#### Supplementary Text for:

# Partial Indium solubility induces chemical stability and colossal thermoelectric figure of merit in Cu<sub>2</sub>Se

A. A. Olvera,<sup>a</sup> N. A. Moroz<sup>a</sup>, P. Sahoo<sup>a</sup>, P. Ren<sup>b</sup>, T.P. Bailey<sup>b</sup>, A. A. Page<sup>b</sup>, C. Uher<sup>b</sup>, P. F. P Poudeu<sup>a,\*</sup>

<sup>a.</sup> Laboratory for Emerging Energy and Electronic Materials, Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI, 48109, USA.

<sup>b.</sup> Department of Physics, University of Michigan, Ann Arbor, MI, 48109, USA.

\* Correspondence to: ppoudeup@umich.edu

# <u>DSC</u>

Differential scanning calorimetry was performed using a Netzsch DSC 404 F1 Pegasus. Approximately 20-30 mg of sample was sealed in a rounded quartz crucible under 1 mtorr. An empty quartz crucible sealed under the same conditions was used as a reference. Measurements were cycled twice from 300 K to 1473 with a heating and cooling rate of 10 K/min.

# <u>SEM</u>

Scanning electron microscopy was performed using a JEOL-7800FLV FE SEM equipped with an Oxford EDAX system operating between 15 and 25 keV for all imaging and electron dispersive spectroscopy mapping. Focused ion beam (FIB) samples for STEM were prepared using an FEI Helios 650 nanolab SEM/FIB.

# STEM

An aberration corrected field emission JEOL 2100f operating at 200 kV was used for High-Angle Annual Dark Field (HAADF) imaging of selected samples. Samples were prepared by wedge polishing using a T-tool by Precision TEM, Inc. and focused ion beam.

# <u>XPS</u>

X-ray photoelectron spectroscopy data was obtained using a Kratos Axis Ultra XPS equipped with a monochromatic Al source (15 kV, 10 mA). Wide scans were acquired using an analyzer pass energy of 160 eV at 1 eV steps. Selected regions were scanned using a pass energy of 10 eV at 0.02 eV steps. Specimens were loaded into the transfer chamber and allowed to evacuate for a 12-hour period reaching less than 5 x  $10^{-7}$  torr. The analysis chamber was kept at approximately 1 x  $10^{-9}$  torr during measurement. Post processing analysis was performed using Casa XPS, where the binding energy (BE) was calibrated to the C 1s (284.4 eV) peak.

# Heat capacity

Specific heat capacity data was measured from 325 K to 750 K under 20 ml/min of argon flow using a Netzsch DSC 404 F1 Pegasus. A Netzsch certified sapphire sample was used for calculating the heat capacity via the ratio method. The heat capacity value was assumed to be constant between at 750 K and 850 K.

# Hall effect

**Fig. S7C** shows a log scaled plot of mobility vs temperature showing the temperature dependence of mobility approximated by the general equation  $\mu \propto T^{r-\frac{3}{2}}$ , where T is the absolute temperature and r is the exponent reflecting the energy dependence of the carrier mean free path. In Fig. 7D, calculation of effective mass assumes a single parabolic band model and scattering parameter A = 1.5 corresponding to the electron scattering mechanism.

#### Electromigration test for chemical stability

Electromigration stability tests were conducted with a custom-built apparatus and monitored via optical microscopy. Hot pressed samples of  $Cu_2Se$  and  $Cu_2Se-1$  mol % In were cut and polished into rectangular prisms with dimensions of  $1.88 \times 1.53 \times 6.73$  mm and  $1.98 \times 1.56 \times 6.91$  mm, respectively. Samples were mounted between graphite electrodes and held up by two metal clamps that provided a gentle, but secure compressive force. Graphite foil was used to ensure a full contact was made between the sample and electrode surface. The graphite electrodes were attached to a ceramic thermal sink, which helped maintain a constant sample temperature. This apparatus was firmly rested on a hot plate, where temperature was monitored via a thermocouple inserted into the ceramic heat sink. Current was provided via a constant current source, where current was adjusted on a sample-to-sample basis to ensure correct current density.

Stability tests were performed in ambient air over 24 hours at a temperature of ~ 523 K and an applied current density of 100 A cm<sup>-2</sup>, which is considered as accelerated conditions for stability testing. Due to the large currents applied to both samples it is expected that the samples increased in temperature higher than the measured base temperature.

