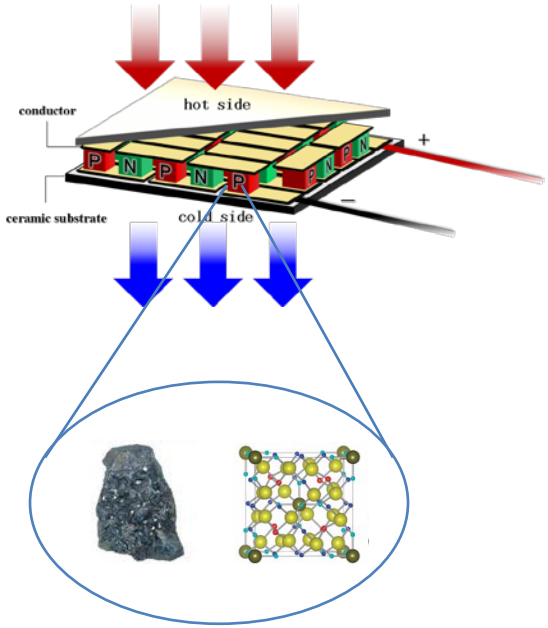
Eco-Friendly Cu-S based Thermoelectric materials



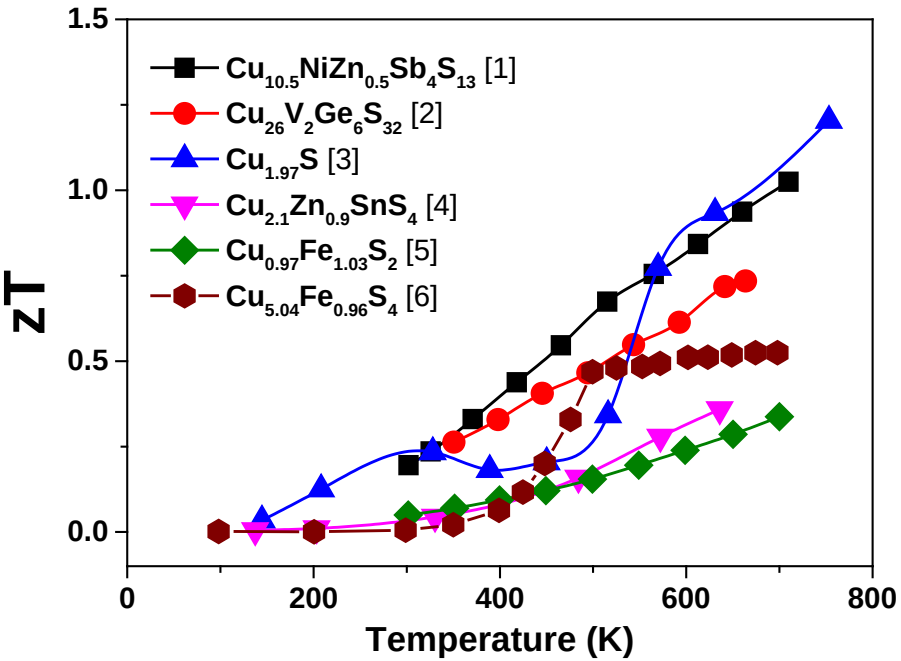
Ruizhi Zhang, Taichao Su, Kan Chen, Baoli Du, Michael J. Reece
Queen Mary University of London

Cono Di Paola, Nicola Bonini, Cedric Weber
King's College London

Matej Balaz, Peter Balaz
Slovak Academy of Sciences

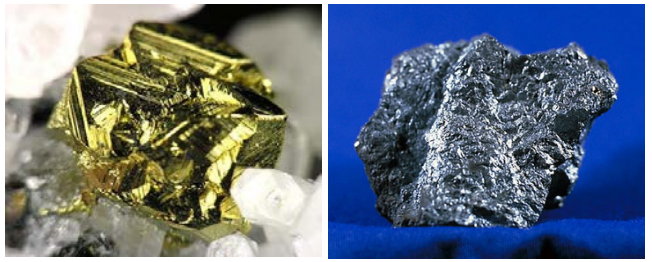
Cu-S based minerals for thermoelectrics

- **Advantages of Cu-S based Thermoelectric Materials**
  - **Potential high thermoelectric performance**
  - **low cost, some are minerals**
  - **Environmentally friendly, compared to Bi_2Te_3**
  - **Large variance of composition (~1000 compounds in ICSD)**



Tetrehidrite($Cu_{12}Sb_4S_{13}$) Bornite(Cu_5FeS_4)

Chalcopyrite ($CuFeS_2$) Chalcocite(Cu_2S)



[1] Lu & Morelli, Chem Mater, 2015 [2] Suekuni, Appl Phys Lett, 2014
[3] He & L. Chen, Adv Mater, 2014 [4] Liu & L. Chen, Appl Phys Lett, 2009
[5] Li & L. Chen, J Appl Phys, 2014 [6] Qiu & L. Chen, Energy Environ Sci, 2014

Collaboration for research on Cu-S compounds

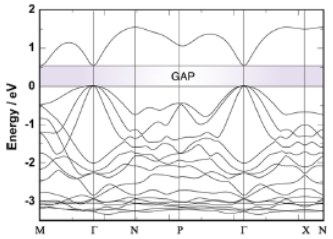
DEFCOM: Designing Eco-Friendly and COst-efficient energy Materials

KING'S College LONDON

Density functional theory modeling

b-initio VASP ackage ienna imulation

QUANTUMESPRESSO



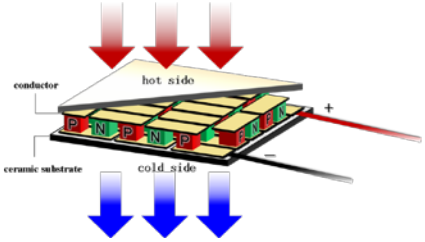
Ball mill + spark plasma sintering **Linsies & Netzsch**

