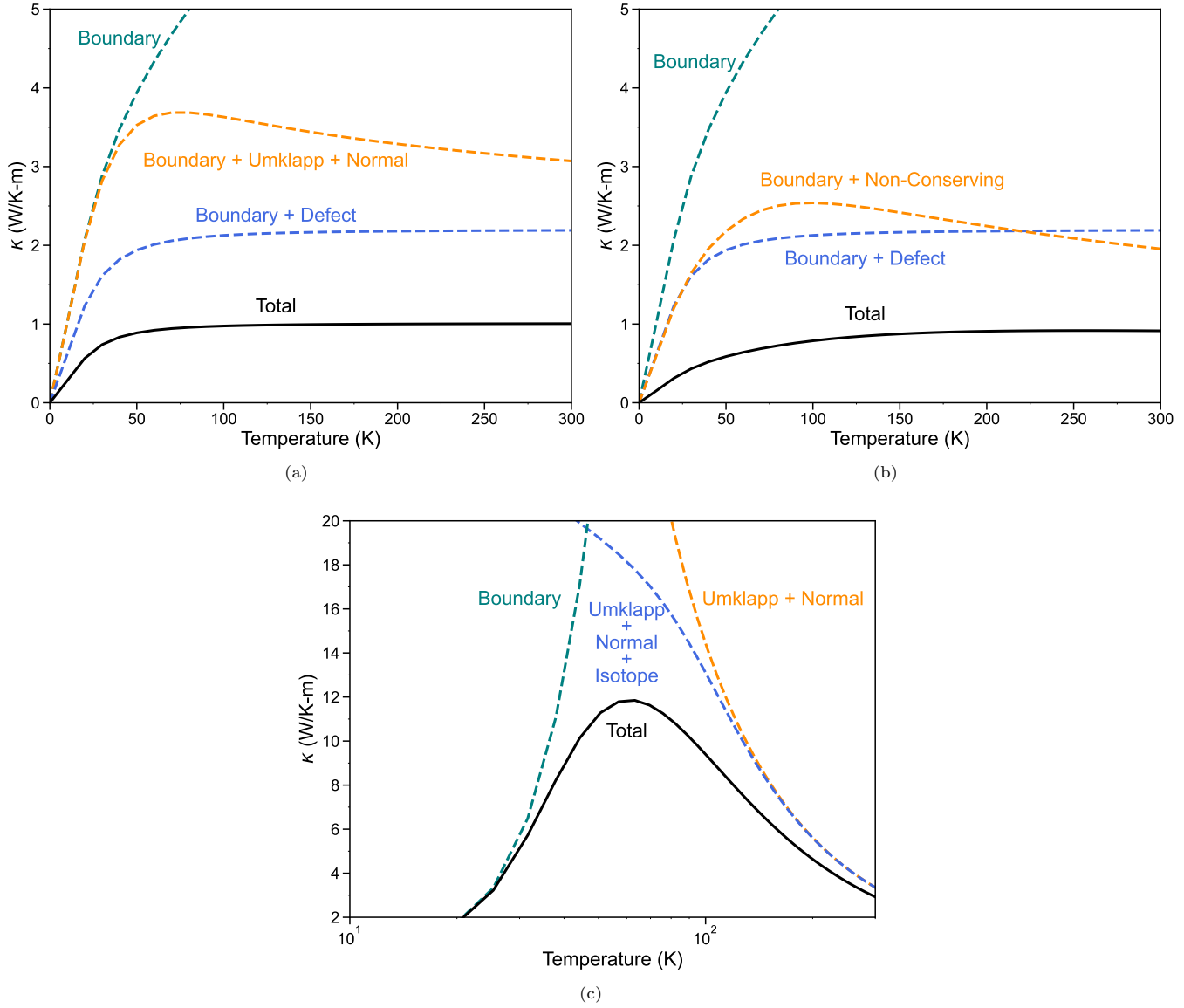


Fig. S21 Analysis of scattering processes in the temperature-dependent thermal conductivity: **a:** A^6WO_4 illustrating parent-averaged phonon-phonon scattering and defect scattering; **b:** A^6WO_4 reanalyzed with a non-conserving phonon scattering process replacing Umklapp and normal scattering; **c:** ZnWO_4 showing distinct contributions from Umklapp and normal scattering, boundary scattering, and isotope scattering (as an example of mass-disorder).