#### Reliability of ZT measurement

When considering the reliability of ZT values it is important to evaluate the consistency of the temperature dependent terms in the figure of merit, which are the electrical conductivity ( $\sigma$ ), Seebeck coefficient (S), and thermal conductivity (k). The consistency of electrical conductivity and Seebeck coefficient can be summarized by the reliability of the power factor,  $\sigma S^2$ . To demonstrate the power factor stability of the highest ZT material several heating and cooling cycles from approximately 300 K to 850 K were measured (see Fig. S8). The power factor differs from the initial run but remains consistent amongst subsequent runs, where the most typical error comes from errors in sample dimension. However, the trend from three heating and two cooling cycles show that the power factor is stable within the measured temperature range. In terms of thermal conductivity, three factors play an important role: the density (r), thermal diffusivity (D), and the specific heat capacity ( $C_{0}$ ). The density of the materials was measured with a commercial helium pycnometer (Quantachrome Micro Ultrapyc 1200e pycnometer) and averaged over 20 runs in order to get the most precise value, where the pycnometer has a machine accuracy of  $< \pm 0.30\%$ . Additionally, heat capacity via differential scanning calorimetry was measured three times, where very little deviation was observed (< ± 2%). Lastly, the laser flash method was used to measure thermal diffusivity, where the laser flash method provides an accuracy of ± 5%. Consequently, the total error in ZT is minimized through the use of these methods, which provides a reliable method for ZT calculation.



**Fig. S1** Chemical transformation of  $CuSe_2$  template into CS/CIS composites. X-ray diffraction (XRD) study of the two step reaction, (**A**)  $CuSe_2 + x \ln$  and (**B**) (1-x) $CuSe_2 + 3x Cu$ . (**C**) Corresponding XRD graphs of the pelletized samples consolidated by uniaxial hot-pressing at 600 ° C.



**Fig. S2** Cu<sub>2</sub>Se - CuInSe<sub>2</sub> phase diagram and DSC of  $(1-x)Cu_2Se/(x)CuInSe_2$  samples. (**A**) Experimental phase diagram of pseudo binary system Cu<sub>2</sub>Se – CuInSe<sub>2</sub>. At low concentrations of indium, Cu<sub>2</sub>Se becomes a better solvent for indium as a function of temperature. It should be noted that the Cu<sub>2</sub>Se  $\alpha$ -to- $\beta$  transition temperature is predicted to remain constant for any multicomponent Cu<sub>2</sub>Se-CuInSe<sub>2</sub> composition. This is confirmed by differential scanning calorimetry (DSC) measurements (**B**) for all (1-x)Cu<sub>2</sub>Se/(x)CuInSe<sub>2</sub> samples, and it shows that the  $\alpha$ -to- $\beta$  transition temperature remains at approximately 400 K. The melting temperature of the Cu<sub>2</sub>Se matrix in various (1-x)Cu<sub>2</sub>Se/(x)CuInSe<sub>2</sub> composites gradually decreases with the increasing CIS content for samples with x ≤ 0.3. This is probably due to the intimate mixing in these composites between the high melting Cu<sub>2</sub>Se matrix and the lower melting CIS phase. Endothermic is down.



**Fig. S3** Backscattered electron micrographs and associated electron dispersive spectroscopy maps of selected  $(1-x)Cu_2Se/(x)CuInSe_2$  samples. (**A**) 1 mol % In; (**B**) 10 mol % In; (**C**) 50 mol % In. At a concentration of 1 mol %, Indium is fully soluble in  $Cu_2Se$  as is evident by the homogenous spread of In. At 10 and 50 mol %, Indium is partially incorporated into the  $Cu_2Se$  matrix, but is clearly phase separated into CuInSe<sub>2</sub>. At 10 mol % In, CuInSe<sub>2</sub> (CIS) phase morphology consists of various micron-scale agglomerations with no distinct grain shape. Further increasing to 50 mol % In, there is still various micron-scale agglomerations of CuInSe<sub>2</sub>, but with a high degree of connectivity between adjacent CIS agglomerations. The size distribution and indistinct shape of CIS agglomerates. Further, SiO<sub>x</sub> particles from 10 nm to less than 1 nm are observed in all samples, where the 1 mol % sample shows the finest SiO<sub>x</sub> particle size.



**Fig. S4** X-Ray photoelectron spectroscopy (XPS) spectra of  $(1-x)Cu_2Se/(x)CuInSe_2$  composites. (A) Cu-2p, In-3d and Se-3d spectra of selected samples confirming the chemical state of copper (+1), indium (+3), and selenium (-2). All patterns were calibrated to the C 1s peak (284.4 eV) (B). It should be noted that the convolution of adventitious carbon peaks produces noticeable error in calibrating the sample containing 50 mol % CIS, which shows a shift to higher binding energies for all spectra including oxygen 1s peaks (B). This indicates that all shifts in the binding energy for that sample are not a result of differences in the oxidation state, but an intrinsic error in the C 1s calibration. Asterisk denotes satellite peaks corresponding copper oxide on sample surface.