QUEEN MARY UNIVERSITY OF LONDON

Synthesis & Characterization

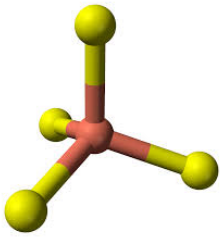
European Thermodynamics

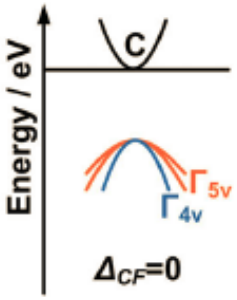
Thermoelectric module



High throughput screening

Screening descriptor:
Cu-S tetrahedral network





> 160,000 entries

Inorganic Crystal Structure Database (ICSD 2015)

965 phases

Cu-S based compounds

324 phases

Contain Cu-S tetrahedral

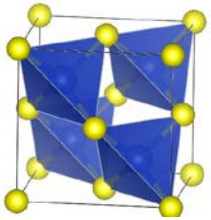
104 compounds

Materials with similar crystal structure

5 groups

Structural relationships of identified 104 compounds

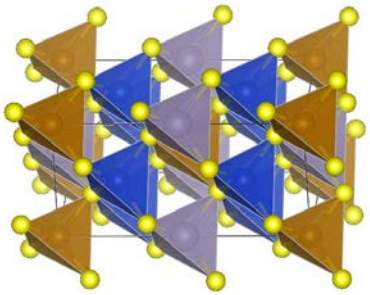
Zincblende
CuS (not exist)



Corner-share Cu-S tetrahedral

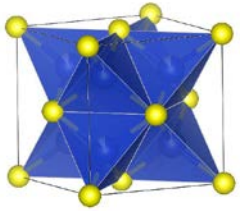
1. Cation Mutation (47)

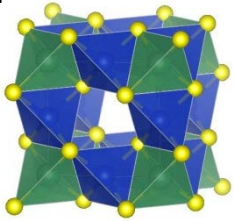
Stannite: Cu_2ZnSnS_4
Chalcopyrite: $CuFeS_2$
Famatinite: Cu_3SbS_4



2. Add/Remove atom (7)

Q-Chalcocite: Cu_2S
Sulvanite: Cu_3VS_4

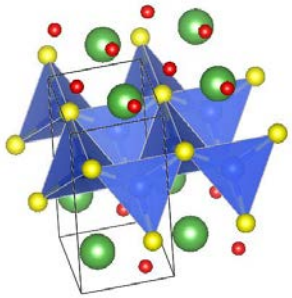


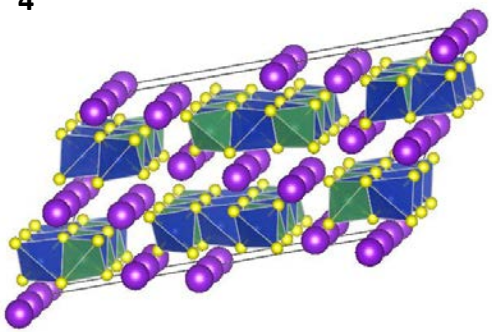


Group 5: all the other phases (11)

4. Add + Cleave (31)

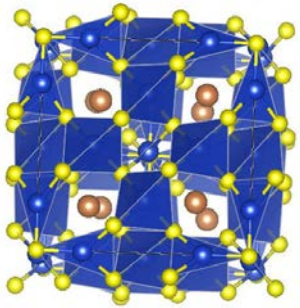
Layer: BiOCuS
Chain: $K_3Cu_3Nb_2S_4$

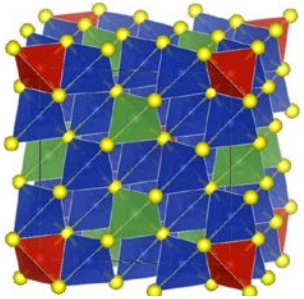




3. Mutation + Add/Remove (8)

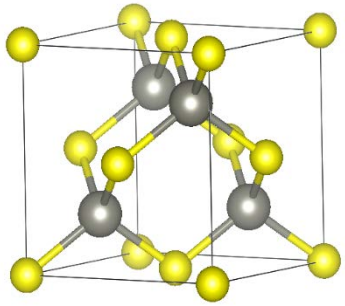
Tetrahidrite: $Cu_{12}Sb_4S_{13}$
Colusite: $Cu_{13}VAs_3S_{13}$





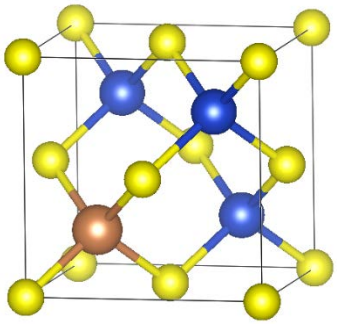
Example: derivative tetrahedrite from ZnS

Zinc Blende ZnS



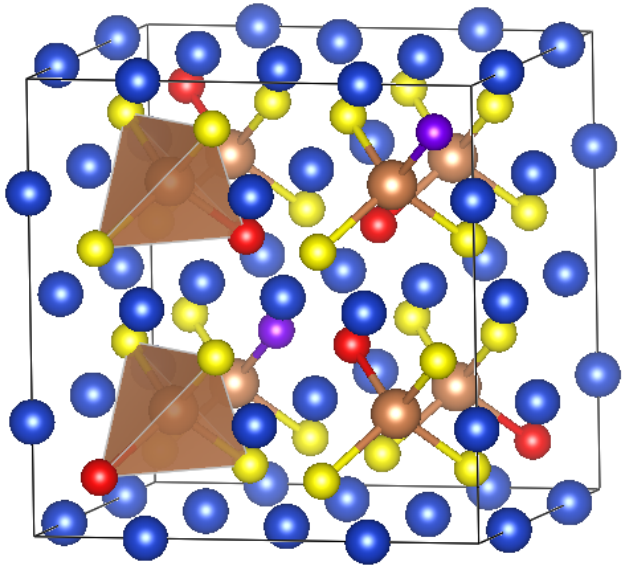
(1)

