Supporting information "Enhanced Thermoelectric Performance of Nanostructured Cu_2SnS_3 (CTS) via Ag Doping"

*Ketan Lohani[a], Himanshu Nautiyal[a], Narges Ataollahi[a], Umberto Anselmi-Tamburini[b], Carlo Fanciulli[c], & Paolo Scardi[a]**

[a] *Department of Civil, Environmental & Mechanical Engineering, University of Trento, Via Mesiano 77, 38123, Trento, Italy.*
[b] *Department of Chemistry, University of Pavia, Viale Taramelli 12, 27100, Pavia, Italy.*
[c] *National Research Council of Italy-Institute of Condensed Matter Chemistry and Technologies for Energy (CNR-ICMATE), Lecco Unit, via Previati 1/E, 23900, Lecco, Italy.*

Email: paolo.scardi@unitn.it & ketan.lohani@unitn.it

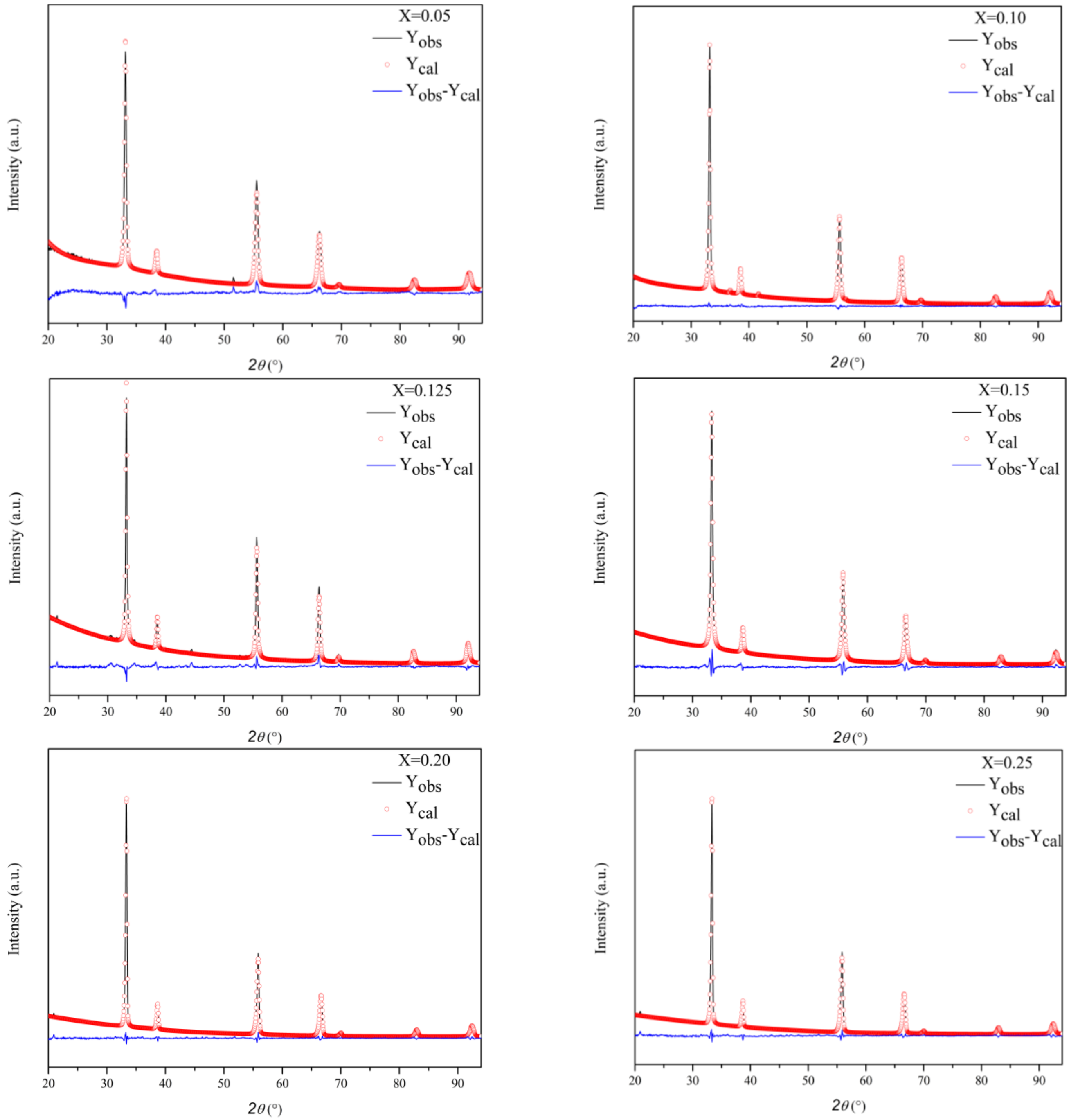

Figure S1. Rietveld refinement data on $Cu_2Ag_{(x)}Sn_{(1-x)}S_3$ (x= 0.05, 0.10, 0.125, 0.15, 0.20, and 0.25) samples.

Table S1: Structural data on Cu_2SnS_3 (space group *F-43m* (216)).

	x	*y*	*Z*	Occupancy	Site	B_{iso}
Cu	0	0	0	2/3	4*a*	1.0
Sn	0	0	0	1/3	4*a*	1.0
S	0.25	0.25	0.25	1.0	4*c*	1.0

