Copper-containing mineral sulfides as thermoelectric materials

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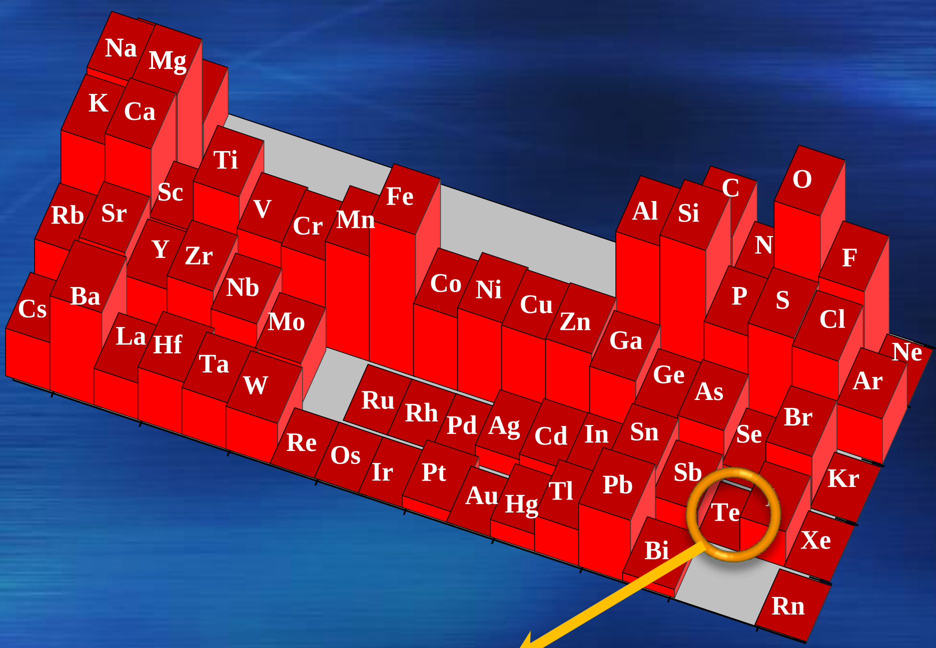
Need for new materials

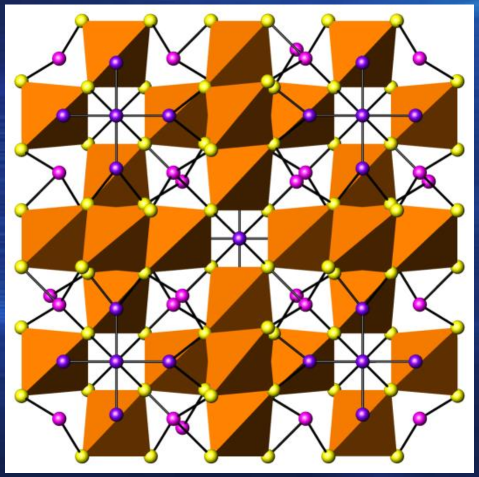
Commercial thermoelectric material:
Bi_2Te_3 (doped) ZT ~ 1 at 25°C

Abundance of elements

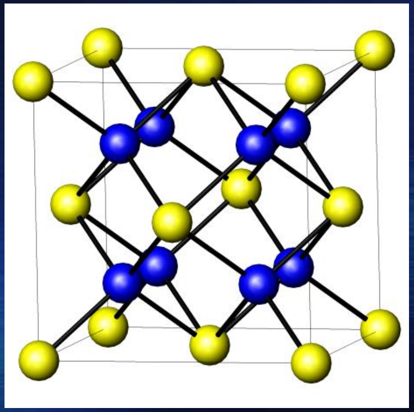


1 ppb in the Earth's crust

Materials made at Reading:



Tetrahedrite (doped)
$Cu_{12}Sb_4S_{13}$
ZT ~ 1 at 450°C
Chem. Mater. 2017, **29**, 4080.