S6 Transmission Electron Microscopy

Transmission electron microscopy (TEM) was done on $A^6\text{WO}_4$ along the $[111]$ zone axis. Due to the polycrystalline nature of the material, we were limited in the orientation of the sample but were nonetheless able to resolve the A site and W atoms in the lattice. High Angle Annular Dark Field-Scanning Transmission Electron Microscopy (HAADF-STEM) and Fast Fourier Transform data agree with the crystal structure determined by X-ray diffraction (Fig. S23).

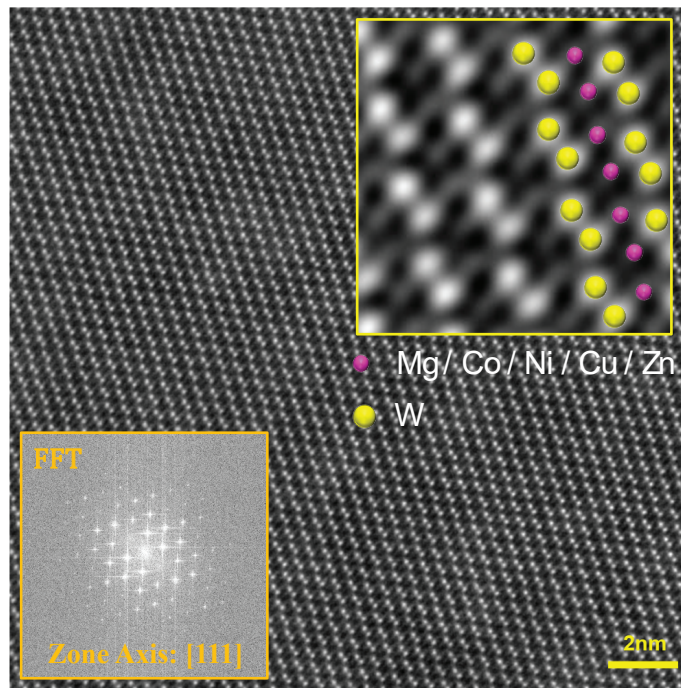


Fig. S22 Drift Corrected HAADF-STEM image and Fast Fourier Transform (FFT) of $A^6\text{WO}_4$ confirming $P2/c$ crystal structure. The yellow inset is zoomed in bandpass-filtered STEM image to highlight the cations in the structure. Since W has the highest atomic number in the system, all the other cations have low intensity in the HAADF-STEM image. The orange inset corresponds to Fast Fourier Transform of STEM image.