For the Rietveld refinement of $Cu_2Sn_{(1-x)}Ag_{(x)}S_3$ samples. The Ag was introduced at Sn site, and the occupancy for Cu and S was kept same as table S1. The variation of various parameters is sown in table S2.

Table S2: Initial occupancy of Cu, Sn and Ag at 4*a* site and lattice parameter (a=b=c) used for the Rietveld refinement of various $Cu_2Sn_{(1-x)}Ag_{(x)}S_3$ samples.

x	Occupancy				(a=b=c) Å
	Cu	Sn	Ag	S	
0.05	0.6667	0.3135	0.0165	1.0	5.43
0.10	0.6667	0.2970	0.0334	1.0	5.43
0.125	0.6667	0.2885	0.04125	1.0	5.43
0.15	0.6667	0.2805	0.0465	1.0	5.43
0.20	0.6667	0.264	0.0667	1.0	5.43
0.25	0.6667	0.2475	0.0825	1.0	5.43

Table S3: After Rietveld refinement final occupancy, Debye Waller factor (B_{iso}), and the goodness of fit (GoF) for various $Cu_2Sn_{(1-x)}Ag_{(x)}S_3$ samples.

x	Occupancy				a=b=c Å	B_{iso}				GoF
	Cu	Sn	Ag	S		Cu	Sn	Ag	S	
0.05	0.6378	0.3141	0.0094	1.15	5.4334(6)	1.5	1.6	1.8	2.1	1.72
0.10	0.6537	0.2920	0.0280	1.14	5.4169(1)	1.2	1.1	2.8	3.1	1.63
0.125	0.6592	0.2899	0.0384	1.04	5.4198(6)	1.4	1.2	2.1	2.4	2.30
0.15	0.6499	0.2737	0.0402	1.17	5.4077(5)	1.8	1.2	2.7	3.2	1.81
0.20	0.6544	0.2587	0.0607	1.11	5.3974(1)	1.7	1.0	1.3	2.5	1.54
0.25	0.6641	0.2440	0.0769	1.06	5.3985(4)	0.9	1.1	1.2	1.6	1.55