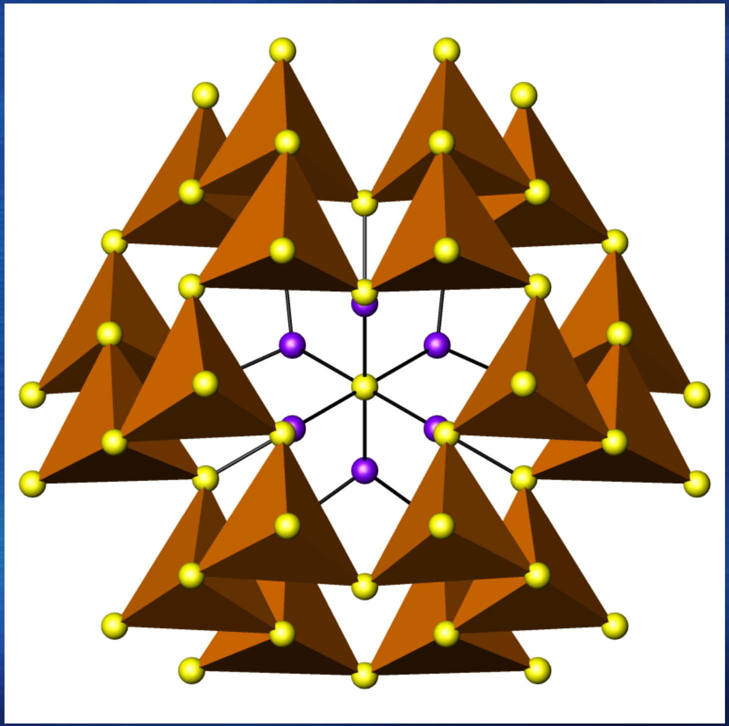
Bornite (doped)
Cu_5FeS_4
ZT~ 0.8 at 280°C
Chem. Mater. 2018, **30**, 456.

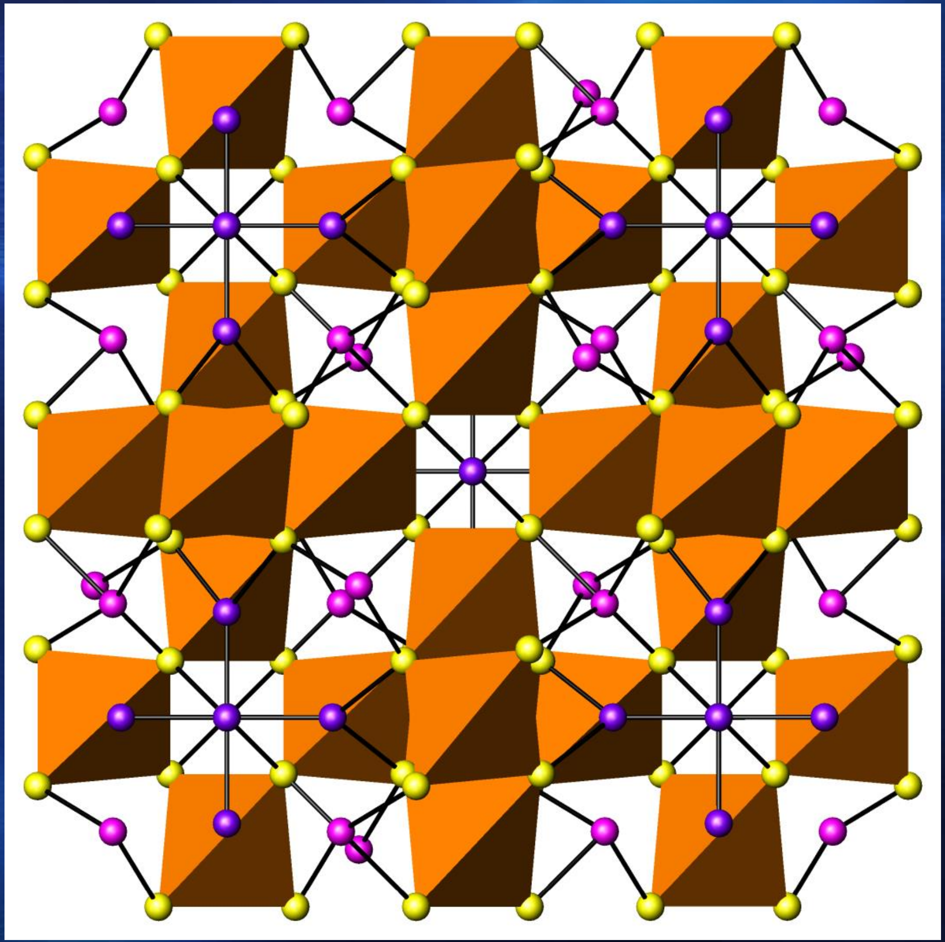
Tetrahedrite

Tetrahedrite is a mineral with the formula $Cu_{12}Sb_4S_{13}$; a common copper ore.

