Electronic Supplementary Information (ESI)

Electronic and Thermoelectric Properties of Zn and Se Double Substituted Tetrahedrite

Sahil Tippireddy[a], Raju Chetty[b], Krushna Kumari Raut[b], Mit H. Naik[d], Prashanta K. Mukharjee[c], Manish Jain[d], R. Nath[c], Krzysztof Wojciechowski[b], Ramesh Chandra Mallik[*a]

[a]*Thermoelectric Materials and Devices Laboratory, Department of Physics, Indian Institute of Science, Bangalore*

[b]*Faculty of Materials Science and Ceramics, AGH University of Science and Technology, Cracow, Poland*

[c]*Indian Institute of Science Education and Research, Thiruvananthapuram, India*

[d]*Department of Physics, Indian Institute of Science, Bangalore*

** Corresponding author Email id:* rcmallik@iisc.ac.in

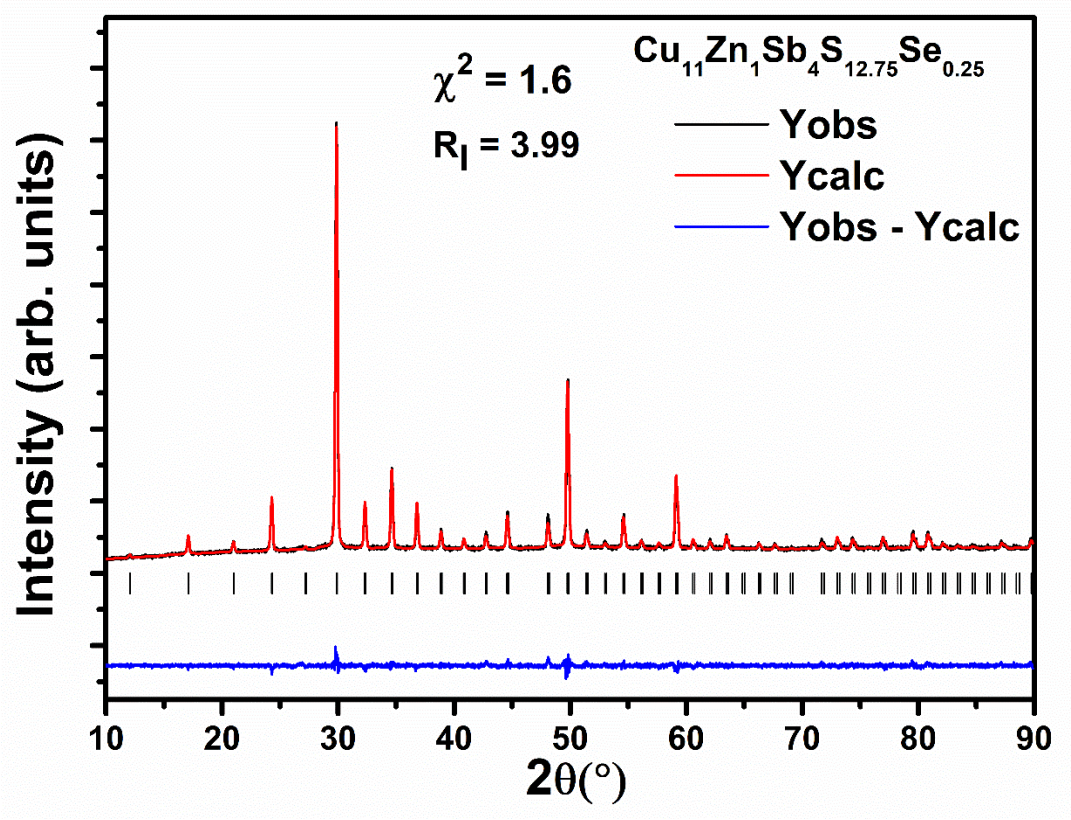

Figure S1: Refined XRD pattern for $Cu_{11}Zn_1Sb_4S_{12.75}Se_{0.25}$ done using Rietveld analysis.

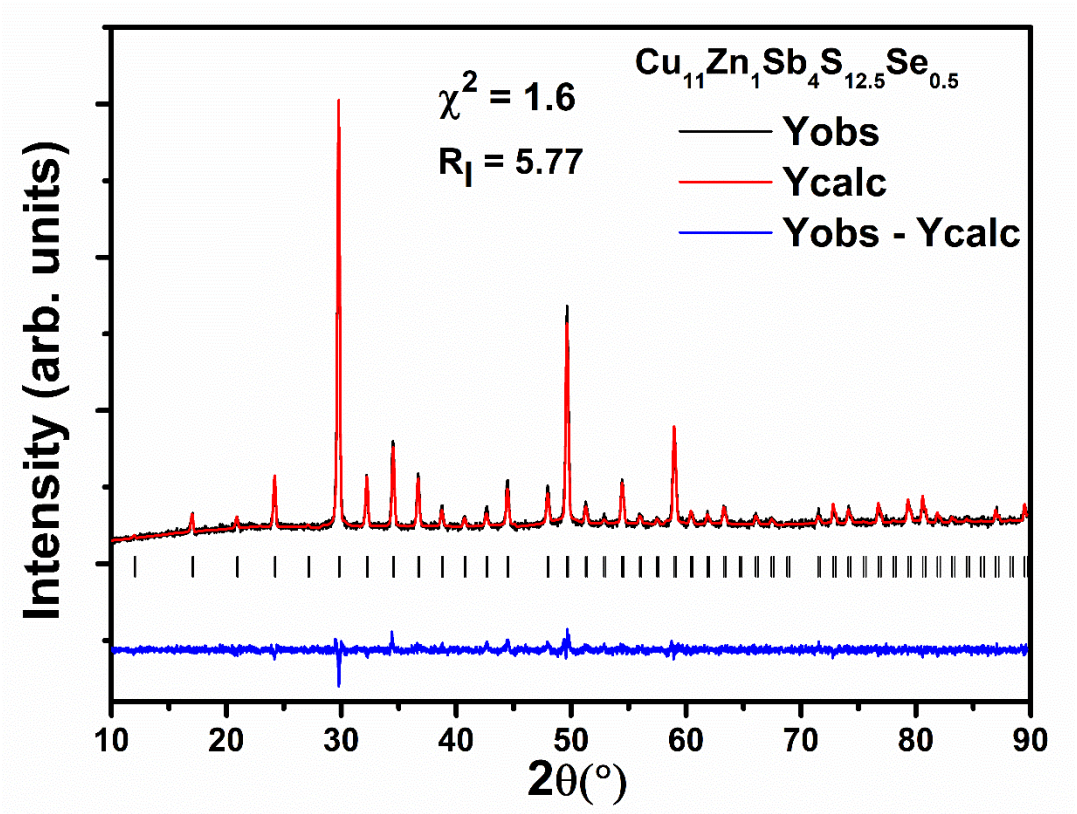

Figure S2: Refined XRD pattern for $Cu_{11}Zn_1Sb_4S_{12.5}Se_{0.5}$ done using Rietveld analysis.

