Supplementary Information: Structural diversity of $CuZn_2InSe_4$ quaternary chalcogenide: electronic and phonon properties from first principles

Long Ma,[1] Wencong Shi,[2] and Lilia M. Woods[1]

[1]*Department of Physics, University of South Florida, Tampa, Florida 33620, USA*

[2]*School of Biological Sciences, Nanyang Technological University, Singapore 639798, Singapore.*

To supplement our results for the energy band structure and DOS, in Figure S2 we show the $s-p-d$ orbitally projected DOS for some of the Cu, In, and Se atoms responsible for most contributions around the energy band gap for the different phases.

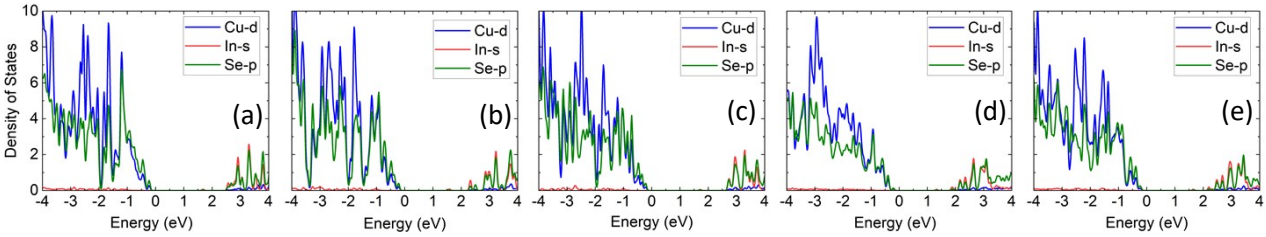

Figure S1. Orbitally projected Density of States (DOS) for $Cu-d$, $In-s$ and $Se-p$ orbitals in (a) KS, (b) PMCA, (c) ST, (d) WKS, and (e) WST phases.

We also present calculations for the conductivity of the considered structural phases of $CuZn_2InSe_4$ using the BoltzTrap code[1], which relies on a constant relaxation approximation. In general, this is a good approximation as long as the energy changes are at a smaller scale as compared to the energy changes in the density of states, which is typically the case for metals and many semiconductors[2]. The input files for the BoltzTrap calculations are generated via the VASPkit[3]. For the transport calculations, the Fermi level is taken as 0.0 eV and the energy grid is set to be 0.0068 eV (0.0005 Ry). The energy cutoff range is about 2.04 eV (0.15 Ry) around the Fermi level. The symmetries of the phases are verified by FINDSYM[4]. After the simulations, the conductivities and the corresponding chemical potentials are extracted at room temperature (300K). In Figure S2, the ratio σ/τ of the electrical conductivity and constant relaxation time τ is shown as a function of chemical potential. For the different structural phases, which clearly reflect their semiconducting band structure.

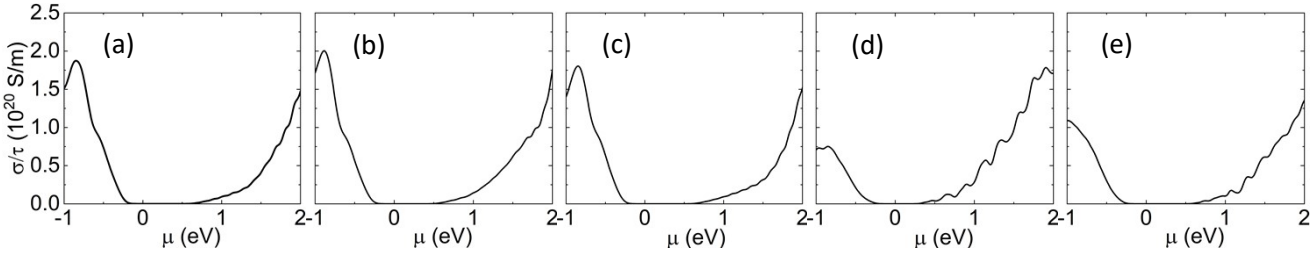

Figure S2. Calculated ratio of the electrical conductivity σ and constant relaxation time τ as a function of chemical potential μ at $T = 300$ K for (a) KS, (b) PMCA, (c) ST, (d) WKS, and (e) WST phases of the $CuZn_2InSe_4$ compound.

Convergence tests for the vibrational properties of this material are also performed. One of the properties that affects the results for the thermal conductivity is the phonon q-grid used in the calculations for the interatomic force constants. All results in the main text are obtained with $(6 \times 6 \times 6)$ q-grid, and in Figure S3 (a) we show κ_{xx} for the KS phase for several other choices. As the grid becomes denser, the deviations in κ_{xx} become smaller. Figure S3 (b) shows that there is about 5% difference between κ_{xx} found with $(6 \times 6 \times 6)$ q-grid and κ_{xx} found with $(7 \times 7 \times 7)$ q-grid. Given the structural similarities of the different phases, it is reasonable to conclude that the $(6 \times 6 \times 6)$ q-grid utilized for the calculations in the main text gives results with good accuracy.