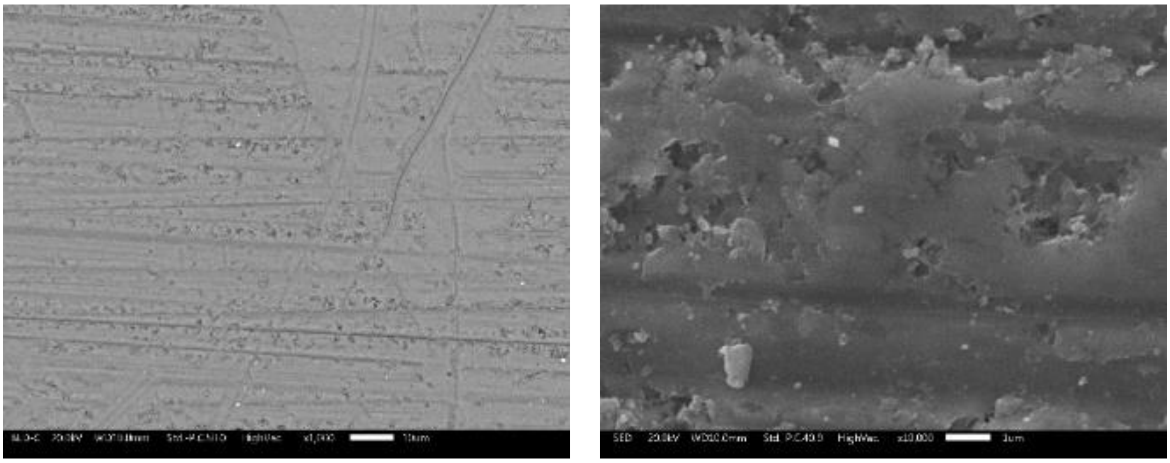

Figure S2. Morphological image on $Cu_2Ag_{(x)}Sn_{(1-x)}S_3$ samples in different magnifications, showing dense microstructure with almost no porosity. Moreover, the grains of the samples are much smaller than the microscope's magnification.