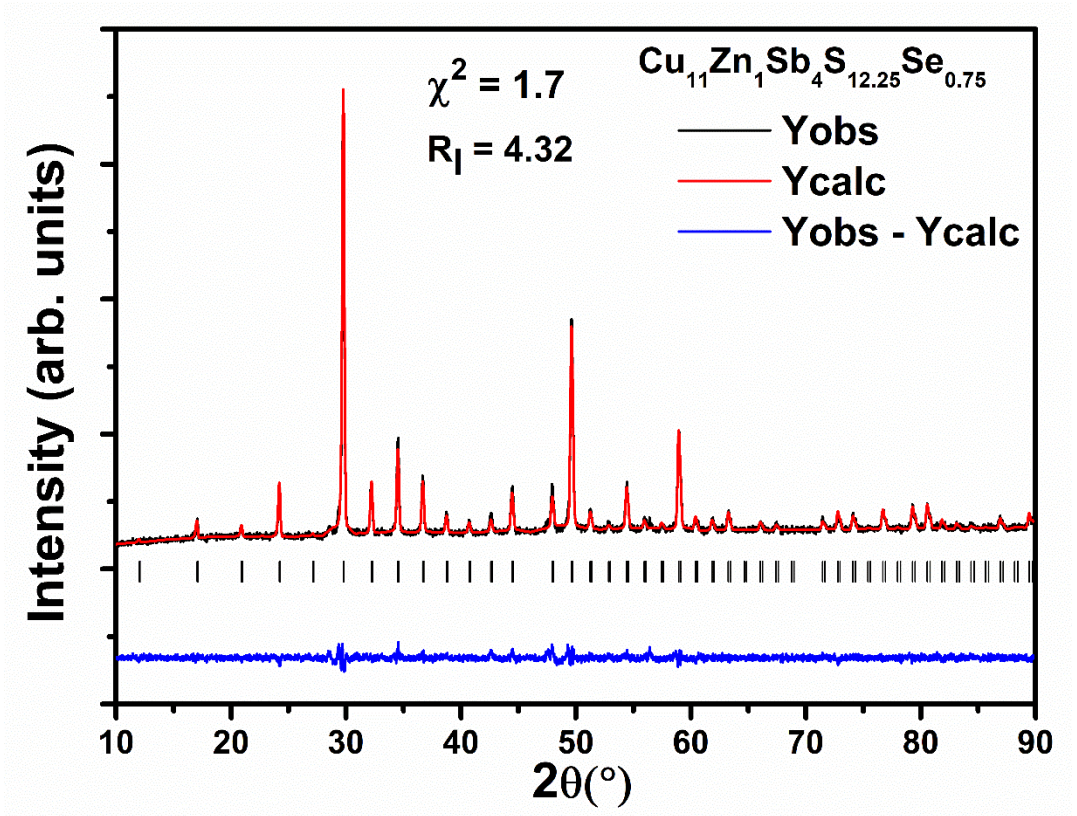

Figure S3: Refined XRD pattern for $Cu_{11}Zn_1Sb_4S_{12.25}Se_{0.75}$ done using Rietveld analysis.

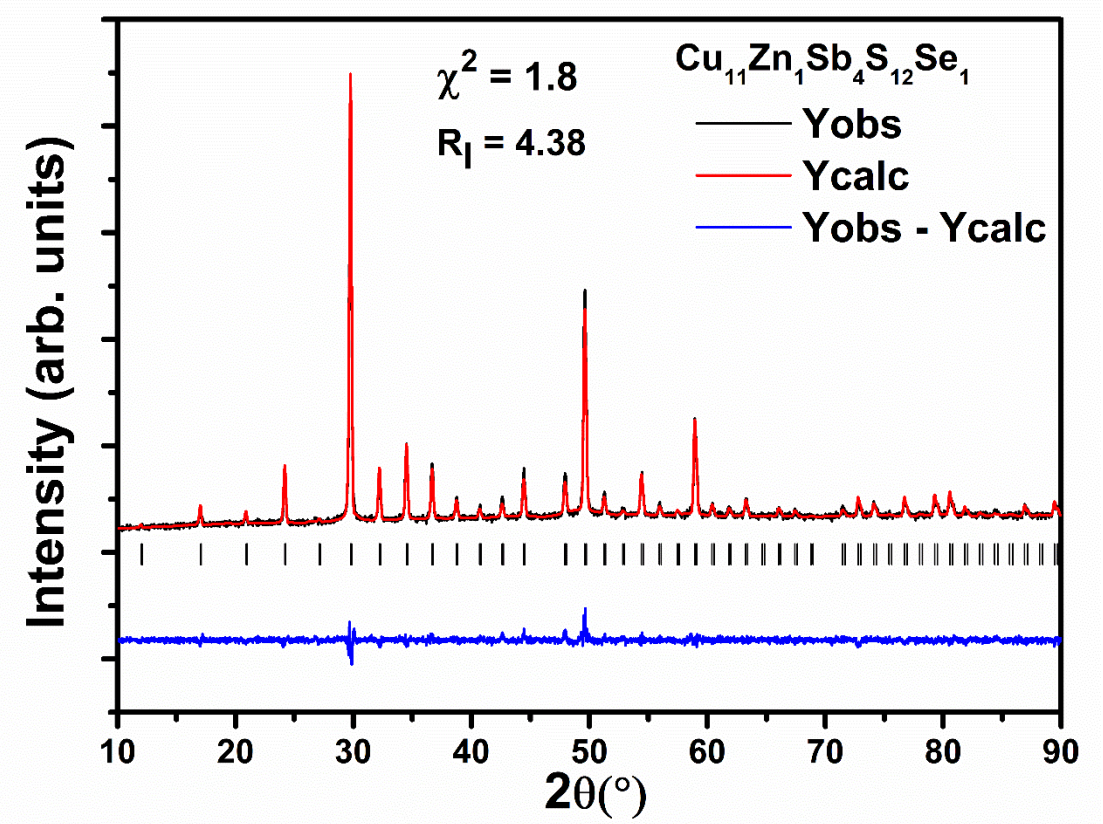

Figure S4: Refined XRD pattern for $Cu_{11}Zn_1Sb_4S_{12}Se_1$ done using Rietveld analysis.