Space group: $I\bar{4}3m$

- ❑ **Sb** trigonal pyramidal site
- ❑ **Cu(1)** tetrahedral site
- ❑ **Cu(2)** trigonal planar site





Tetrahedrite: a collapsed sodalite

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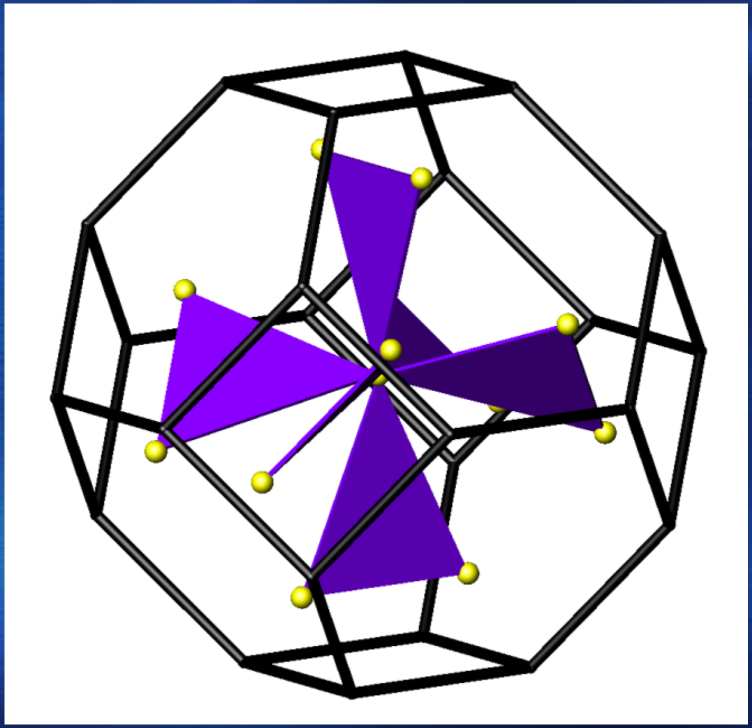
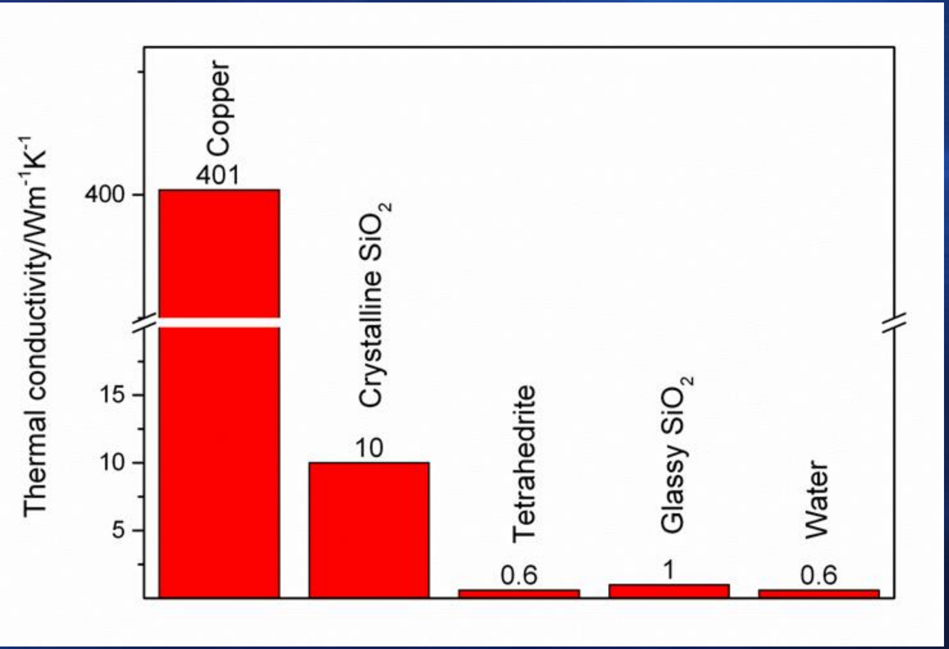
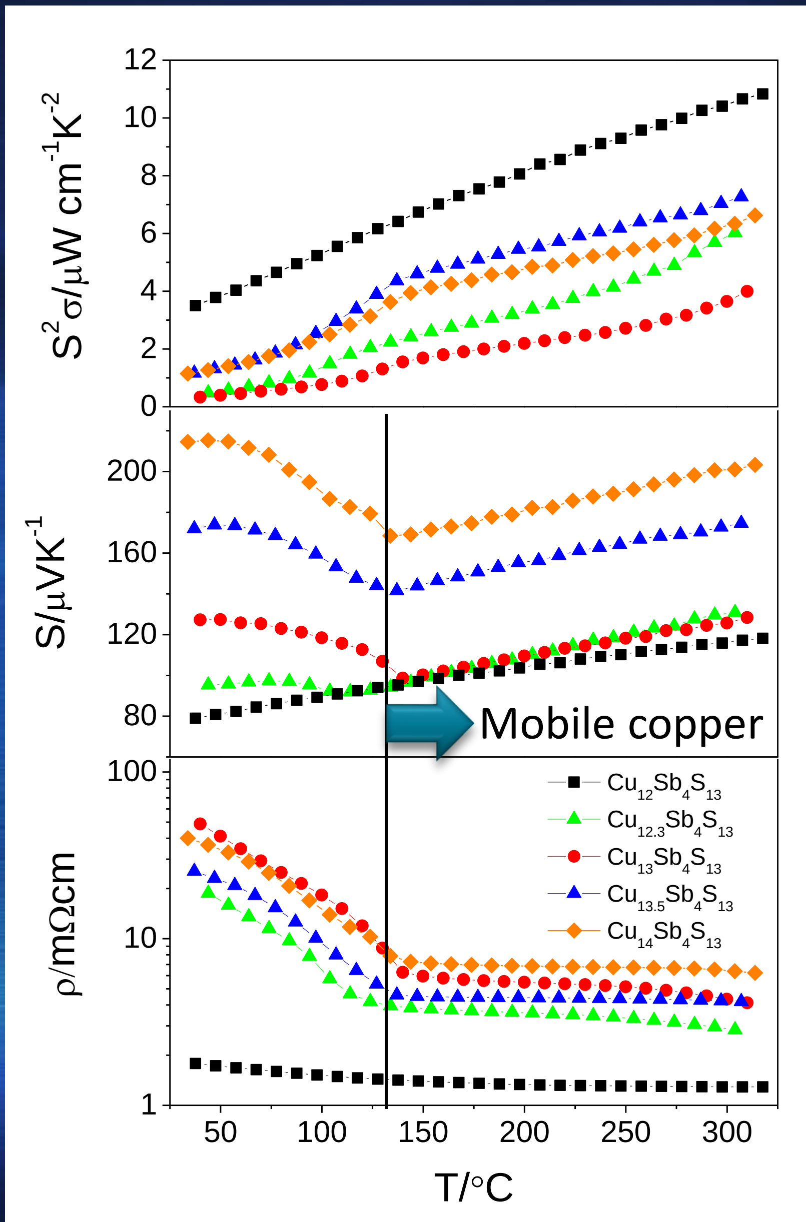
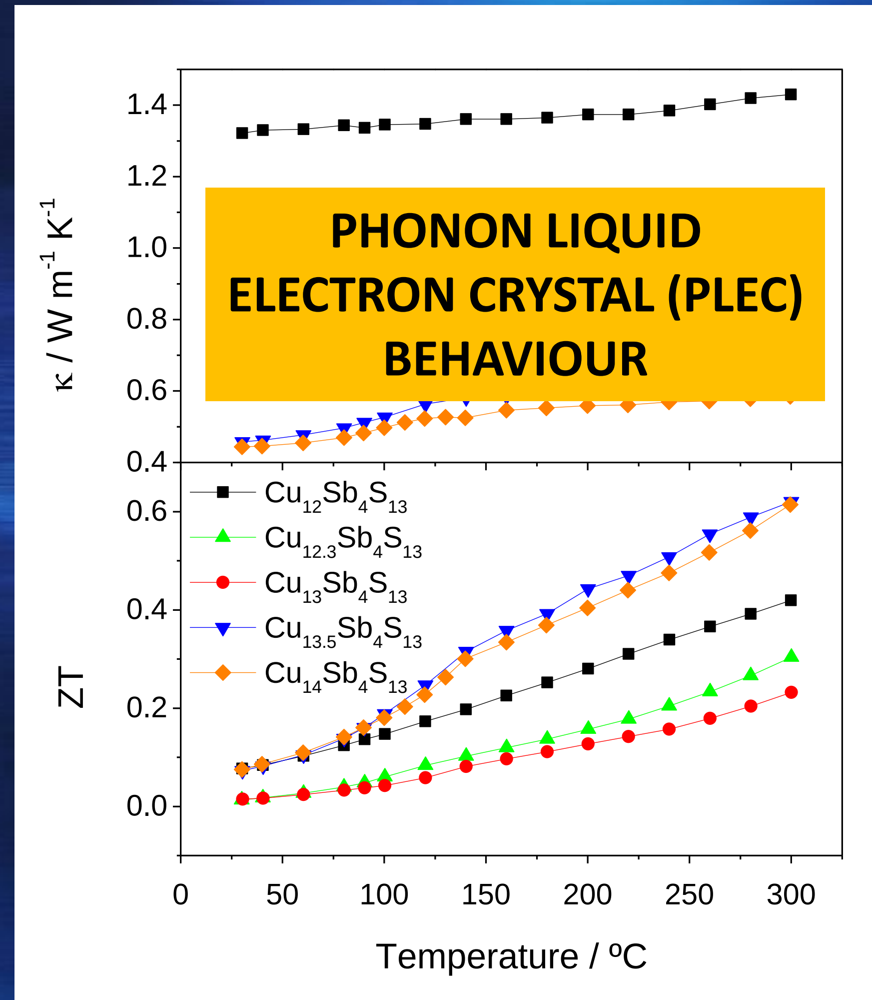