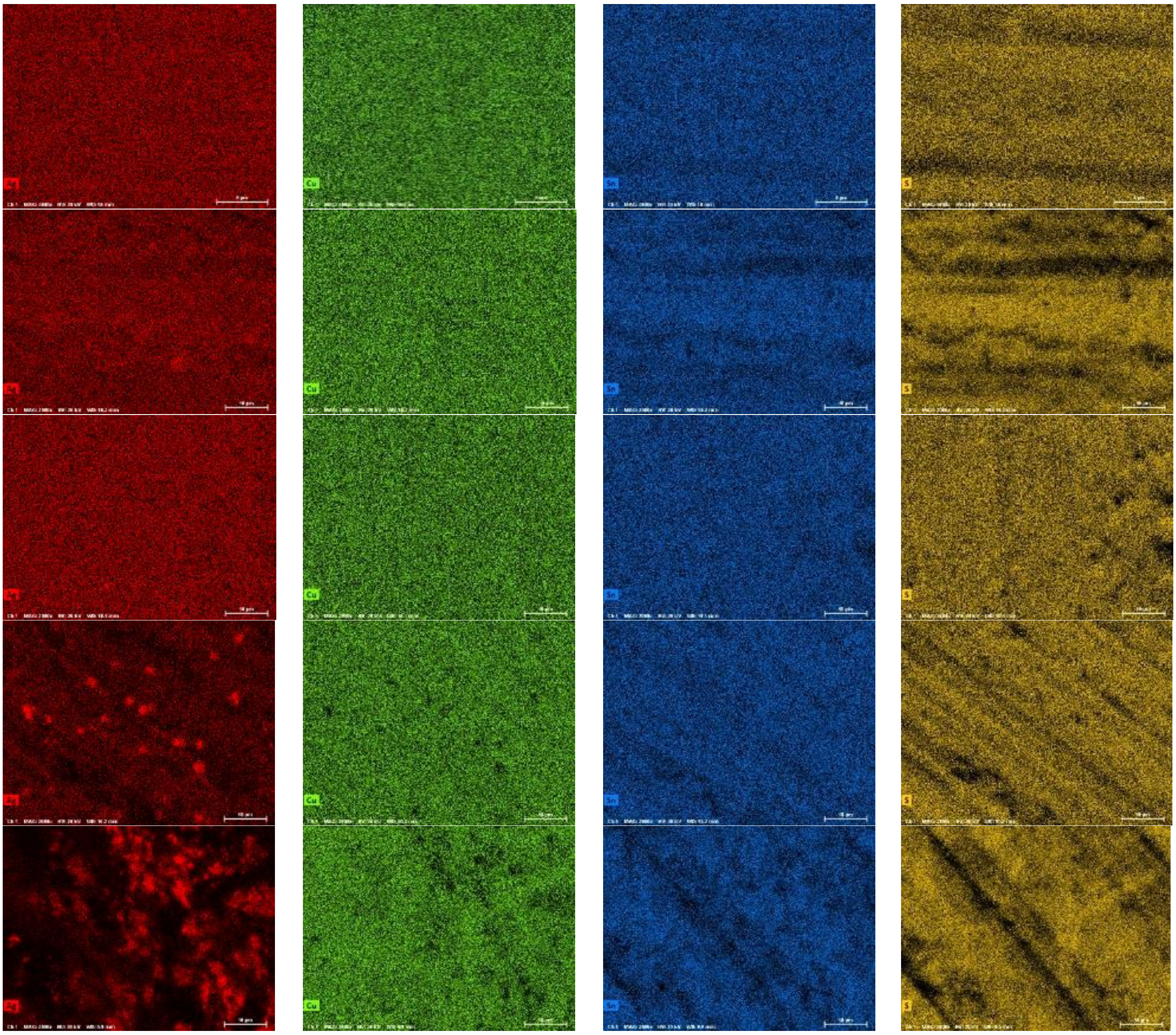

Figure S3. Chemical maps collected on $Cu_2Ag_{(x)}Sn_{(1-x)}S_3$ samples (x= 0.05, 0.10, 0.15, 0.20, and 0.25), respectively. Chemical maps for Cu (Green), Sn (Blue), and S (Yellow) are homogeneous for all the samples. However, $x \leq 0.20$ samples show a non-homogeneous Ag (Red) distribution.

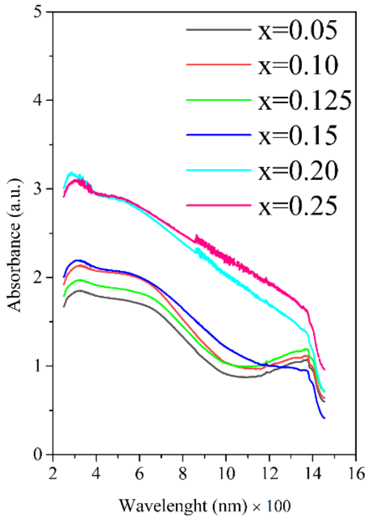

Figure S4. Optical absorption spectra collected on $Cu_2Ag_{(x)}Sn_{(1-x)}S_3$ (x= 0.05, 0.10, 0.125, 0.15, 0.20, and 0.25) samples.