Cu_3SbS_4



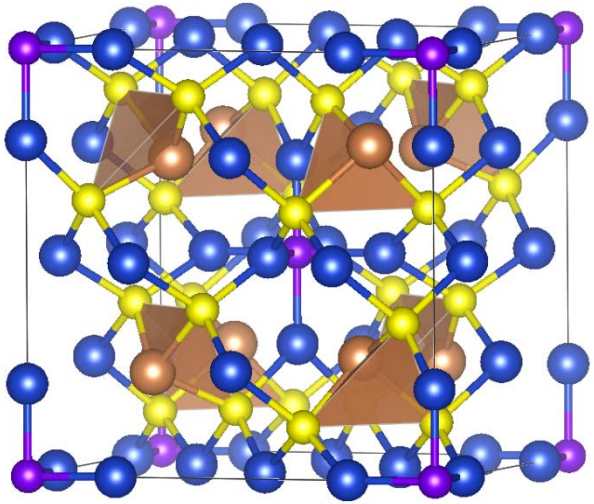
Operations:
Cation(Cu) mutation + atoms(S) removing

(2)



8 x Cu_3SbS_4

(3)



$Cu_{24}Sb_8S_{26}$ ($Cu_{12}Sb_4S_{13}$)

Group 3 compounds

Group	ICSD Number	ICSD formula	Mineral name	Reported zT_{Max}	Notes
(a). Sb(As)-S_3 pyramid	25707	$Cu_{12}S_{13}Sb_4$	Tetrahedrite	1.13@575K [1]	RF* $Cu_{11}MnSb_4S_{13}$
	33588	$As_4Cu_{12}S_{12}$	Tennantite		
	236895	$As_8Cu_{12}S_{18}$	Sinnerite		
(b). Unusual sulphur coordination	40047	$Cu_6Fe_2S_8Sn_1$	Mawsonite		
	41894	$Cu_{16}Fe_{4.3}S_{24}Sn_4Zn_{1.7}$	Stannoidite		
	64787	$Cu_{13}Fe_2Ge_2S_{16}$	Germanite	0.17@575K [2]	RF $Cu_{22}Fe_8Ge_4S_{32}$
	156238	$Cu_6Ge_1S_8W_1$	Catamarcaite		
	610353	$As_3Cu_{13}S_{16}V_1$	Colusite	0.73@663K [3]	RF $Cu_{13}VGe_3S_{16}$

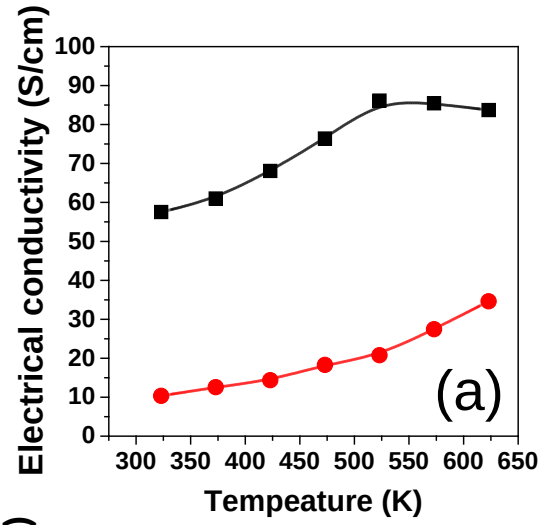
Red: compounds for further experiments

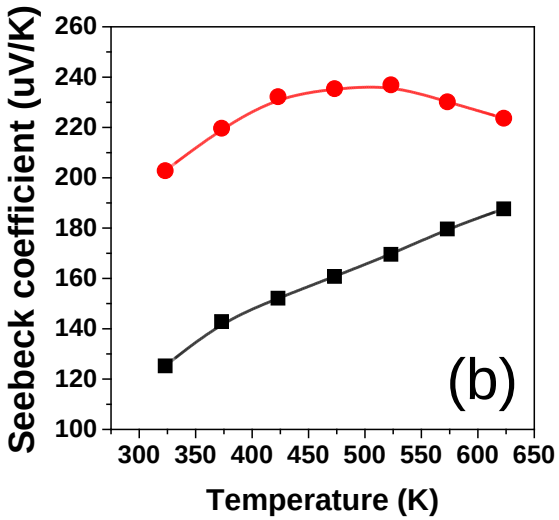
Orange: compounds have been reported as thermoelectrics

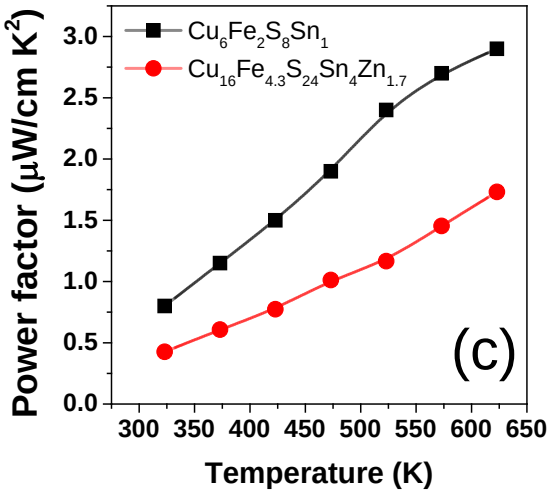
*** RF= reported formula**

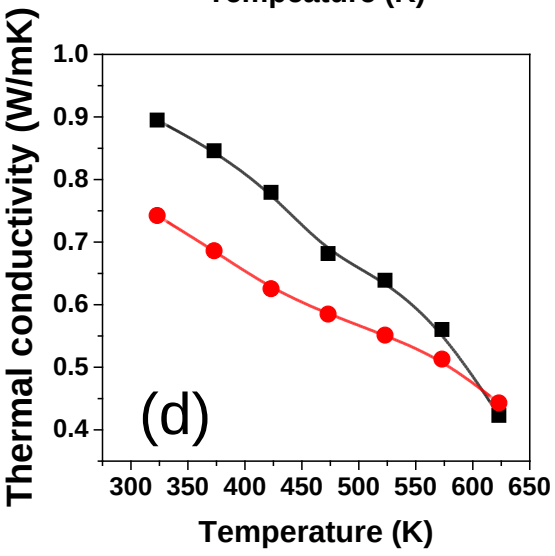
Ref: [1] Morelli, ChemMater 2015; [2] Guilmeau, Inorg Chem 2017; [3] Suekuni, APL 2014

