Electronic Supporting Information

Solution-Based Synthesis and Characterization of Earth Abundant Cu$_3$(As,Sb)Se$_4$ Nanocrystal Alloys: Towards Scalable Room-Temperature Thermoelectric Devices

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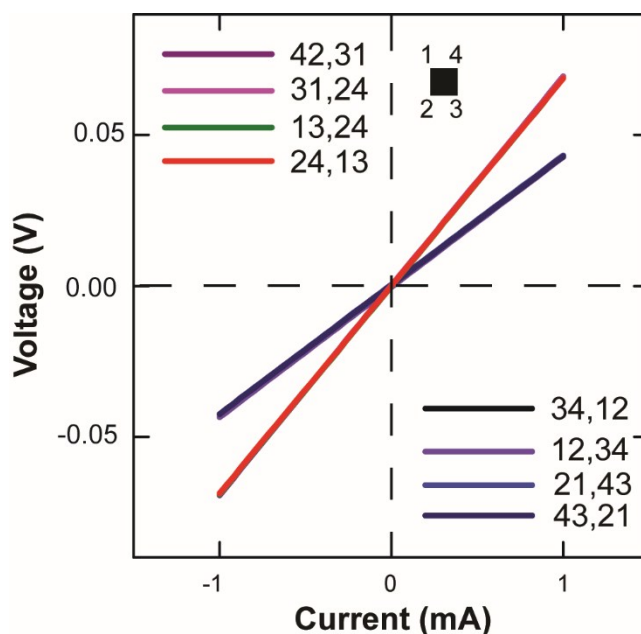
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Figure S1. Electrical characterization obtained using the van der Pauw method from one representative thin film with a composition of Cu$_3$(As$_{0.5}$,Sb$_{0.5}$)Se$_4$ collected and at a temperature of 313 K. The first two numbers in the key denote the direction of applied current, while the last two numbers denote the direction of measured voltage. A schematic labeling the device contacts is inset on the figure.
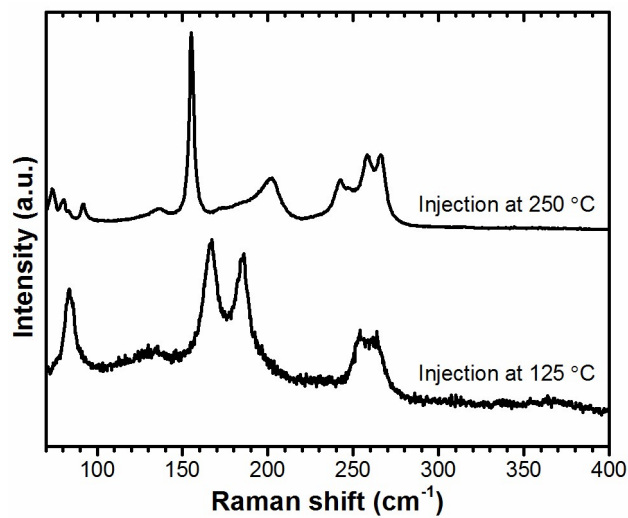
Figure S2. Effect of the selenium precursor injection temperature on the Raman spectra for Cu_3AsSe_4 nanocrystals. The injection temperature of 125 °C is necessary to maintain phase purity throughout all $Cu_3(As,Sb)Se_4$ nanocrystal compositions.