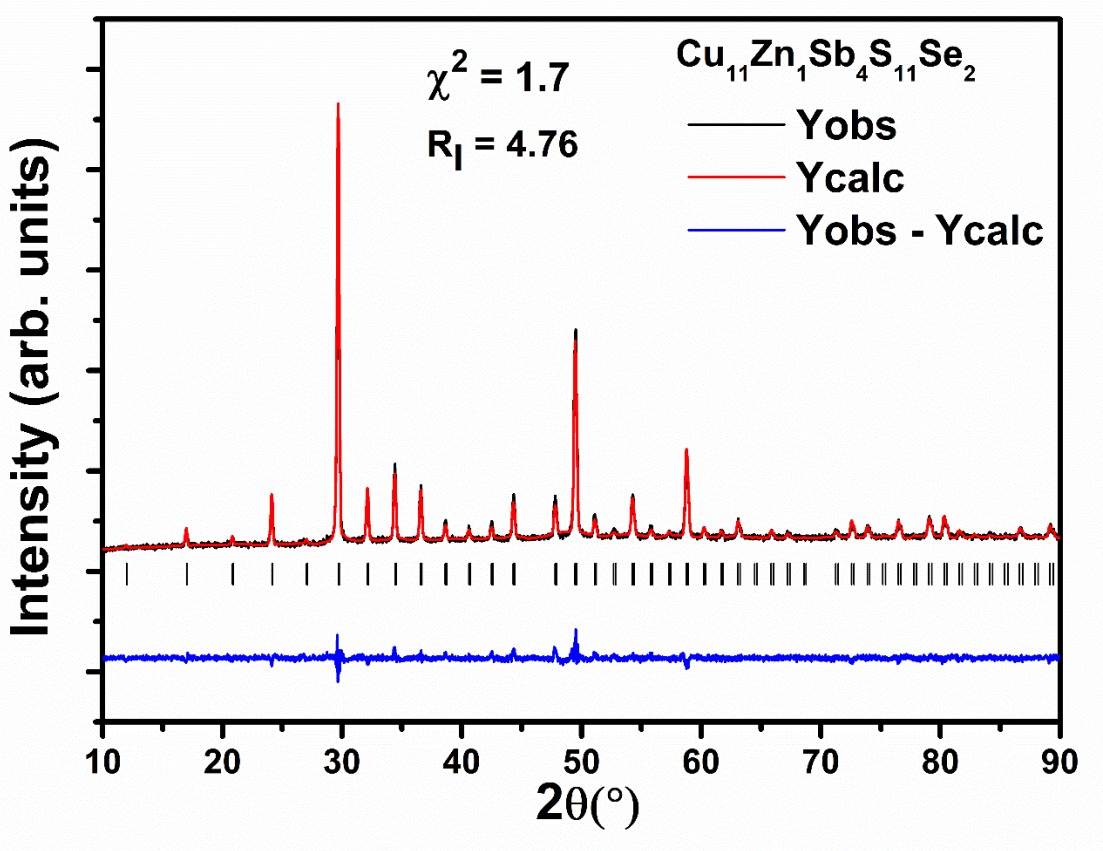

Figure S5: Refined XRD pattern for $Cu_{11}Zn_1Sb_4S_{11}Se_2$ done using Rietveld analysis.

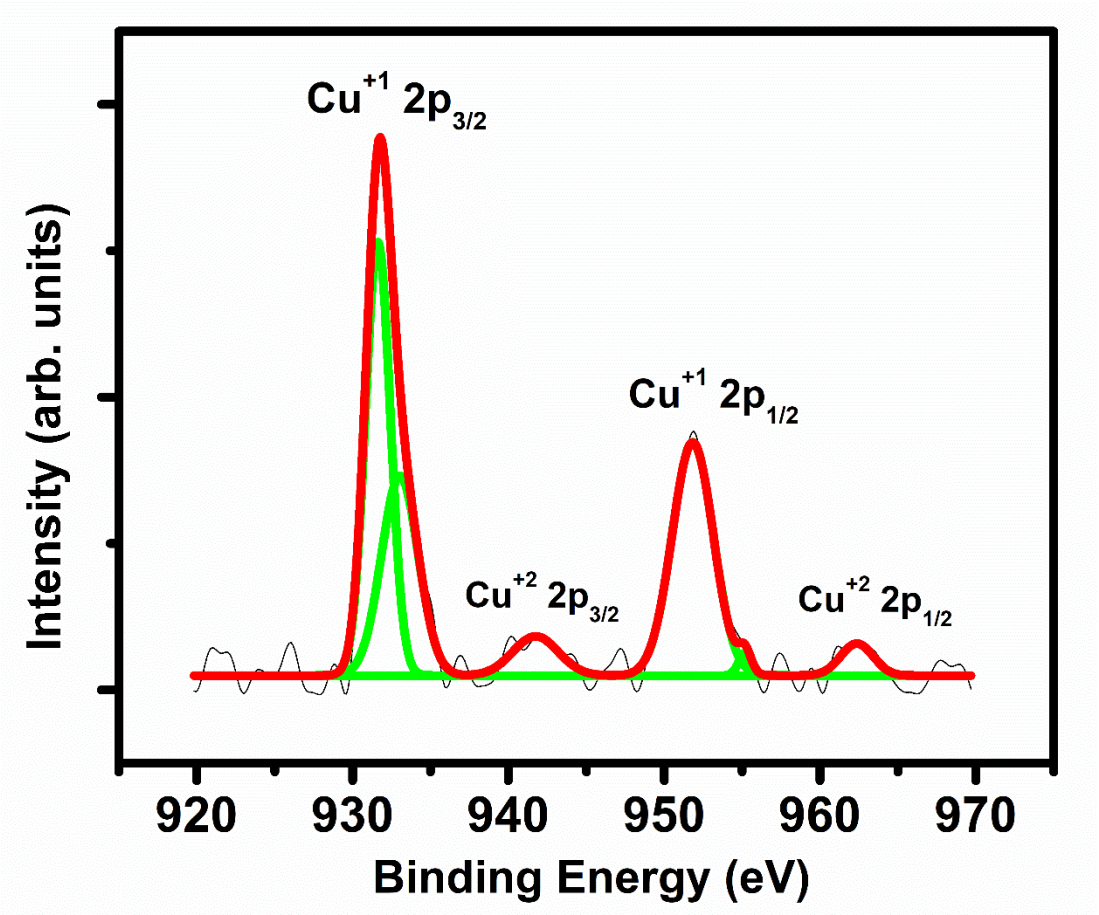

Figure S6: X – ray photoelectron spectroscopy (XPS) spectrum of Cu in $Cu_{11}Zn_1Sb_4S_{12.5}Se_{0.5}$