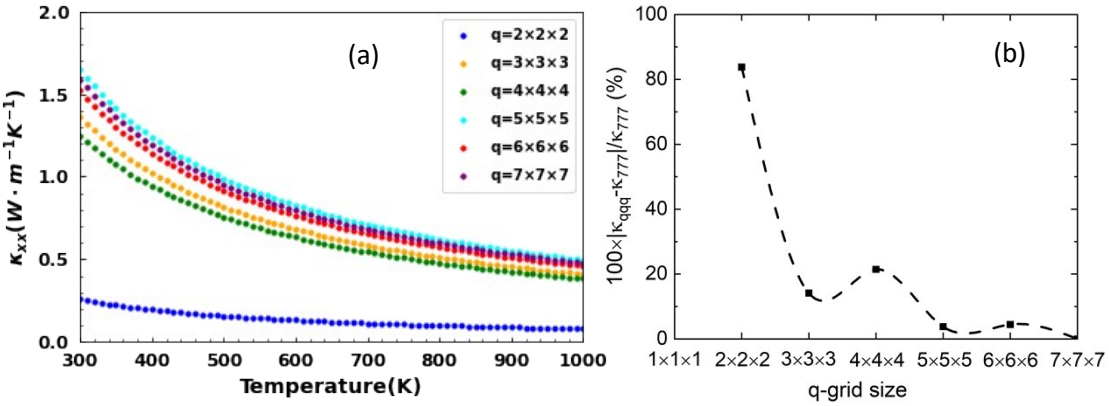

Figure S3 (a) Lattice thermal conductivity along the $x-$ axis for the $CuZn_2InSe_4$ KS phase for different phonon q-grids; (b) Relative difference of κ_{xx} for the $CuZn_2InSe_4$ KS phase at $T = 300$ K as a function of the q-grid.

The numerical results for the lattice thermal conductivity are also affected by the separation between the atoms that are being displaced as implemented in the PHONO3PY code. In Figure S4 (a), we show how the lattice thermal conductivity along the x-axis for the $CuZn_2InSe_4$ KS phase behaves as a function of temperature at different cutoff displaced atomic pair distances. The calculations show that there is about 8% difference between κ_{xx} at 6 Å and 7 Å (Figure S4 (b)). This indicates that the 6 Å cutoff distance used for the simulations in presented in the main text have very good accuracy within the utilized numerical approach.

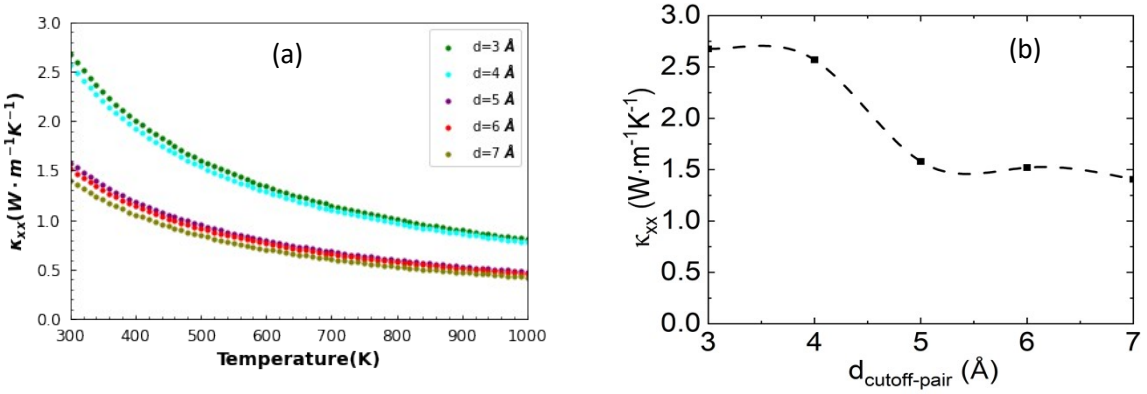

Figure S4. Lattice thermal conductivity along the $x-$ axis for the $CuZn_2InSe_4$ KS phase for varied cutoff-pair distances: (a) as a function of temperature, (b) as a function of cut-off pair distance at $T = 300$ K.

References:

1 G. K. H. Madsen and D. J. Singh, *Computer Physics Communications*, 2006, **175**, 67–71.

2 D. Parker and D. J. Singh, *Physical Review B - Condensed Matter and Materials Physics*, 2010, **82**, 035204.

3 V. Wang, N. Xu, J. C. Liu, G. Tang and W. T. Geng, *Computer Physics Communications*, 2021, **267**, 108033.

4 H. T. Stokes and D. M. Hatch, *J. Appl. Cryst*, 2005, **38**, 237–238.