S7 Other Characterization of $A^6\text{WO}_4$ Samples

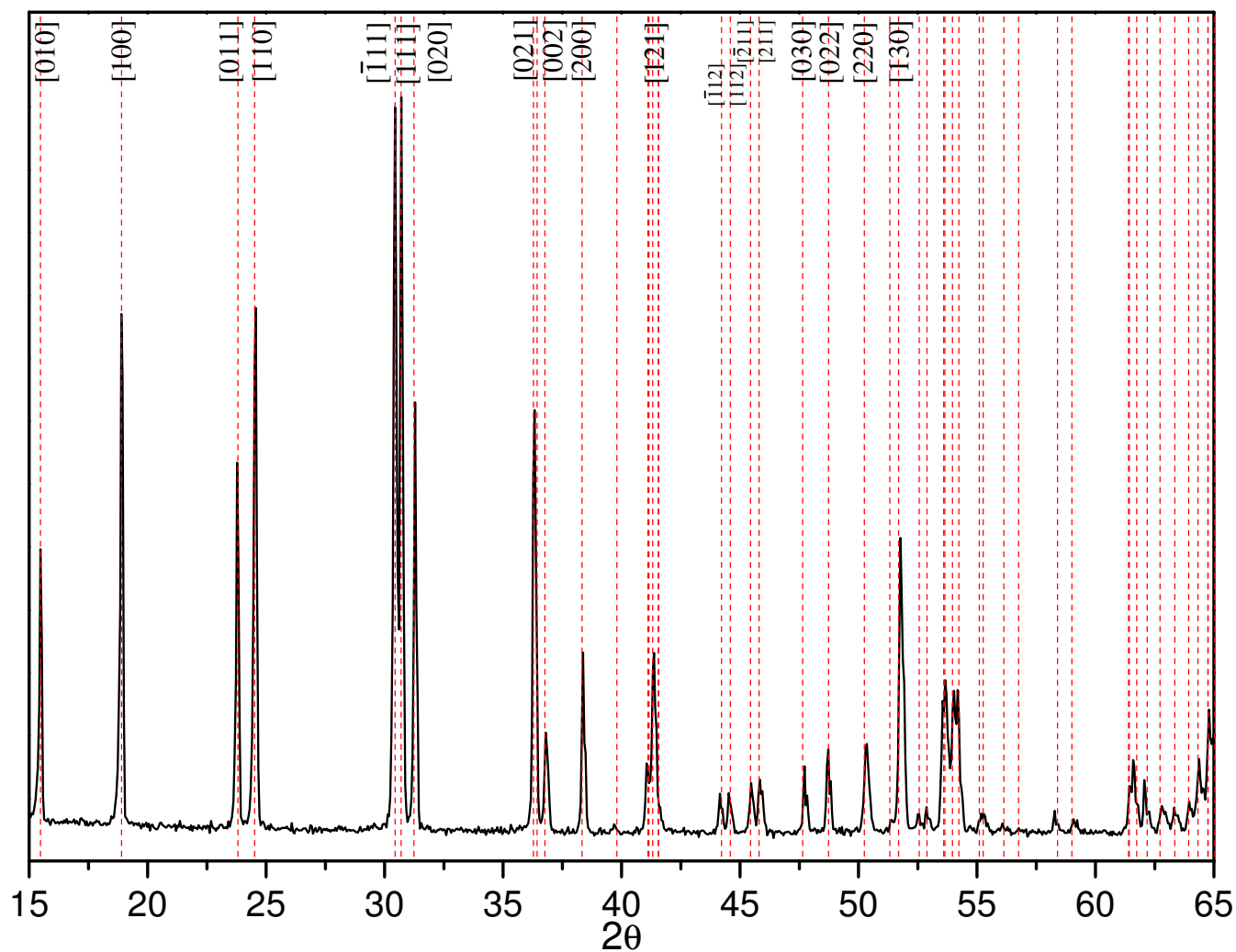


Fig. S23 Experimental X-ray diffraction data for A^6WO_4 , calculated peak positions (dashed red lines) and indices of major peaks are also included. The experimental and calculated peaks are in good agreement, indicating that the A^6WO_4 sample is phase pure.