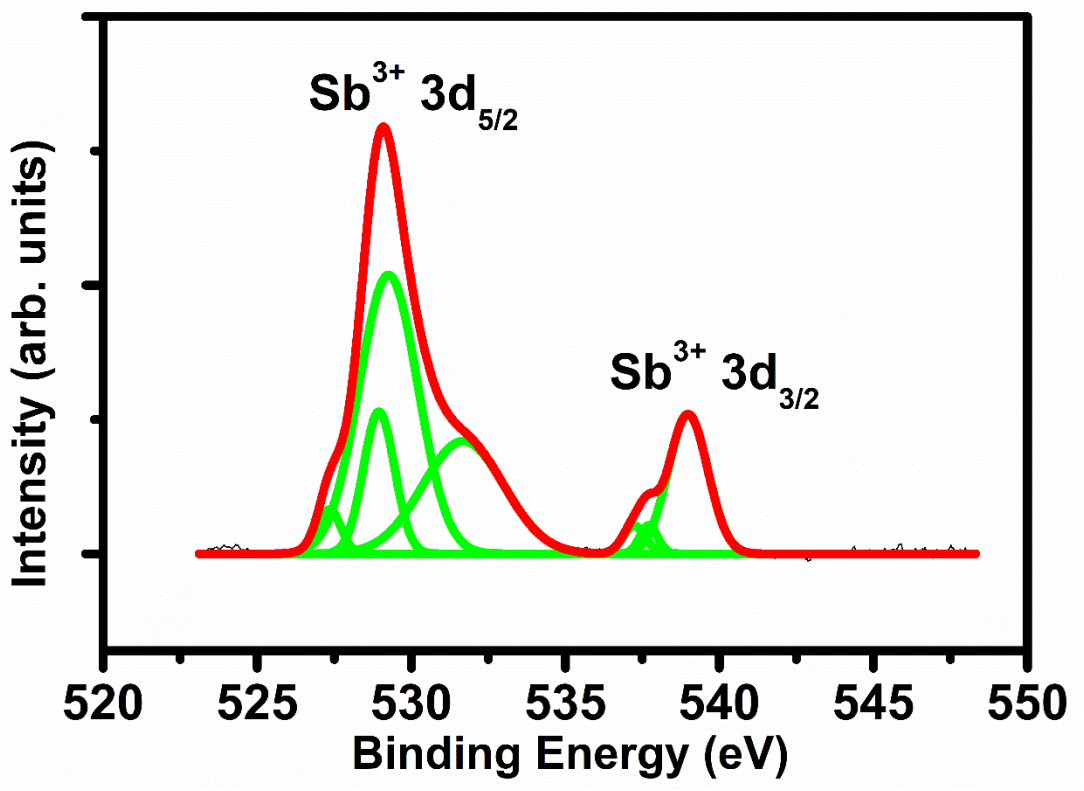

Figure S7: X – ray photoelectron spectroscopy (XPS) spectrum of Sb in $Cu_{11}Zn_1Sb_4S_{12.5}Se_{0.5}$

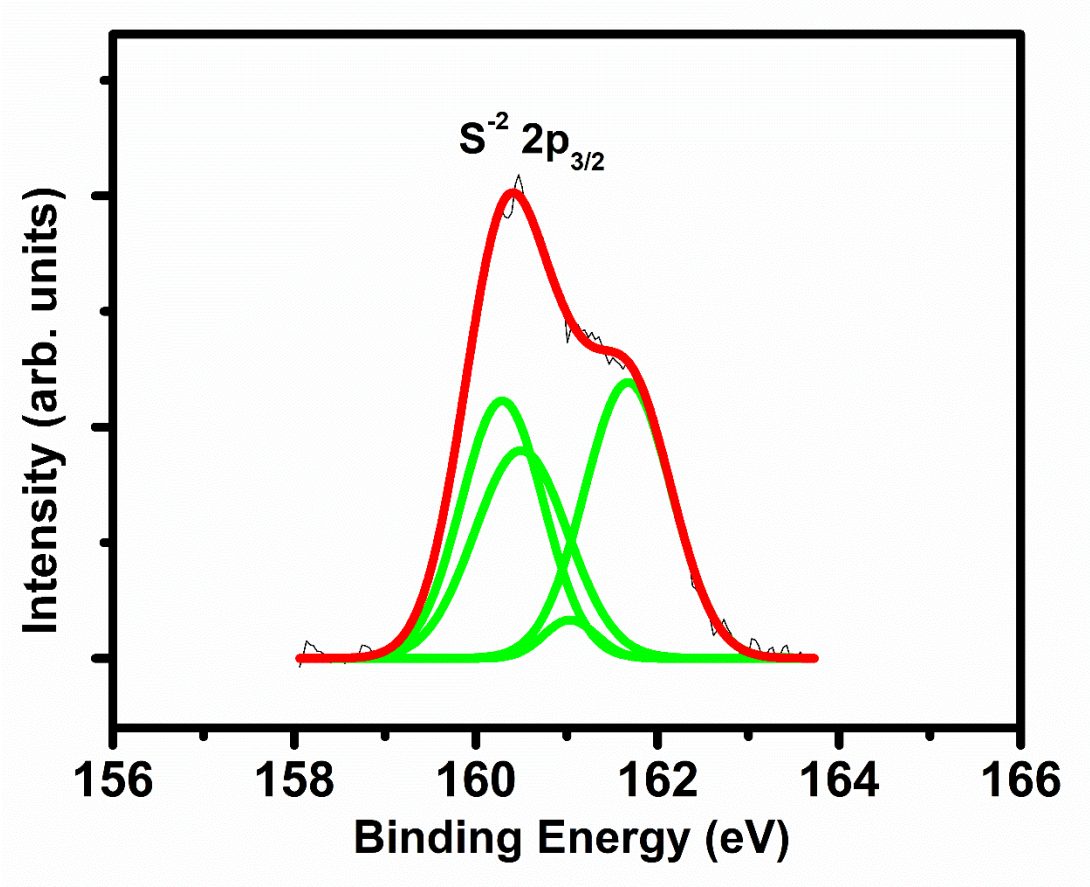

Figure S8: X – ray photoelectron spectroscopy (XPS) spectrum of S in $Cu_{11}Zn_1Sb_4S_{12.5}Se_{0.5}$