ZT ~ 1 at 450°C

Copper-rich tetrahedrites: $Cu_{12+x}Sb_4S_{13}$





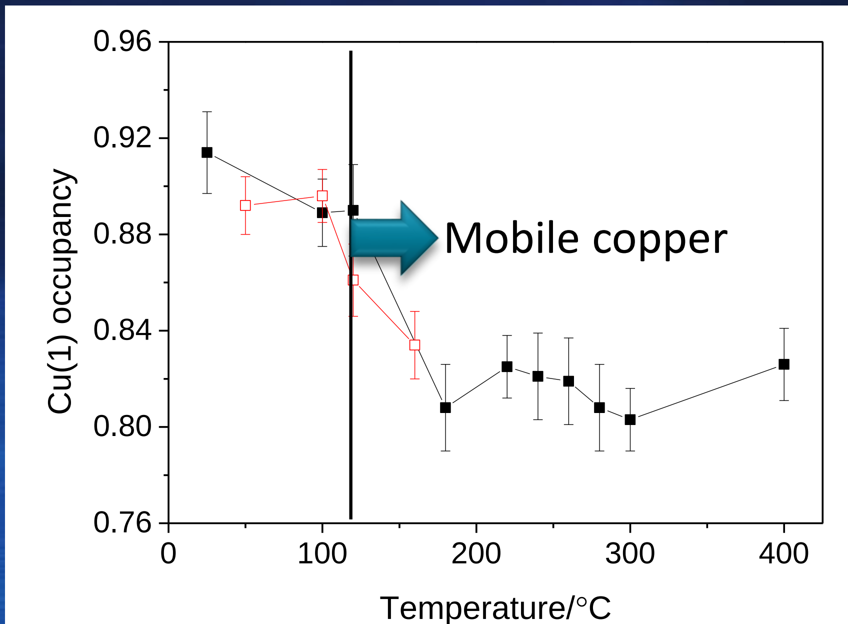
ZT~ 0.6 at 300°C

Estimated ZT ~ 1 at 450°C

Vaqueiro et al., *Chem. Mater.*, 2017, **29**, 4080.

Copper mobility

$Cu(1)S_4$ in "$Cu_{14}Sb_4S_{13}$"



Anomaly in lattice parameters at the onset of copper mobility.