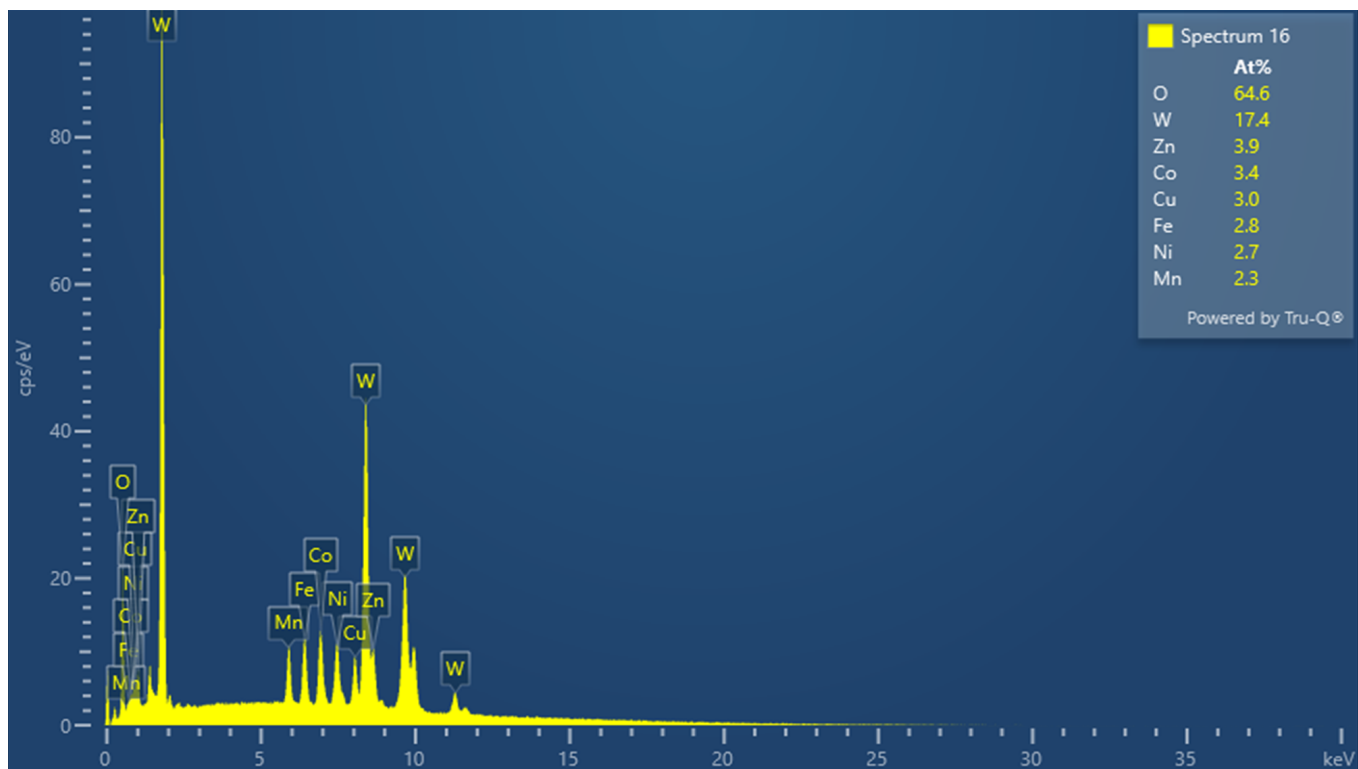


Fig. S24 Quantitative atomic percentage results for A^6WO_4 via Scanning Electron Microscope Energy Dispersive X-ray Spectrometry (EDX) at millimeter scale. All 6 A site cations are present in the same proportions and close to a 1:1 ratio with W. EDX is not able to accurately find atomic percentage of oxygen, hence the under-reporting.