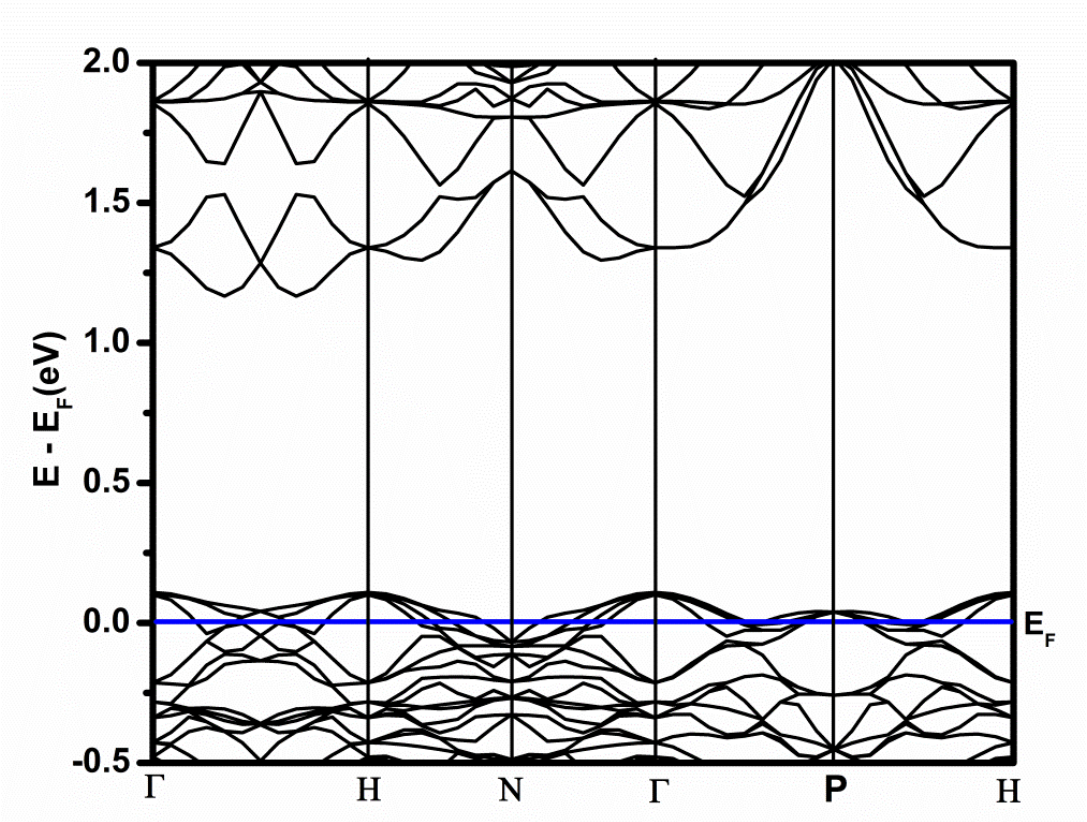

Figure S9: Bandstructure of pristine compound $Cu_{12}Sb_4S_{13}$

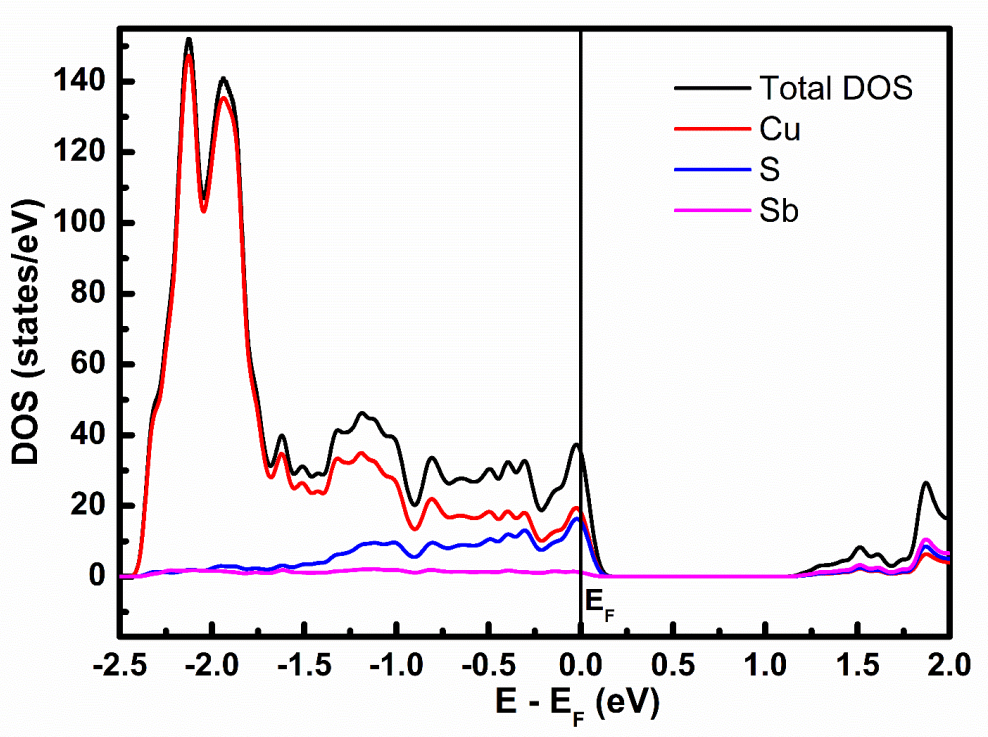

Figure S10: Projected density of states (PDOS) of the pristine compound $Cu_{12}Sb_4S_{13}$

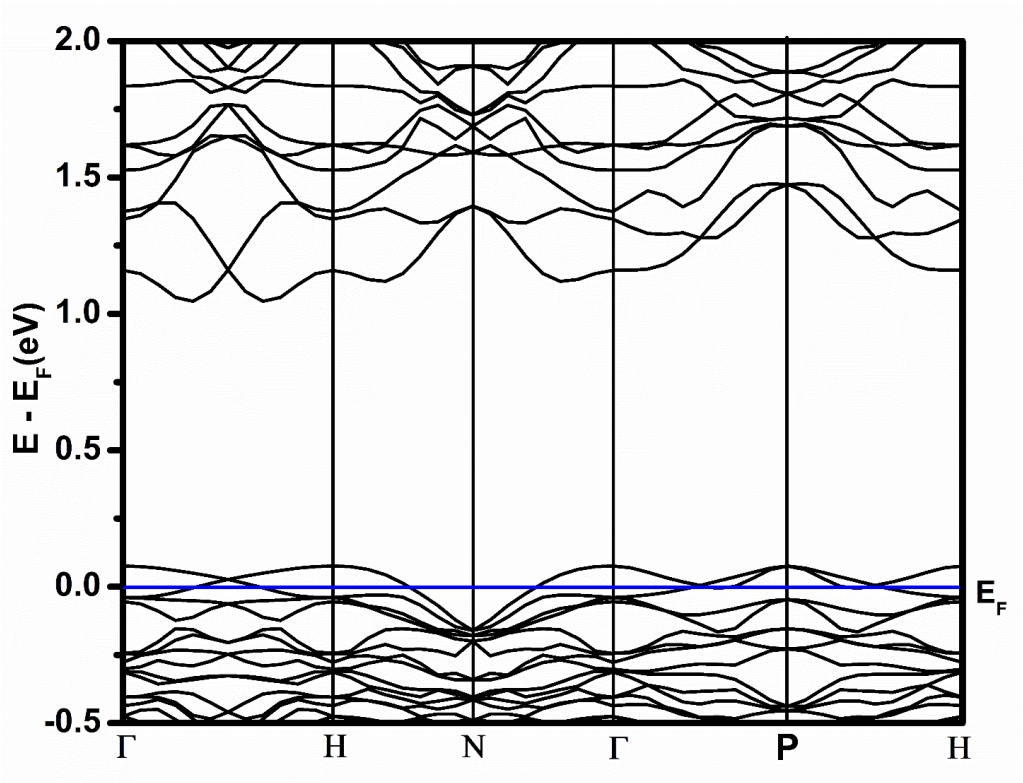

Figure S11: Bandstructure of Zn only substituted compound $Cu_{11}Zn_1Sb_4S_{13}$