**Fig. S5** Electronic properties of Cu<sub>2</sub>Se samples containing various mole fractions of indium up to 50 mol % In. (**A**) Temperature dependent electrical conductivity; (**B**) Temperature dependent Seebeck coefficient; (**C**) Effect of In content on electrical conductivity and carrier mobility; (**D**) Effect of In content on Seebeck coefficient and carrier density.



**Fig. S6** (**A**) Temperature dependent thermal conductivity and (**B**) figure of merit, ZT, for  $Cu_2Se$  samples containing various mole fractions of indium up to 50 mol % In.



**Fig. S7** Electronic transport in CS/CIS composites. **(A)** Temperature dependence of the carrier concentration of all samples extracted from Hall effect measurements. At 300K, the carrier concentration initially decreases upon incorporation of 1 mol% CIS and then gradually increases with a further addition of CIS. Samples containing more than 1 mol% CIS show an increase in the carrier concentration with rising temperature. Samples with large CIS content (30mol% and 50 mol%) showed the strongest temperature dependence of the carrier concentration. This unusual characteristic is possibly a result of carrier doping by the CuInSe<sub>2</sub> phase. **(B)** Temperature dependent Hall mobility calculated using the measured electrical conductivity and carrier concentration. Note the large increase in the mobility for the sample containing 1 mol % CIS compared to the pristine Cu<sub>2</sub>Se despite the small change in the carrier concentration. **(C)** Log-scale plot of the mobility as a function of temperature

indicating that the temperature dependence of the mobility follows the general equation  $\mu \propto T^{-\frac{1}{2}}$ , where T is the absolute temperature and r is the exponent reflecting the energy dependence of the carrier mean free path. From the experimental data, the mobility of pristine Cu<sub>2</sub>Se shows relatively weak energy dependence below the  $\alpha$ - $\beta$  transition temperature, which is proportional to T<sup>-1</sup>. After the structural transition, a T<sup>-3</sup> dependence is observed, presumably due to the high interaction of mobile and disordered copper ions with the charge carriers. For the sample with 1 mol % CIS, the mobility proportionality begins with T<sup>-2</sup> before the structural transition and on average maintains the T<sup>-2</sup> proportionality. (**D**) Pisarenko plot showing the relationship between the Seebeck coefficient and the carrier concentration in various CS/CIS samples. The lower effective mass observed in the 1mol% CIS sample, compared to other compositions, explains its very high electrical conductivity. Calculations of

the effective mass assume a single parabolic band model and scattering parameter A = 1.5, corresponding to the ionized impurity electron scattering mechanism.



**Fig. S8** Power factor,  $\sigma$ S<sup>2</sup>, stability testing for sample with 1 mol % indium. The repeatability of power factor demonstrates the stability of Cu<sub>2</sub>Se-1 mol % In over four heating and cooling cycles.



**Fig. S9** Chemical electromigration tests. (A) Top view schematic of the experimental set-up; (B) front view and (C) side view of the experimental set-up. Low magnification backscattered electron imaging of post 24 hour current stress test at 100 A cm<sup>-2</sup> for (D) Cu<sub>2</sub>Se and (E) Cu<sub>2</sub>Se – 1 mol % In. Photos were taken of sample surface at negative contact. A large quantity of Cu is extruded from the pristine Cu<sub>2</sub>Se sample, whereas the 1% In sample shows no sign of copper extrusion. Both samples were kept at a temperature of ~520 K during the 24 hours of applied current.



# Fig. S10

SEM and EDS failure analysis of  $Cu_2Se$  after applying 100 A cm<sup>-2</sup> at ~ 520 K for 24 hours. (A) Partial sample surface at negative contact; (B) Zoomed in view of a bundle of extruded copper wires with accompanying Cu, Se, O, and C EDS mapping; (C) Other examples of copper extrusion found throughout the sample surface, where it is clear that copper migrates out of  $Cu_2Se$  as wires instead of a homogenous surface layer.

#### Movie S1

Time-lapse of the first 30 minutes of the  $Cu_2Se$  electromigration test. The start of the recording was synced with the application of 100 A cm<sup>-2</sup>. Within 2 minutes, surface deformation can be seen at the V(-) terminal, where this deformation has been verified as copper extrusions. Additionally, the sample bar is seen to oxidize throughout the video, showing color changes reminiscent of thin film interference. Changes in color are a result of changes in oxide layer thickness.

#### Movie S2

Time-lapse of the first 30 minutes of the  $Cu_2Se - 1 \mod \%$  In electromigration test. The start of the recording was synced with the application of 100 A cm<sup>-2</sup>. The sample bar is seen to oxidize throughout the video, showing distinct color changes similar to those observed in  $Cu_2Se$ . Changes in color are a result of change in oxide layer thickness. No copper extrusion was observed for this sample, confirming the stabilization of Cu diffusion through incorporation of In within the  $Cu_2Se$  crystal lattice.