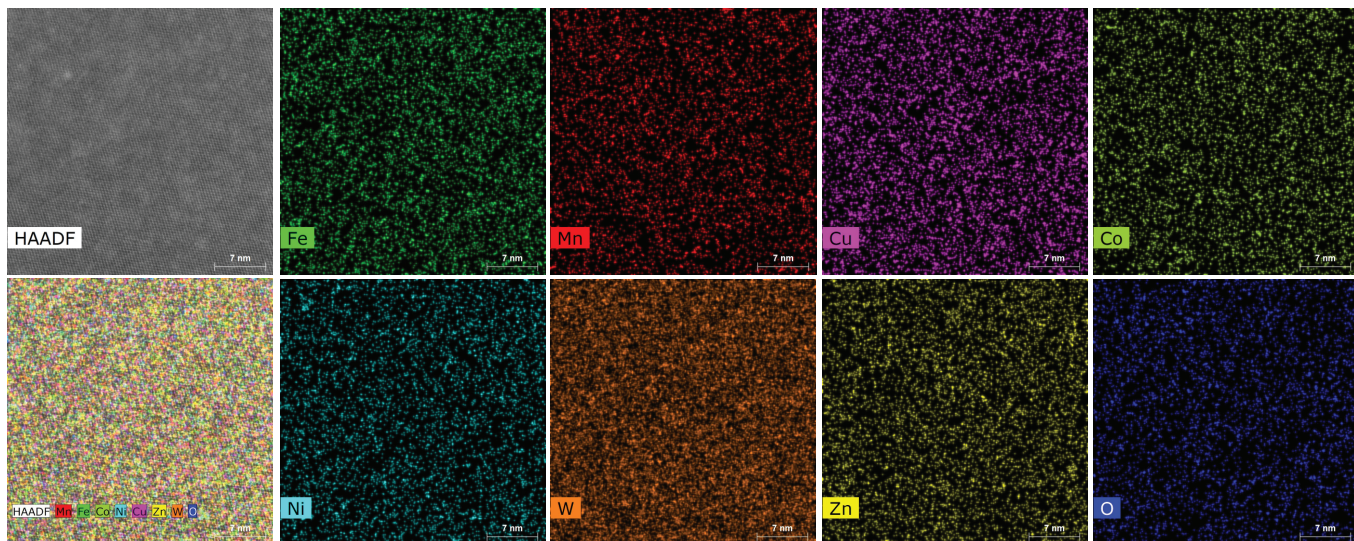


Fig. S25 High-Angle Annular Dark-Field imaging - Scanning Transmission Electron Microscopy (HAADF-STEM) and EDX elemental maps for A^6WO_4 . HAADF shows good crystallinity and maps show an even distribution of each element indicating that the sample is homogeneous at this scale.

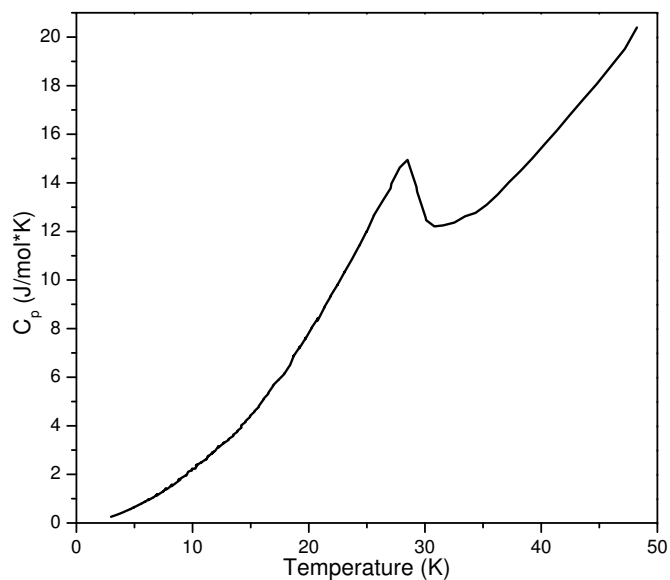


Fig. S26 Specific Heat vs. Temperature for A^6WO_4 . The peak near 30 K corresponds to the antiferromagnetic transition in the material.