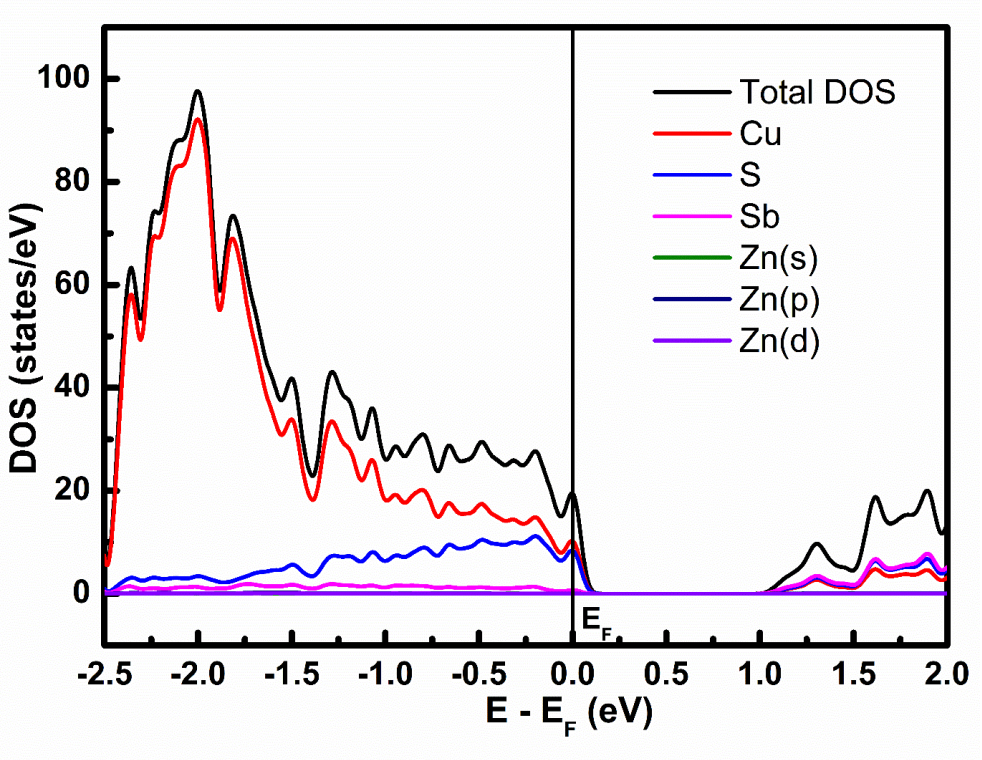

Figure S12: Projected density of states (PDOS) of the Zn only substituted compound

$Cu_{11}Zn_1Sb_4S_{13}$

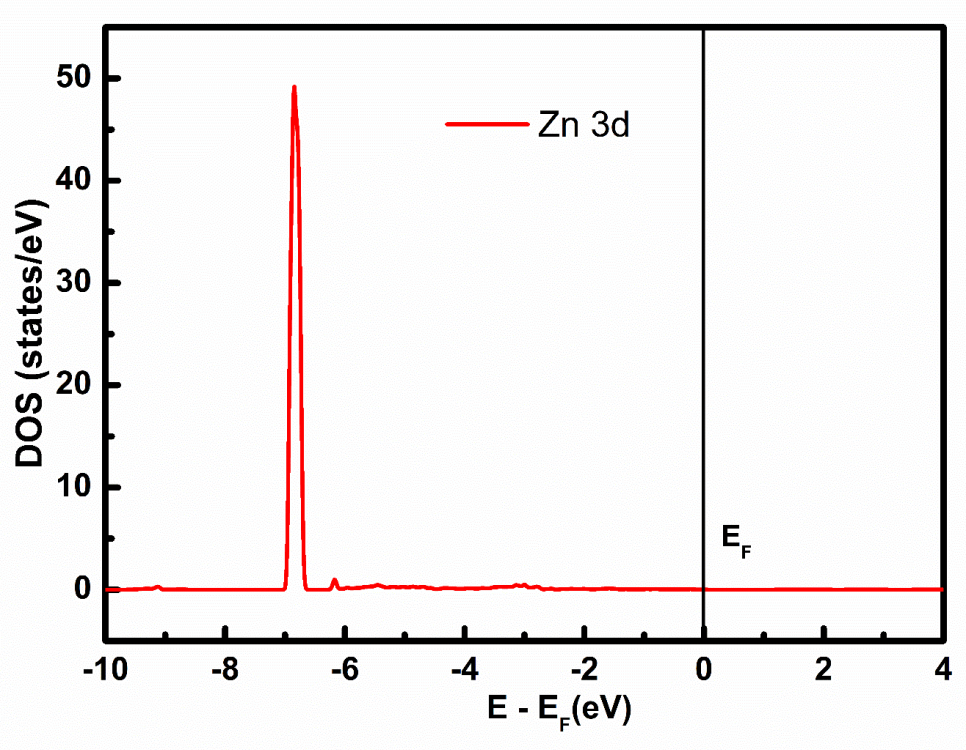

Figure S13: Zn 3d states lying around 7 eV below E_F

Table S1: XPS peak assignment corresponding to the oxidation states of individual elements.

Element	Peak	B.E(eV)[a]	Oxidation state
Cu	$2p_{3/2}$	931.6 eV	+1
	$2p_{3/2}$	941.7 eV	+2
	$2p_{1/2}$	951.8 eV	+1
	$2p_{1/2}$	962.3 eV	+2
Sb	$3d_{5/2}$	529.3 eV	+3
	$3d_{3/2}$	538.9 eV	+3
S	$2p_{3/2}$	160.2 eV	-2
	$2p_{3/2}$	161.6 eV	-2

[a] The binding energy of the XPS peaks are indexed from the NIST database.