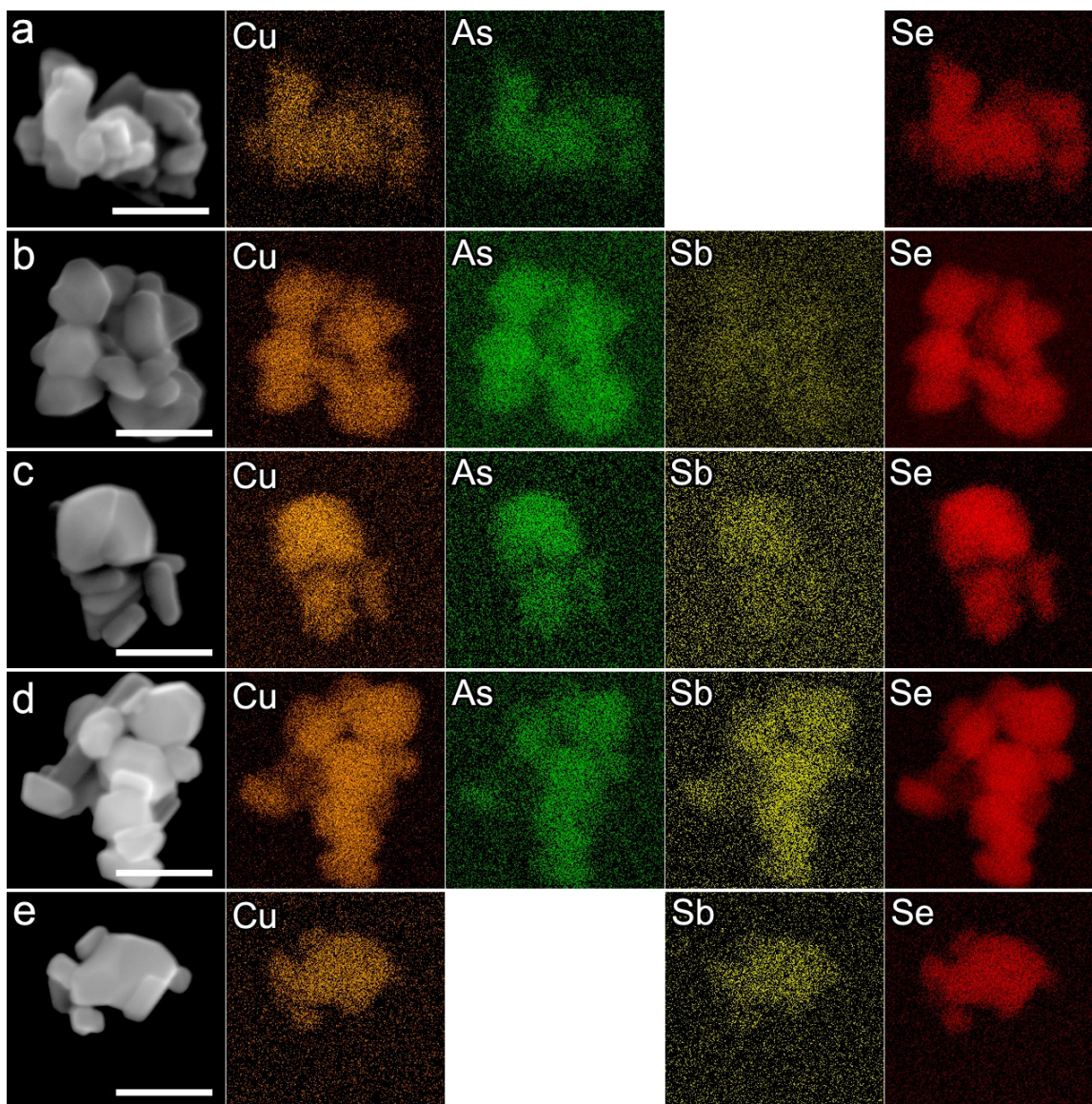
Figure S3. Scanning electron microscopy energy dispersive X-ray spectroscopy elemental maps of the $Cu_3(As,Sb)Se_4$ nanocrystals showing uniform elemental distribution for all compositions. (a) Cu_3AsSe_4, (b) $Cu_3(As_{0.75},Sb_{0.25})Se_4$, (c) $Cu_3(As_{0.5},Sb_{0.5})Se_4$, (d) $Cu_3(As_{0.25},Sb_{0.75})Se_4$, and (e) Cu_3SbSe_4. All scale bars represent 500 nm.