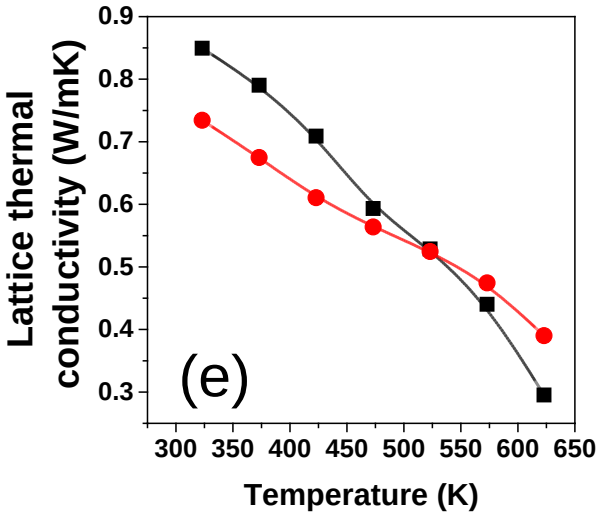
Thermoelectric properties of identified compounds

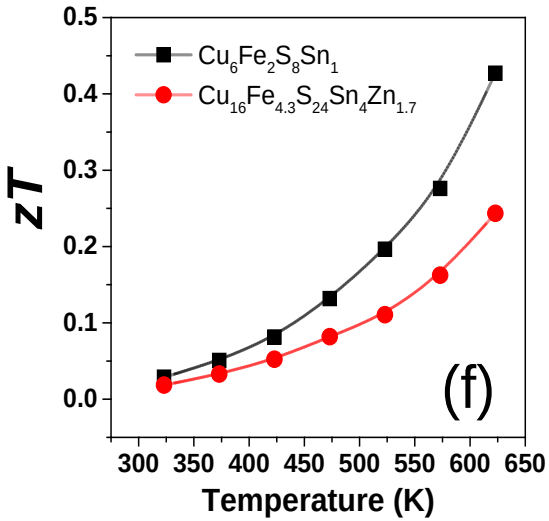






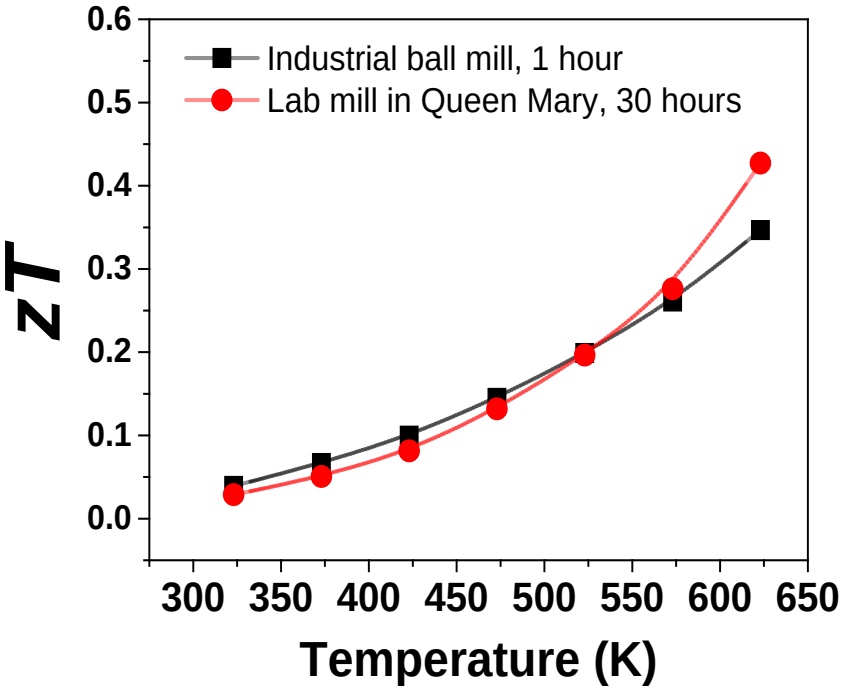


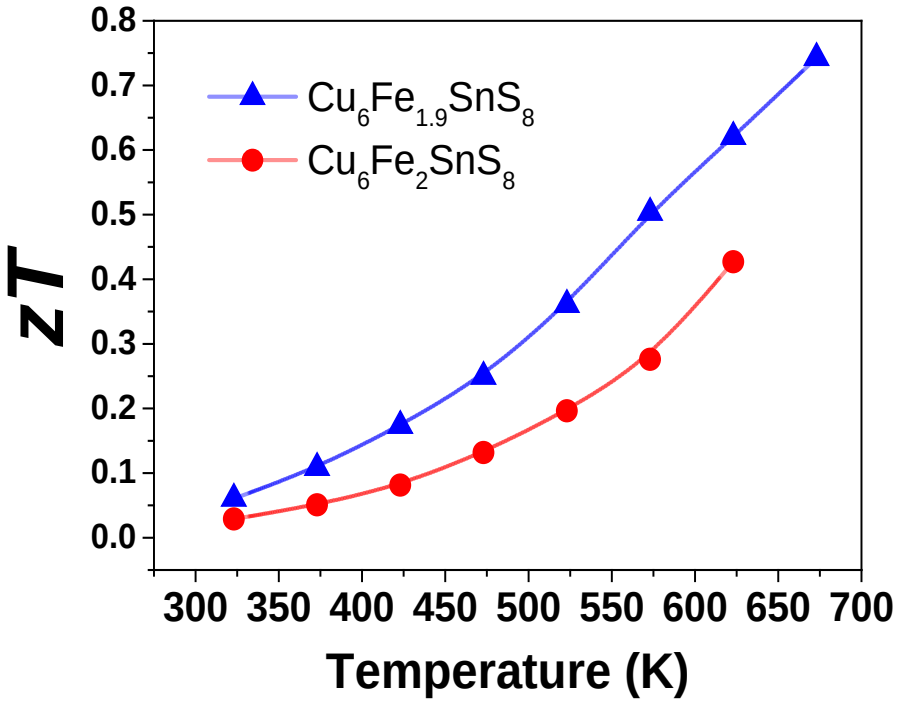


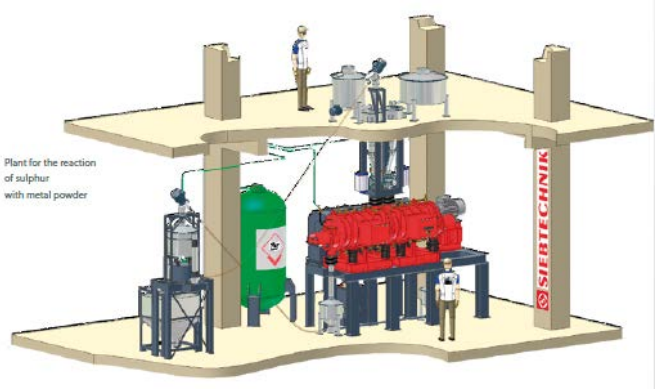


Improved synthesis routine and properties

Mawsonite, $Cu_6Fe_2SnS_8$

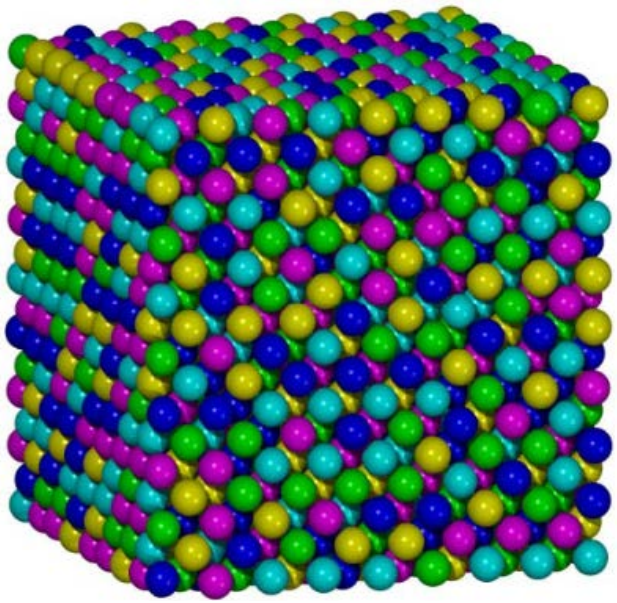






By introducing Fe vacancies, zT can be improved to 0.74@673K

Group 1: make it complex



Atomic structure model of FCC CoCrFeMnNi

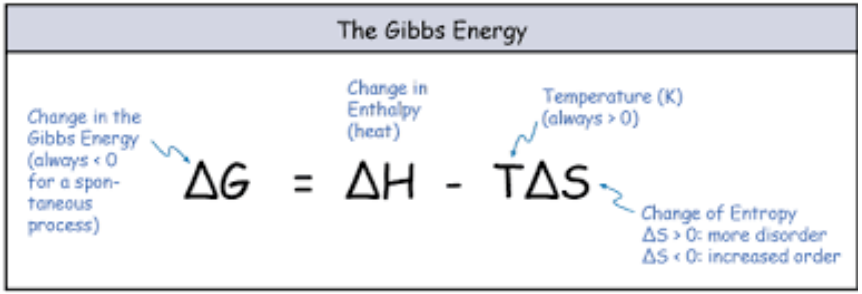
- High Entropy Alloys, by Professors Brian Cantor and Jien-Wei Yeh, 2004
  - Solid solution high entropy mixtures of several (>4) different alloying elements in near-equal amounts
  - Structural order, chemical disorder
- Single or two-phase solid solutions can be formed => "Entropy stabilised"

$$\Delta G = \Delta H - T\Delta S$$

High entropy (or multi-component) sulfides

Selection criteria

- **Reduce enthalpy of formation**
  - **Only compounds forming zinc blende or wurtzite derived structure were considered**