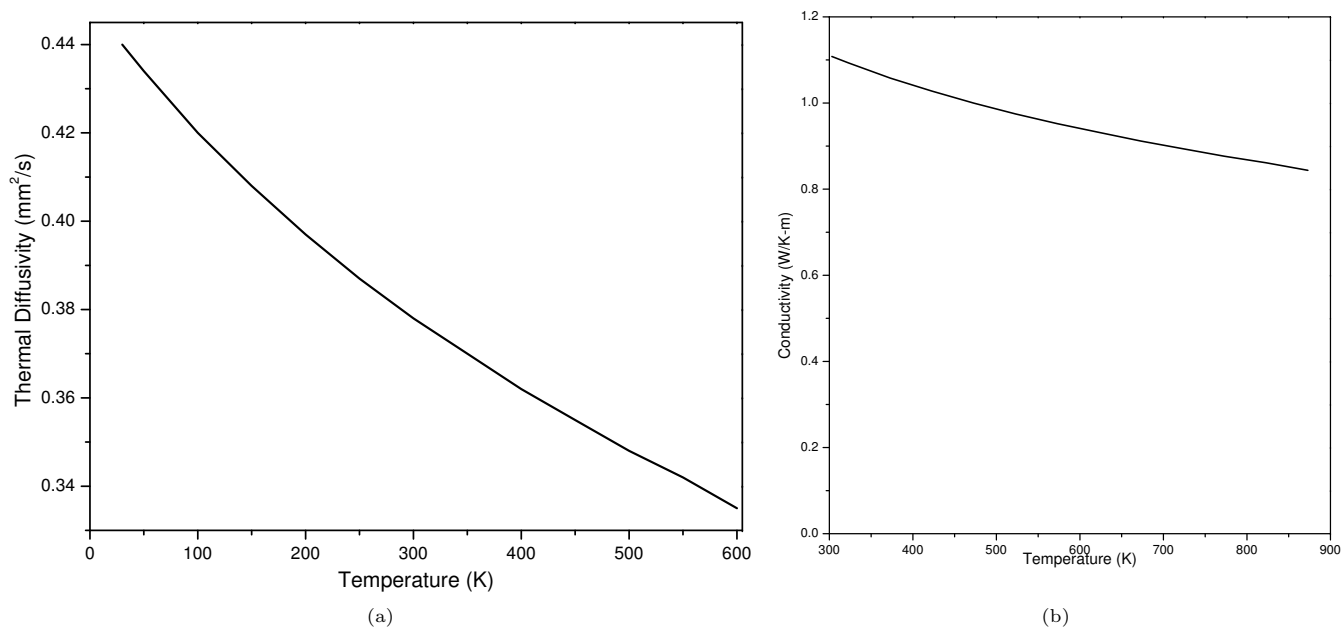


Fig. S27 **a:** Thermal Diffusivity vs. Temperature for A^6WO_4 from 300-900 K. **b:** κ vs. Temperature for A^6WO_4 from 300-900 K. Calculated from thermal diffusivity data.

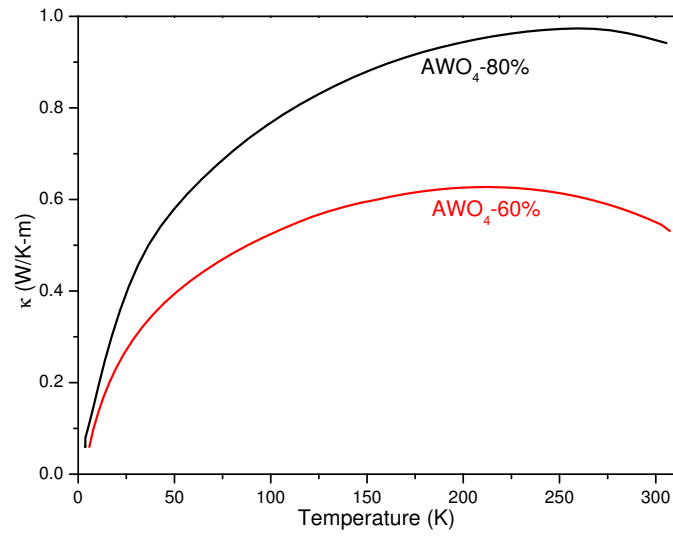


Fig. S28 Thermal conductivity of A⁶WO₄ samples of different densities. Even with large variance in sample density, the magnitude of the thermal conductivity is similar.

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