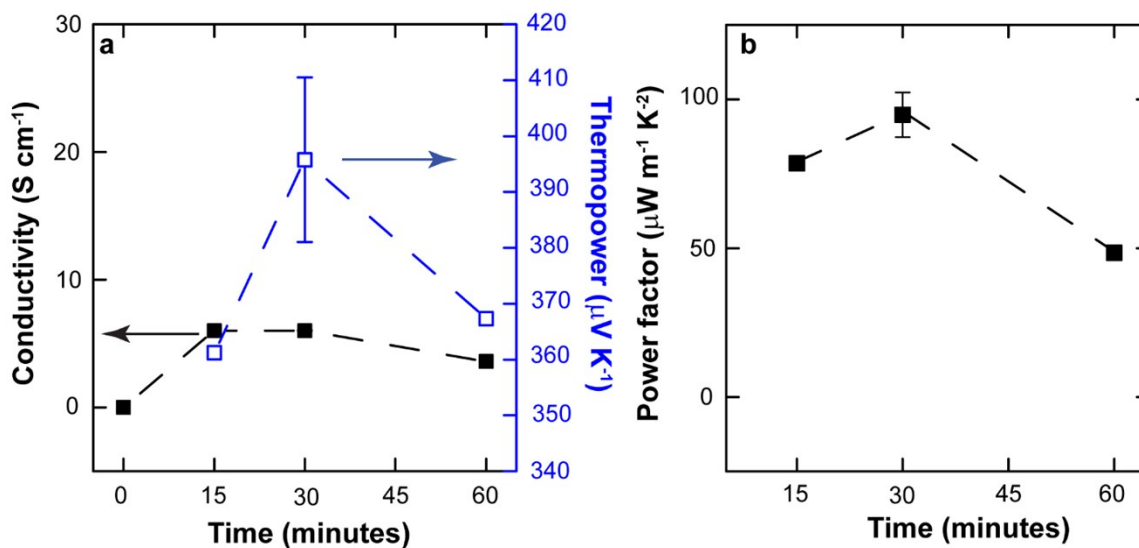
Figure S4. Optimization of the 340 °C heat treatment process time at 100 Torr pressure for thin films containing equal molar ratio of As and Sb. (a) The left vertical axis shows changes in electrical conductivity as a function of heat treatment time (black squares). Each point outside of 30 minutes represents a single film. The data for 30 minutes represents the average and standard error of 4 thin films. The right vertical axis shows the measured thermopower for the different heat treatment times (blue hollow squares). Thermopower could not be acquired for the thin films without heat treatment due to the low signal-to-noise ratio. (b) The power factor as a function of heat treatment time at 340 °C is plotted. The largest power factor was obtained by heat treating the drop-cast nanocrystal thin films for 30 min.
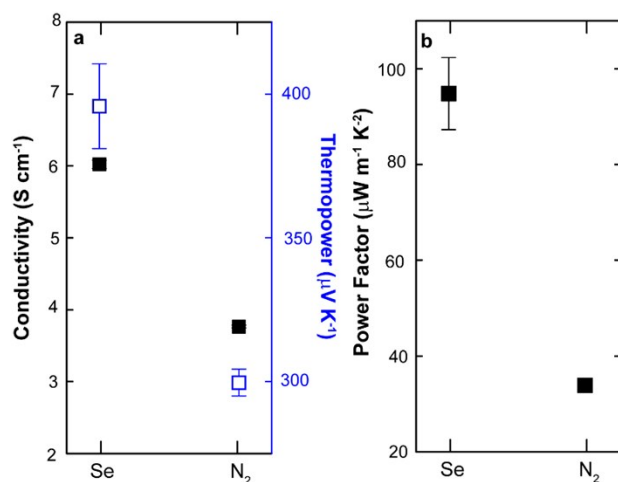
Figure S5. A comparison between the atmosphere conditions of the heat treatment process and the thermoelectric device performance for films containing equal molar ratios of Sb and As. (a) A heat treatment under a selenium atmosphere increased both the electrical conductivity (black squares) and the thermopower (blue hollow squares) when compared to similar heat treatment conditions under nitrogen. (b) The resulting power factor is significantly larger for the devices heat treated under selenium compared to nitrogen. Therefore, the incorporation of selenium, in addition to the densification of the thin films, is critical to achieving higher thermoelectric performance.
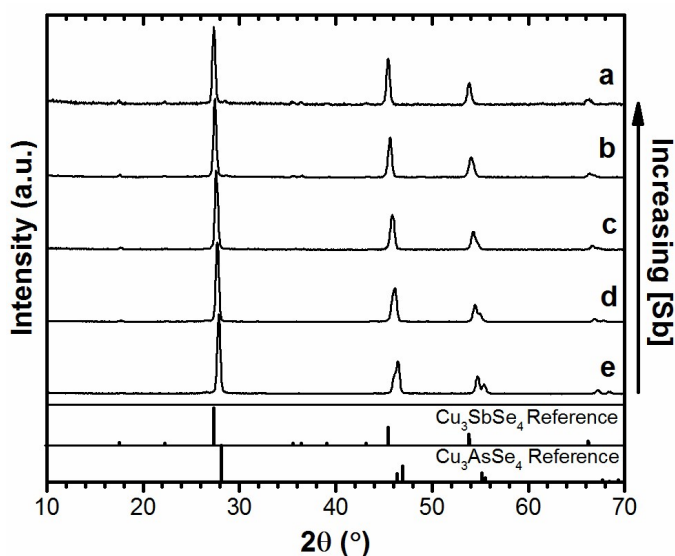

Figure S6. Grazing incidence X-ray diffraction patterns of (a) Cu_3SbSe_4, (b) $Cu_3(As_{0.25},Sb_{0.75})Se_4$, (c) $Cu_3(As_{0.50},Sb_{0.50})Se_4$, (d) $Cu_3(As_{0.75},Sb_{0.25})Se_4$ and (e) Cu_3AsSe_4 thin films after heat treating in selenium vapor at 100 Torr and 340 °C for 30 min. For reference, Cu_3SbSe_4 (ICSD Collection Code 628993) and Cu_3AsSe_4 (ICSD Collection Code 610361) are provided.