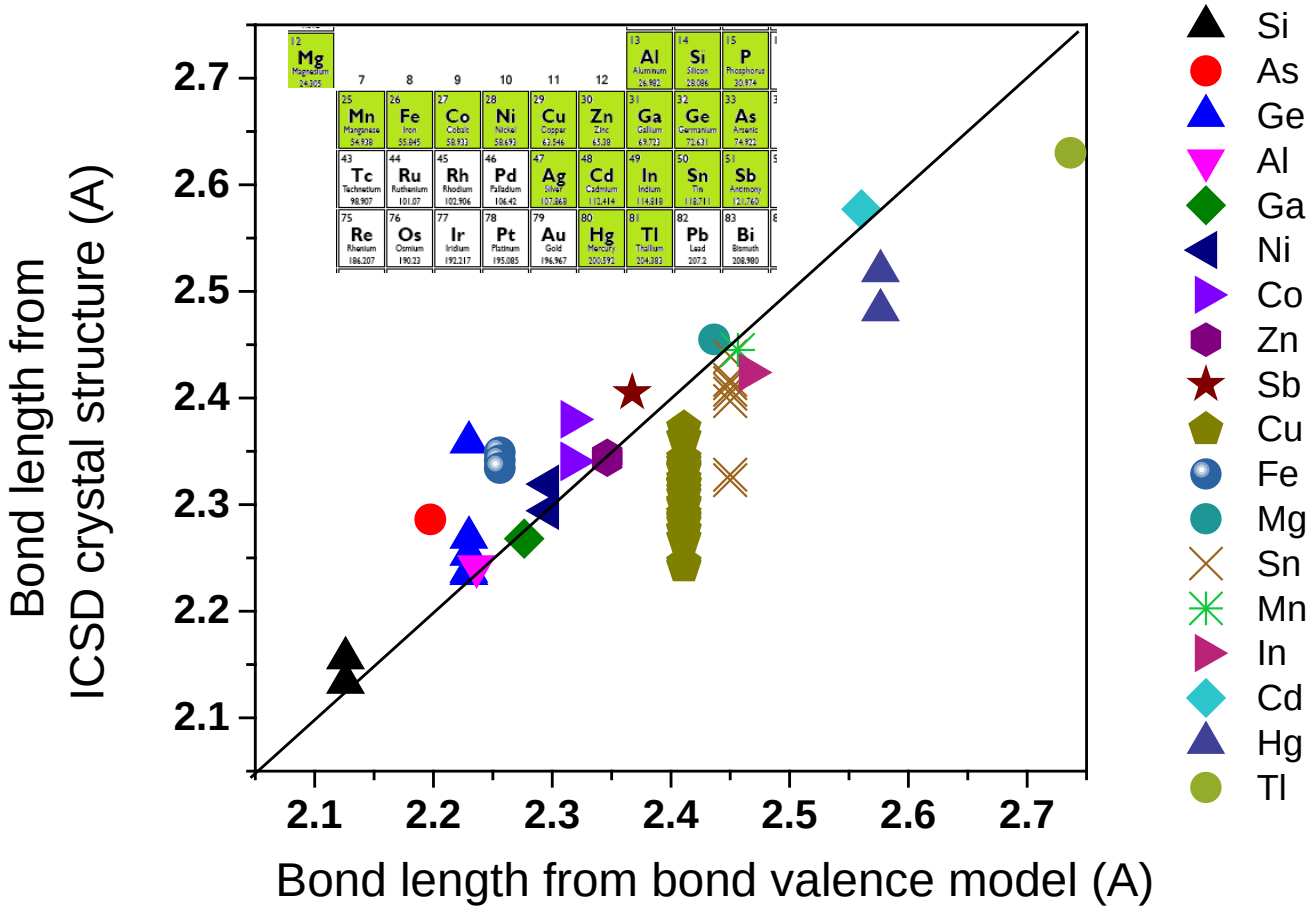
- **Importance of Cu_3SnS_4**
  - **Known metallic compounds with zinc blende derived structure**
  - **Several existing thermoelectric containing Cu_3SnS_4**

Composition	Breakdown	Reference
$Cu_3Sn_{0.1}Sb_{0.9}S_4$	$0.9Cu_3SbS_4+0.1Cu_3SnS_4$	zT~0.7@623K, Kan, to be published
$Cu_{2.1}Zn_{0.9}SnS_4$	$0.9Cu_2ZnSnS_4+0.1Cu_3SnS_4$	zT~0.3@623K, Liu & L. Chen, APL, 2009
$Cu_{2.15}Co_{0.85}SnS_4$	$0.85Cu_2CoSnS_4+0.15Cu_3SnS_4$	zT~0.6@773K, Qinghui, Nano energy 2017
$Cu_2Sn_{0.9}Zn_{0.1}S_3$	$0.7Cu_2SnS_3+0.2Cu_3SnS_4+0.1ZnS$	zT~0.6@723K, Wang , Scitific report, 2016

Data driven – structure data from ICSD

Zinc blende-related(29)		Wurtzite-related(18)	
ICSD number	Formula	ICSD number	Formula
2518	$Cu_1Fe_1S_2$	16924	$Cd_1Cu_2S_4Si_1$
2857	$Cu_3S_4Sb_1$	24132	$Cu_2S_3Si_1$
28742	$Cu_1S_2Tl_1$	24530	$Cu_3P_1S_4$
30368	$Cu_3S_4Sb_1$	26150	$Cd_1Cu_2Ge_1S_4$
42516	$As_1Cu_3S_4$	31999	$Cu_5S_7Si_2$
47165	$Cu_2Fe_1Ge_1S_4$	42672	$Cu_3S_4Sb_1$
85138	$Cu_2Ge_1S_3$	70057	$Cu_2S_3Si_1$
88235	$Cu_2S_3Si_1$	152762	$Cu_2Ge_1Hg_1S_4$
100778	$Cu_4Ni_1S_7Si_2$	185597	$Cu_2S_4Sn_1Zn_1$
107606	$Cu_2S_3Sn_1$	236248	$Cu_2S_4Si_1Zn_1$
152752	$Cu_2Ge_1S_4Zn_1$	261367	$Cu_2S_4Si_1Zn_1$
156786	$Cu_1Ga_1S_2$	415452	$Cu_2Mn_1S_4Si_1$
165738	$Al_1Cu_1S_2$	415453	$Cu_2Ge_1Mn_1S_4$
165739	$Al_1Cu_1S_2$	425554	$Cu_2Mg_1S_4Si_1$
171978	$Cu_2Fe_1S_4Sn_1$	425555	$Cu_2Ge_1Mg_1S_4$
181166	$Cu_2Fe_1S_4Sn_1$	627355	$Cu_2Fe_1S_4Si_1$
186714	$Cu_1In_1S_2$	627793	$Cu_2Ge_1S_4Zn_1$
187020	$Cu_2Ge_1Hg_1S_4$	627928	$Cu_2Hg_1S_4Si_1$
189286	$Cu_2S_4Sn_1Zn_1$		
415454	$Cu_2Mn_1S_4Sn_1$		
415927	$Co_1Cu_2Ge_1S_4$		
619773	$Cd_1Cu_2S_4Sn_1$		
622576	$Co_1Cu_2S_4Si_1$		
622578	$Co_1Cu_2S_4Sn_1$		
627755	$Cu_4Ge_2Ni_1S_7$		
627779	$Cu_2Ge_1S_3$		
627929	$Cu_2Hg_1S_4Sn_1$		
	$Cu_2Mg_1S_4Sn_1$		
	$Cu_2Ni_1S_4Sn_1$		
	$Cu_3S_4Sn_1$		
602043	$Cu_2S_4Sn_1W_1$ (wrong structure)		
156413	$B_1Cu_1S_2$ (only HPHT)		