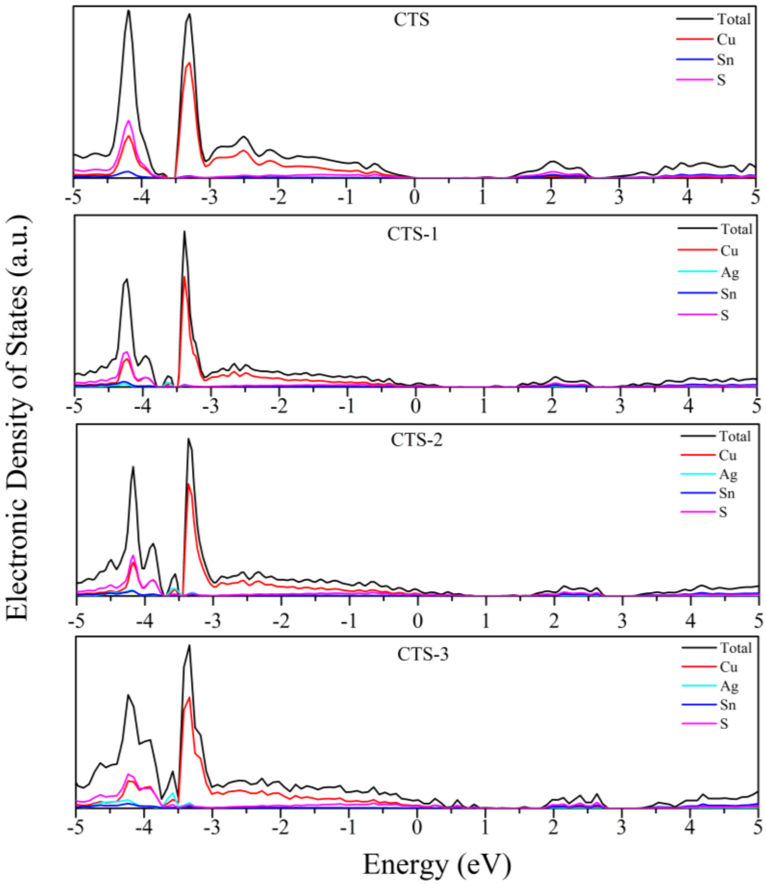

Figure S5. Atomic projected Density of States (DOS) plot for monoclinic CTS, 1 Ag atom, 2 Ag, and 3 Ag atom substituted CTS systems, shown as CTS (Cu_2SnS_3), CTS-1 ($Cu_2Ag_{0.083}Sn_{0.91}S_3$), CTS-2 ($Cu_2Ag_{0.16}Sn_{0.84}S_3$), and CTS-3 ($Cu_2Ag_{0.25}Sn_{0.75}S_3$), respectively. Here, the Fermi level is set at zero.

Table S4. Specific heat capacity values for $Cu_2Ag_{(x)}Sn_{(1-x)}S_3$ at 50 °C.

$Cu_2Ag_{(x)}Sn_{(1-x)}S_3$	Temperature (°C)	Cp (J/g°C)
x=0.05	50	0.387 ± 0.01
x=0.10	50	0.364 ± 0.01
x=0.125	50	0.369 ± 0.01
x=0.15	50	0.394 ± 0.01
x=0.20	50	0.378 ± 0.01
x=0.25	50	0.394 ± 0.01