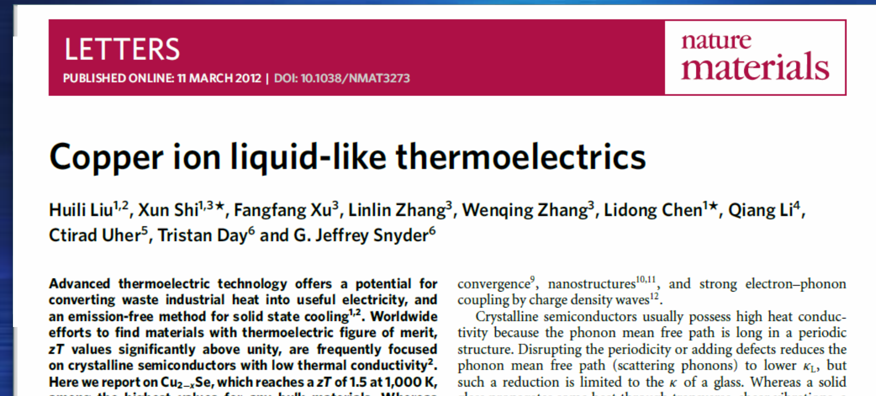
At 400˚C:

Refined composition for "$Cu_{12.3}Sb_4S_{13}$":

$Cu_{11.6(1)}Sb_4S_{13}$

Refined composition for "$Cu_{14}Sb_4S_{13}$":

$Cu_{11.7(1)}Sb_4S_{13}$



LETTERS

nature materials

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Copper ion liquid-like thermoelectrics

Huili Liu[1,2], Xun Shi[1,3]*, Fangfang Xu[3], Linlin Zhang[3], Wenqing Zhang[3], Lidong Chen[1]*, Qiang Li[4], Ctirad Uher[5], Tristan Day[6] and G. Jeffrey Snyder[6]

Advanced thermoelectric technology offers a potential for converting waste industrial heat into useful electricity, and an emission-free method for solid state cooling[1,2]. Worldwide efforts to find materials with thermoelectric figure of merit, zT values significantly above unity, are frequently focused on crystalline semiconductors with low thermal conductivity[2]. Here we report on $Cu_{2-x}Se$, which reaches a zT of 1.5 at 1,000 K,

convergence[9], nanostructures[10,11], and strong electron–phonon coupling by charge density waves[12].

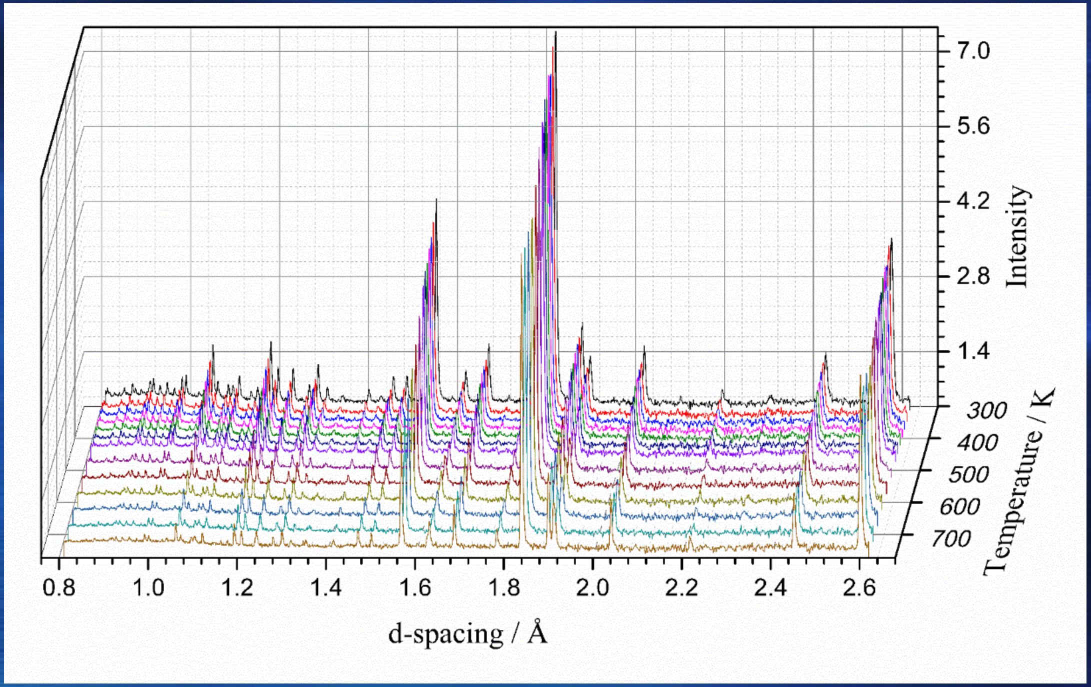
Crystalline semiconductors usually possess high heat conductivity because the phonon mean free path is long in a periodic structure. Disrupting the periodicity or adding defects reduces the phonon mean free path (scattering phonons) to lower κ_L, but such a reduction is limited to the κ of a glass. Whereas a solid