Analysis of bond length

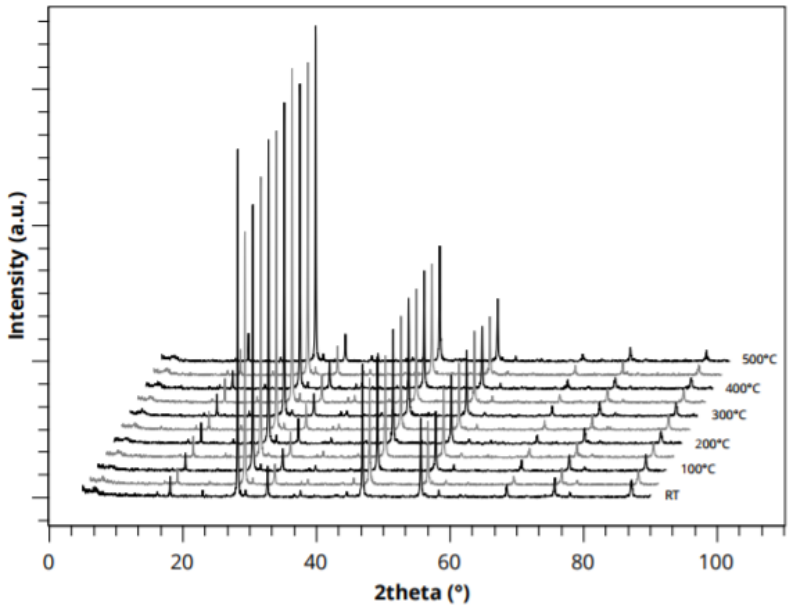


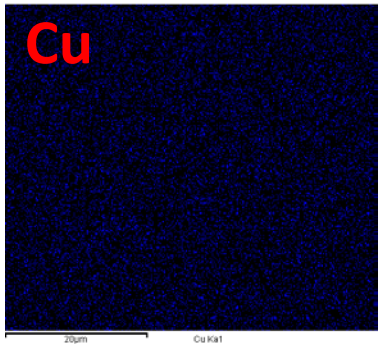
Two compositions were designed

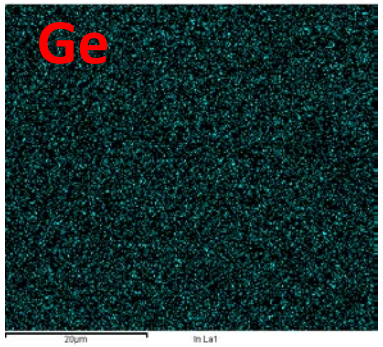
Metallic, $Cu_5Ge_1Zn_1Mg_1Sn_1S_8$ (Cu_3SnS_4-Cu_2MgGeS_4-ZnS)

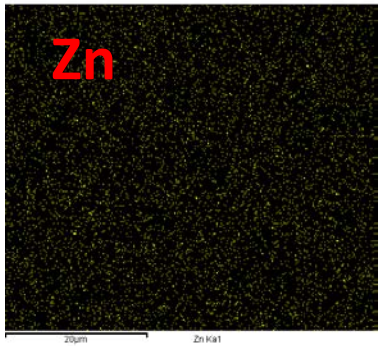
Semiconductor, $Cu_3Mg_1In_1Sn_1Zn_1S_9$ (Cu_2MgSnS_4-$CuInS_4$-ZnS)