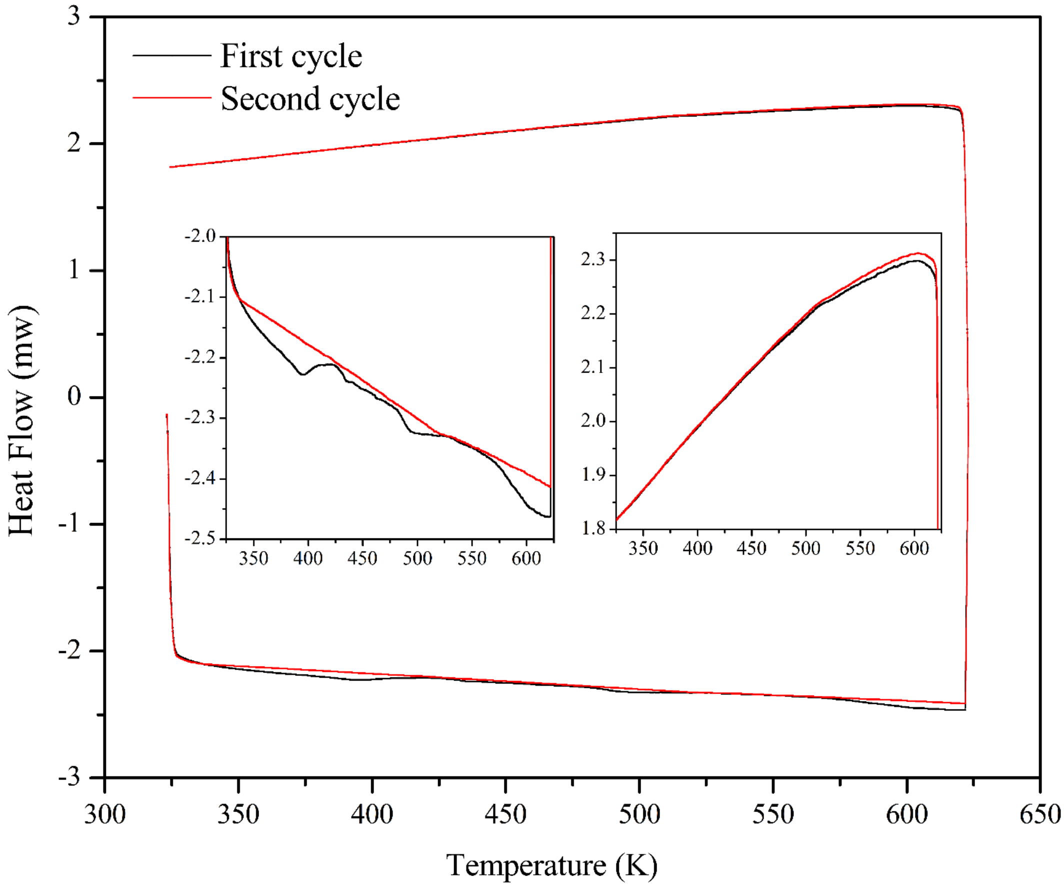

Figure S6. Two temperature-dependent heat flow measurement cycles were performed on $Cu_2Ag_{(x)}Sn_{(1-x)}S_3$, $x = 0.15$ sample. Two insets show magnified heating and cooling cycles.

The heat flux measurements were carried out on $x = 0.15$ sample in two successive heating and cooling cycles in temperature span 325 K to 625 K. In the first cycle, while heating, an endothermic peak from ~350 K to ~425 K is associate to the release of water, which could be present in the samples due to humidity. Other than this, four features are evident in the first cycle of heat flux line and 435 K, 460 K, 500 K, and 600K, respectively. The enthalpy associated with first two peaks is very small ~0.0167 J/g and ~0.0024 J/g. The enthalpy associated with the third peak around 500 K has one order of magnitude higher (~ 0.1511 J/g) than peaks at 435 K and 460 K. The last peak in heat flux measurement is around 600 K. All these peaks are very small and possibly related to release of S and or oxidization of the sample. Moreover, these peaks completely disappeared in second cycle. Thus, confirming the thermal stability of $Cu_2Ag_{(x)}Sn_{(1-x)}S_3$, $x = 0.15$ sample.

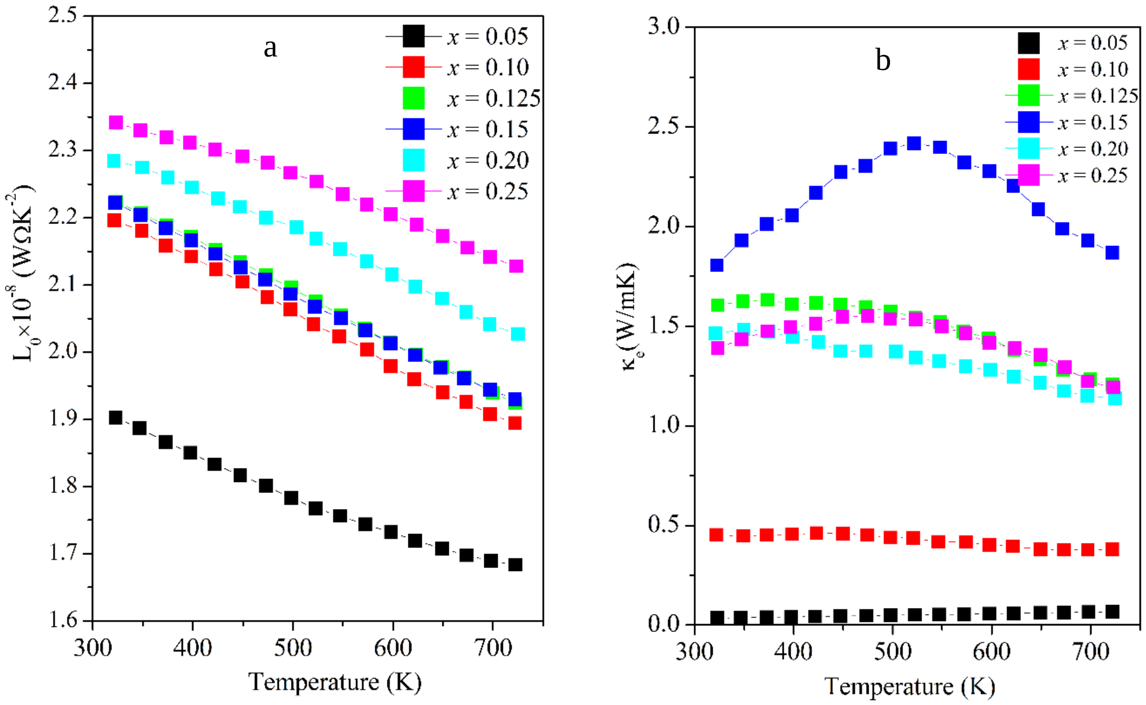

Figure S7. (a) Calculated Lorenz number (L_o), and (b) electronic contribution to the thermal conductivity (κ_e).