For comparison of the Zn (only) and Se (only) substituted samples, Figures S14 – S18 show the transport properties of $Cu_{11}Zn_1Sb_4S_{13}$ (ref: Tippireddy et al., *J. Phys. Chem. C*., **122**, 8735 - 8749) and $Cu_{12}Sb_4S_{12}Se_1$ (The data reprinted with permission from Lu et al., *Chem. Mater*, 2016, **28**, 1781-1786. Copyright (2016) American Chemical Society).

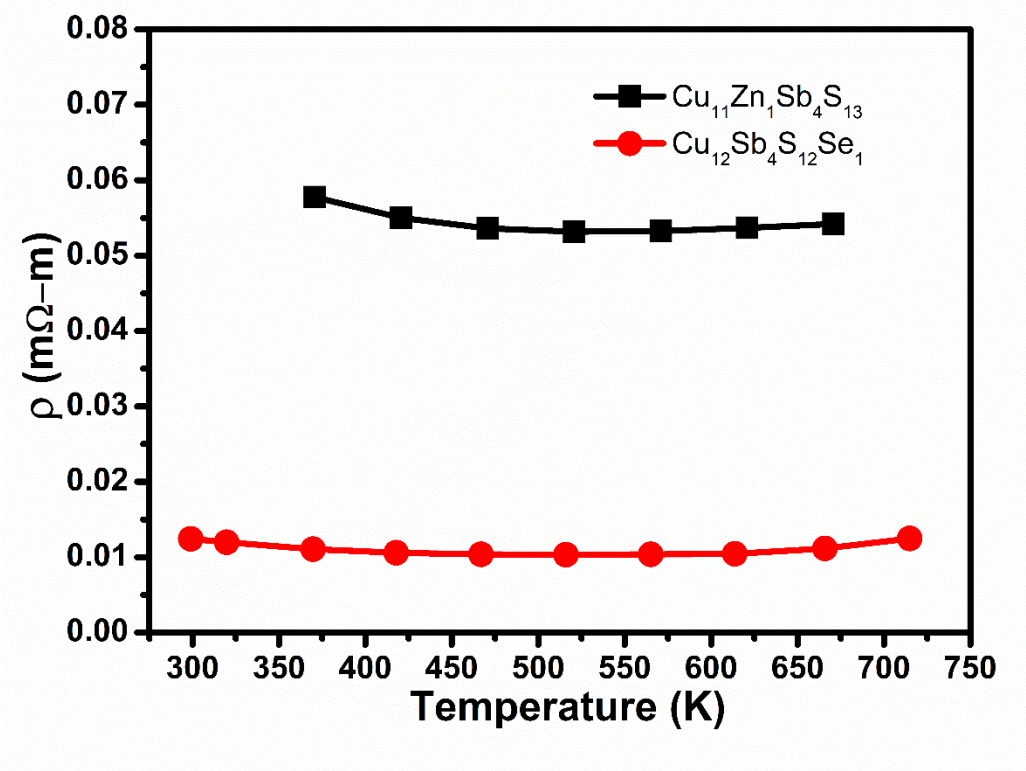

Figure S14

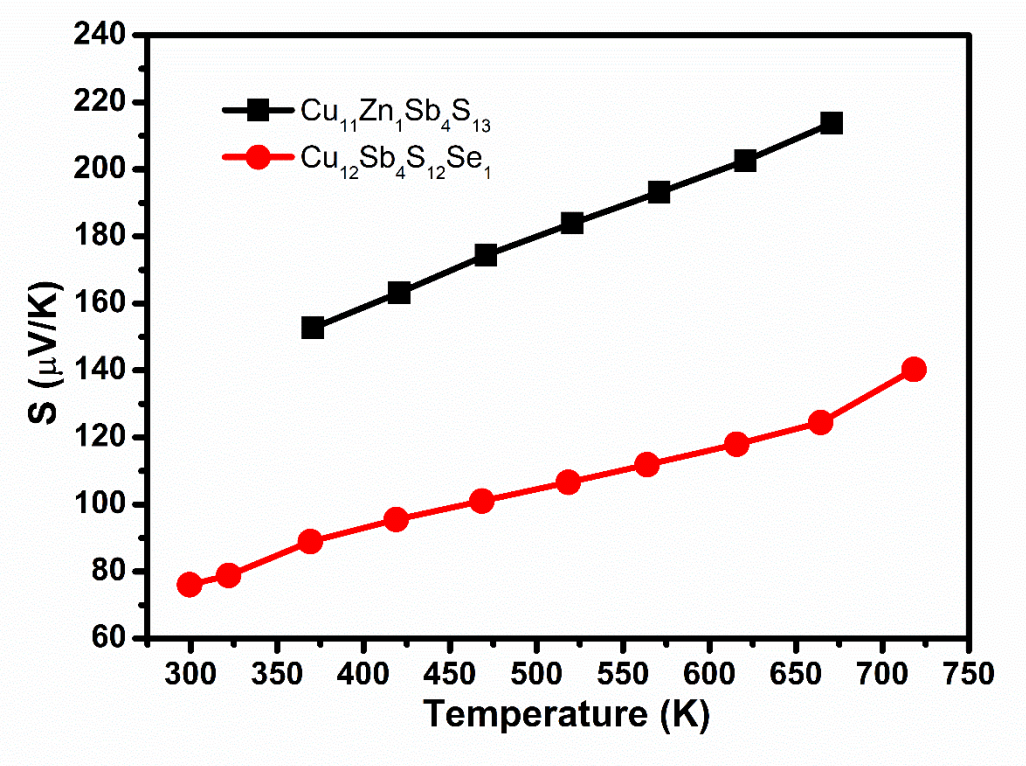

Figure S15

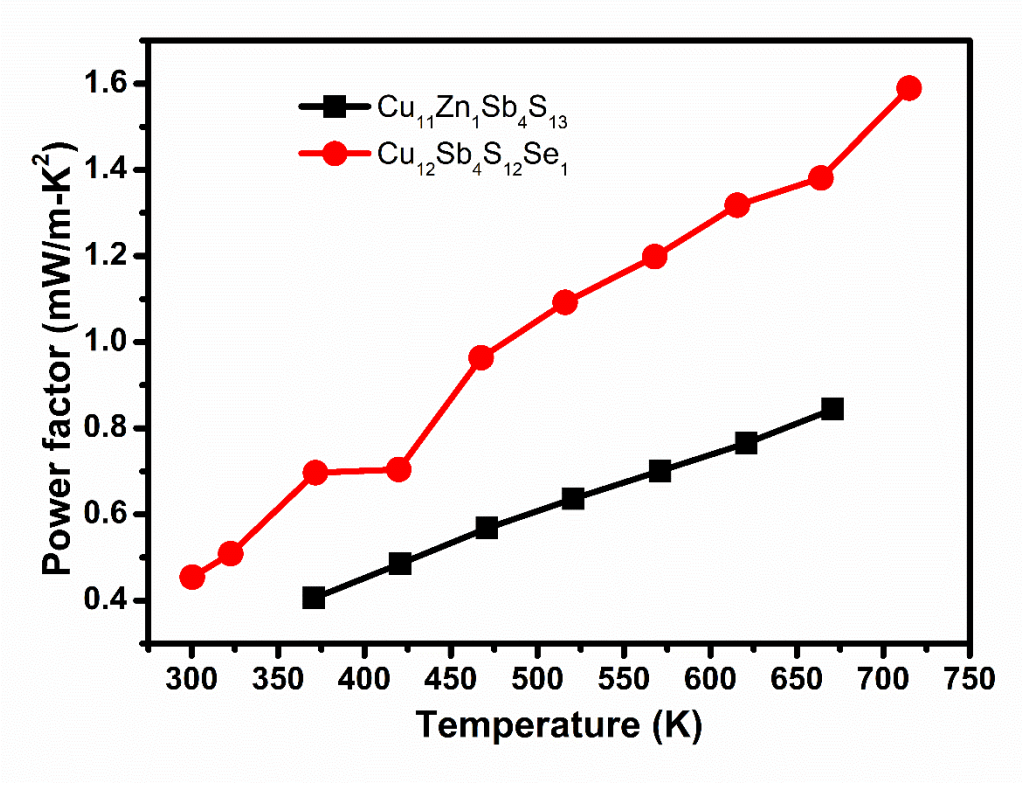

Figure S16

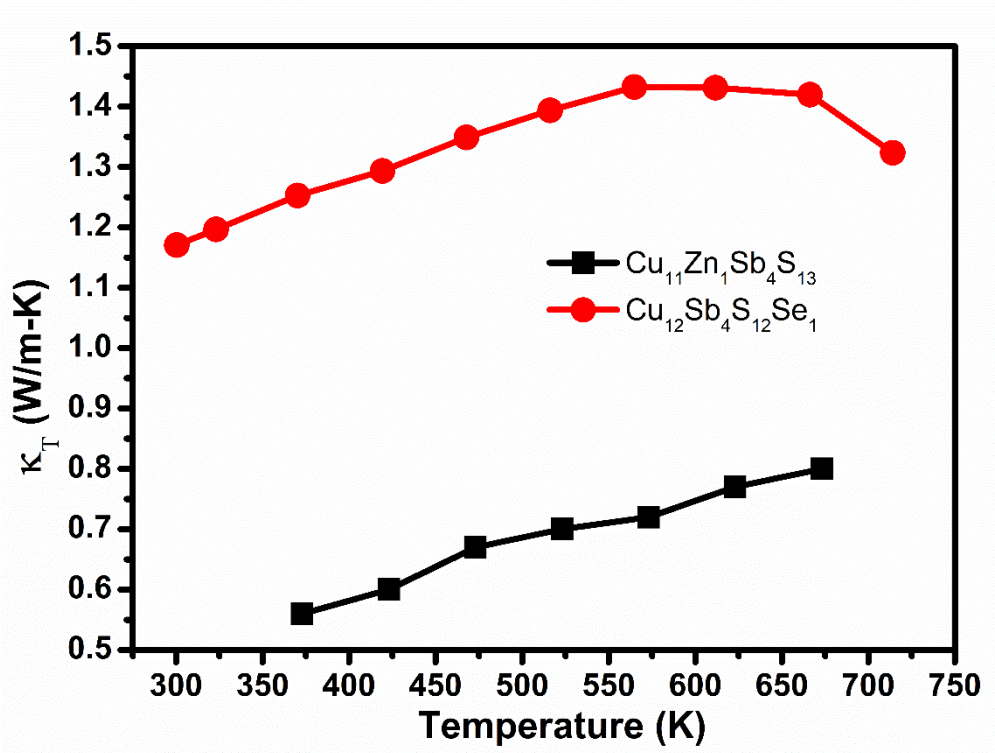

Figure S17

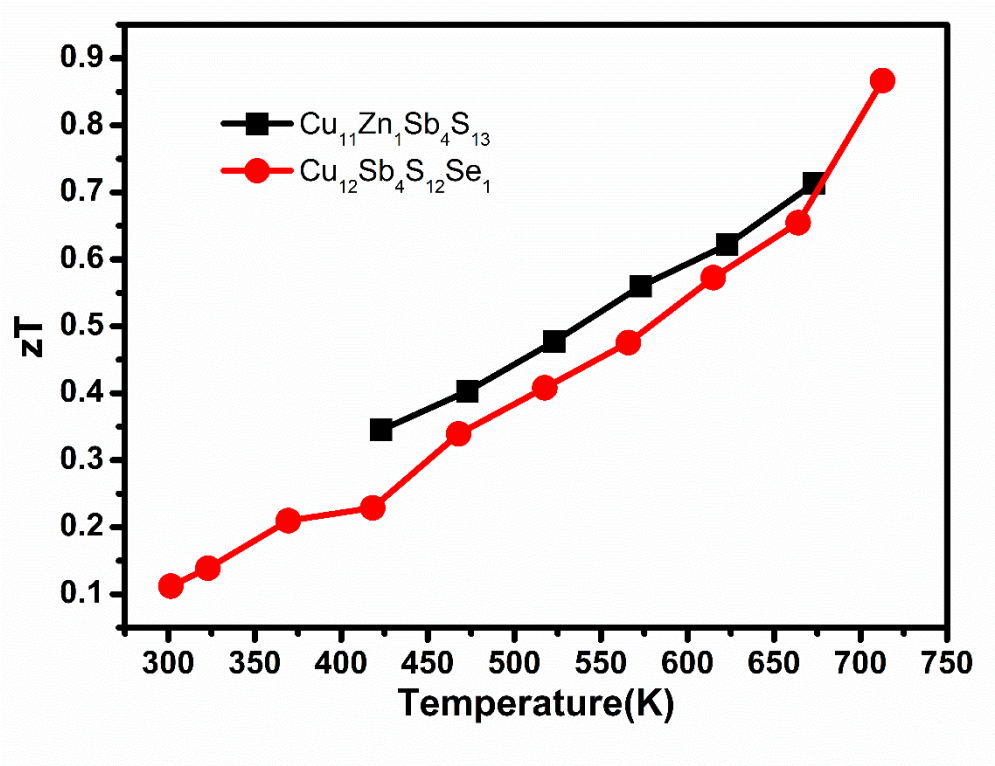
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
zT
300
350
400
450
500
550
600
650
700
750
Temperature(K)
Cu11Zn1Sb4S13
Cu12Sb4S12Se1

Figure S18