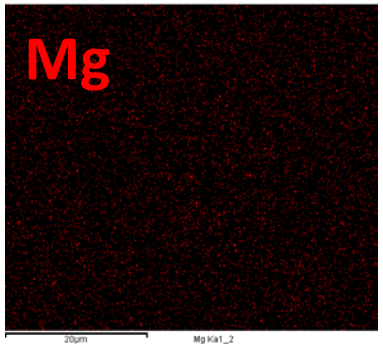
Structures of multi-component sulfides

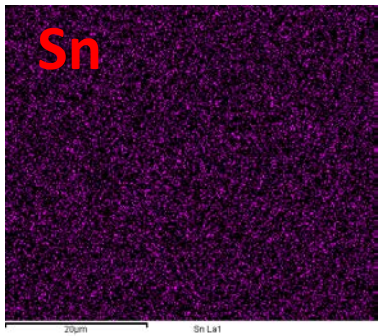


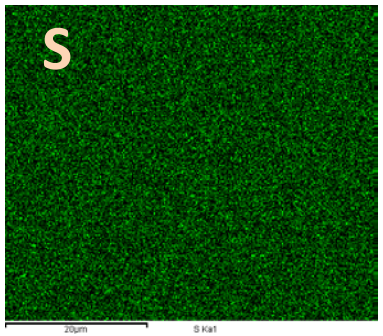






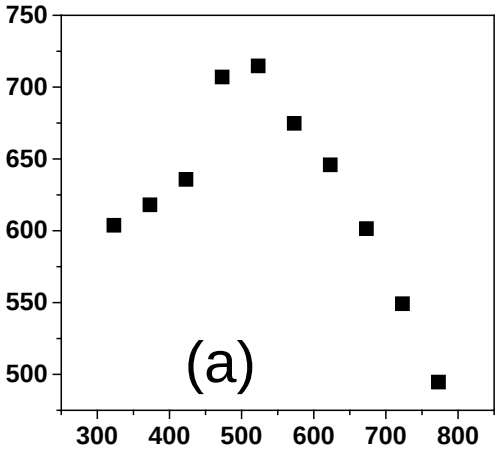


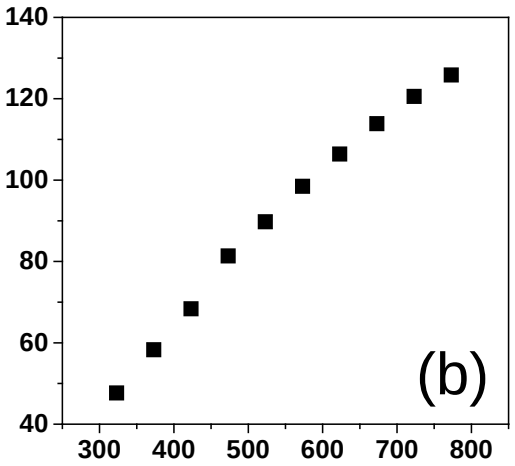


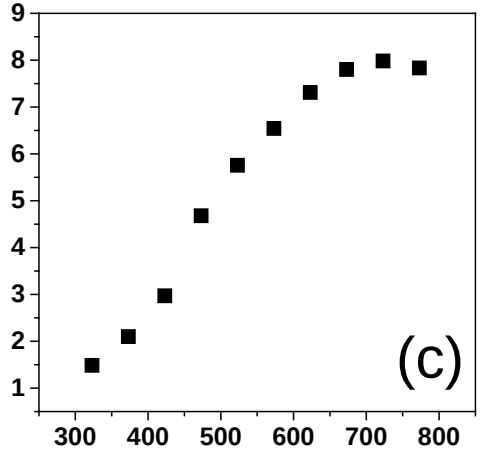


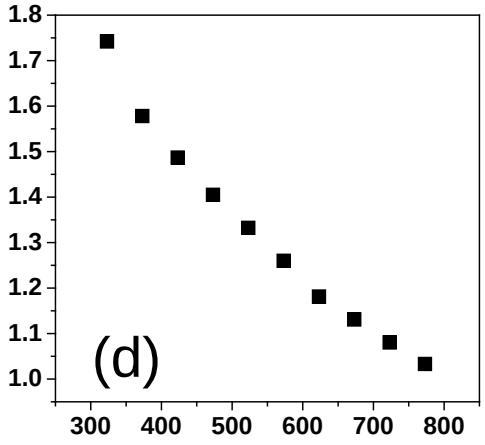
- **Single phase upto 500 ℃**
- **All the elements are distributed homogeneously at micro scale**

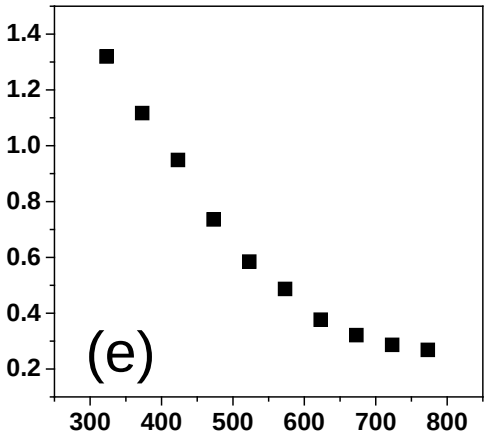
Thermoelectric $Cu_3Sn_{1.2}S_4$-Cu_2MgGeS_4-ZnS

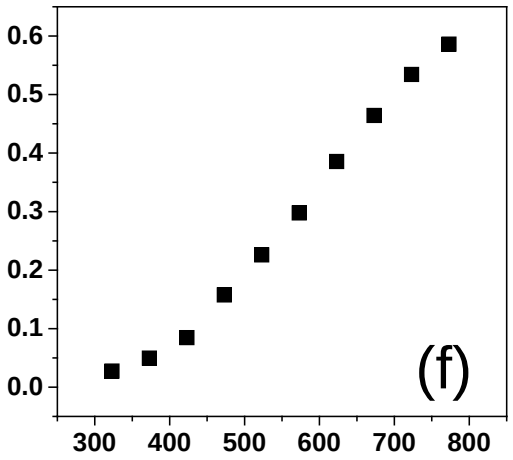






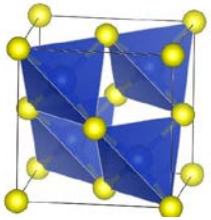






Conclusions

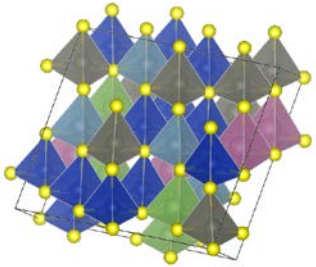
Zincblende
CuS (not exist)



Corner-share Cu-S tetrahedral

1. Cation Mutation (47)

- Data driven multi-component sulfide design
- Single phase, homogenous ceramics
- zT ~ 0.6 @ 773K

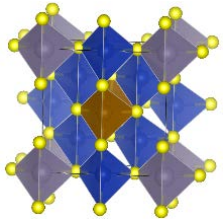


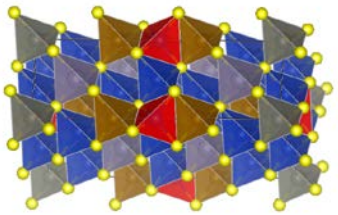
2. Add/Remove atom (7)

Synthesis problem: cannot get single phase or correct phase

3. Mutation + Add/Remove (8)

- Mawsonite and stannoidite were indentified as thermoelectric materials
- zT ~ 0.7 @ 673K for single phase mawsonite ceramics





4. Add + Cleave (31)

Further work for textured ceramics of layer/chain compounds