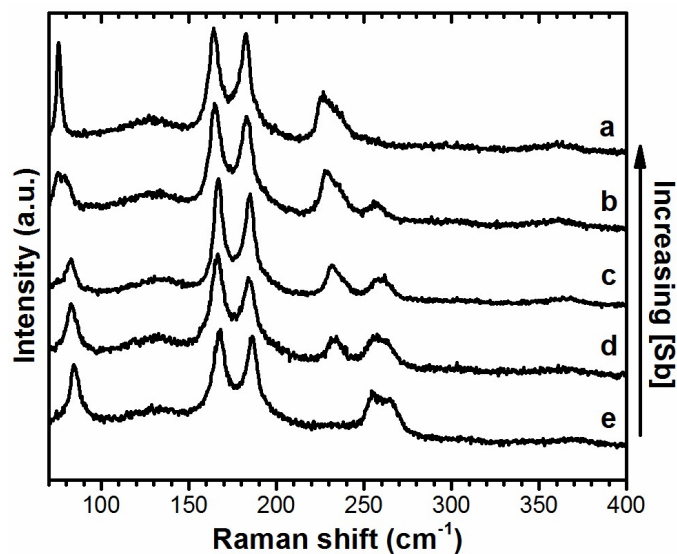
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Figure S7. Raman spectra of (a) Cu_3SbSe_4, (b) $Cu_3(As_{0.25},Sb_{0.75})Se_4$, (c) $Cu_3(As_{0.50},Sb_{0.50})Se_4$, (d) $Cu_3(As_{0.75},Sb_{0.25})Se_4$ and (e) Cu_3AsSe_4 thin films after a heat treatment in selenium vapor at 100 Torr pressure and 340 °C for 30 min.

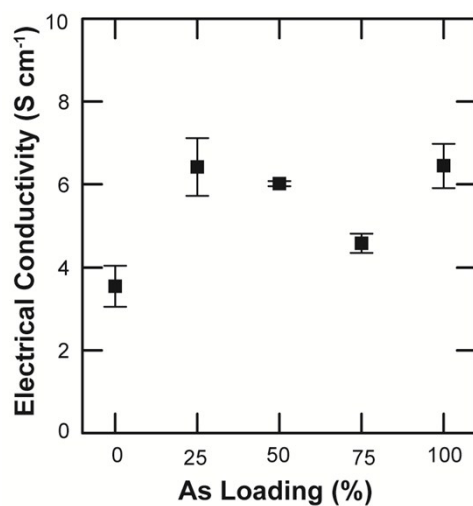**Figure S8**. Electrical conductivity of the heat treated thin films of $Cu_3(As,Sb)Se_4$ nanocrystal alloys as a function of arsenic composition. The error bars correspond to standard error.

Table S1. Comparison of the bulk elemental compositions of the $Cu_3(As,Sb)Se_4$ nanocrystals after heat treating in a selenium atmosphere for 30 min at 100 Torr and 340 °C obtained by scanning electron microscopy energy dispersive X-ray spectroscopy.

Post Heat Treatment (Se)	Atomic Fraction		
Desired Composition	$\dfrac{Cu}{(As+Sb)}$	$\dfrac{Se}{(Cu+As+Sb)}$	$\dfrac{As}{(As+Sb)}$
Cu_3SbSe_4	2.99 ± 0.04	1.06 ± 0.01	0
$Cu_3(As_{0.25}Sb_{0.75})Se_4$	2.99 ± 0.01	1.03 ± 0.01	0.24 ± 0.00
$Cu_3(As_{0.50}Sb_{0.50})Se_4$	2.91 ± 0.04	1.02 ± 0.01	0.50 ± 0.02
$Cu_3(As_{0.75}Sb_{0.25})Se_4$	3.31 ± 0.02	1.06 ± 0.01	0.71 ± 0.05
Cu_3AsSe_4	3.17 ± 0.13	1.05 ± 0.02	1