Table S5: AIMD temperature-dependent RMSD values and error for simulated CTS-1 ($Cu_2Ag_{0.083}Sn_{0.91}S_3$), CTS-2 ($Cu_2Ag_{0.16}Sn_{0.84}S_3$), and CTS-3 ($Cu_2Ag_{0.25}Sn_{0.75}S_3$) supercells, respectively.

CTS-1

Temperature	Total	Error	Cu	Error	Ag	Error	Sn	Error	S	Error
450 K	0.27	0.029	0.317	0.037	0.217	0.091	0.243	0.047	0.242	0.029
550 K	0.285	0.034	0.332	0.045	0.235	0.104	0.256	0.048	0.255	0.031
650 K	0.298	0.028	0.355	0.039	0.262	0.119	0.258	0.039	0.262	0.026

CTS-2

Temperature	Total	Error	Cu	Error	Ag	Error	Sn	Error	S	Error
450 K	0.254	0.029	0.301	0.041	0.269	0.09	0.215	0.035	0.223	0.026
550 K	0.275	0.03	0.325	0.039	0.27	0.095	0.238	0.042	0.241	0.028
650 K	0.291	0.028	0.348	0.041	0.313	0.101	0.243	0.039	0.254	0.024

CTS-3

Temperature	Total	Error	Cu	Error	Ag	Error	Sn	Error	S	Error
450 K	0.251	0.025	0.296	0.038	0.275	0.069	0.207	0.032	0.219	0.021
550 K	0.264	0.024	0.308	0.034	0.286	0.077	0.222	0.036	0.232	0.022
650 K	0.289	0.032	0.345	0.043	0.309	0.099	0.233	0.039	0.251	0.028

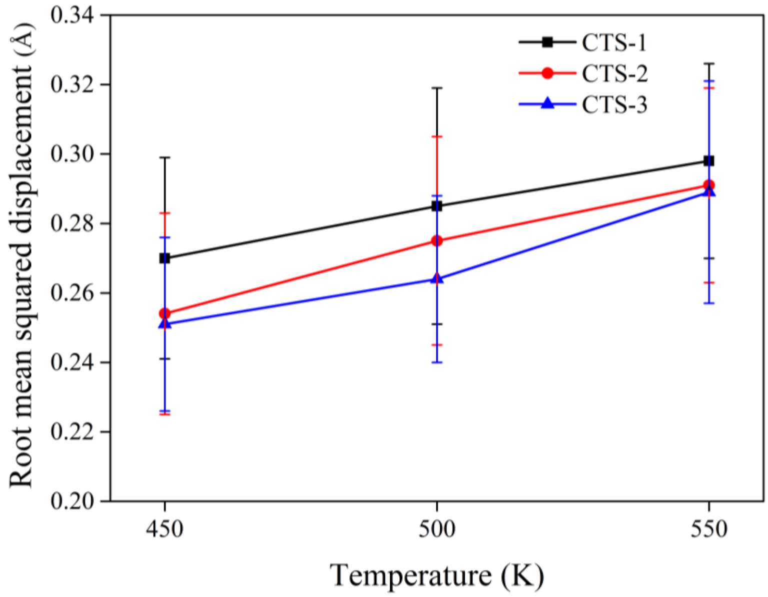

Figure S8. Temperature dependent total RMSD for 1 Ag, 2 Ag, and 3 Ag atom substituted CTS systems, shown as CTS-1 ($Cu_2Ag_{0.083}Sn_{0.91}S_3$), CTS-2 ($Cu_2Ag_{0.16}Sn_{0.84}S_3$), and CTS-3 ($Cu_2Ag_{0.25}Sn_{0.75}S_3$) respectively.