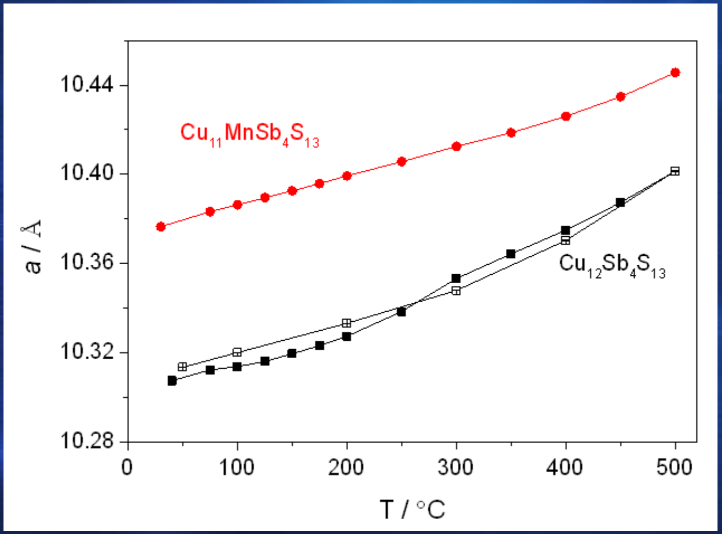
Cu_2Se after DC current for 24 hours…

Adv. Energy Mater. 2014, 1301581

Are all tetrahedrites PLEC materials?

Neutron diffraction data for $Cu_{12}Sb_4S_{13}$
POLARIS diffractometer (ISIS)





NO EVIDENCE FOR COPPER MOBILITY

Thermal expansion

$Cu_{12}Sb_4S_{13}$	$2.31(6) \times 10^{-4}$ Å K^{-1}
$Cu_{11}MnSb_4S_{13}$	$1.39(4) \times 10^{-4}$ Å K^{-1}

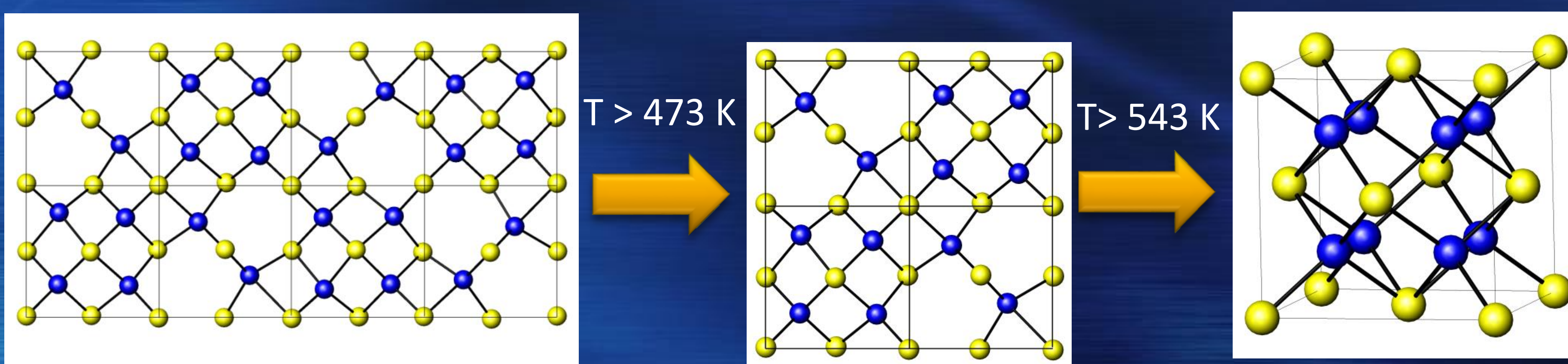
Sample in sealed ampoule

Manuscript in preparation

Bornite: Cu_5FeS_4

- Mineral $Cu_5Fe\square_2S_4$, where $\square$ represents a vacancy
- Structure related to antifluorite / zinc blende

Antifluorite $M_2S \equiv M_8S_4$ Bornite M_6S_4 Zinc blende $MS \equiv M_8S_8$

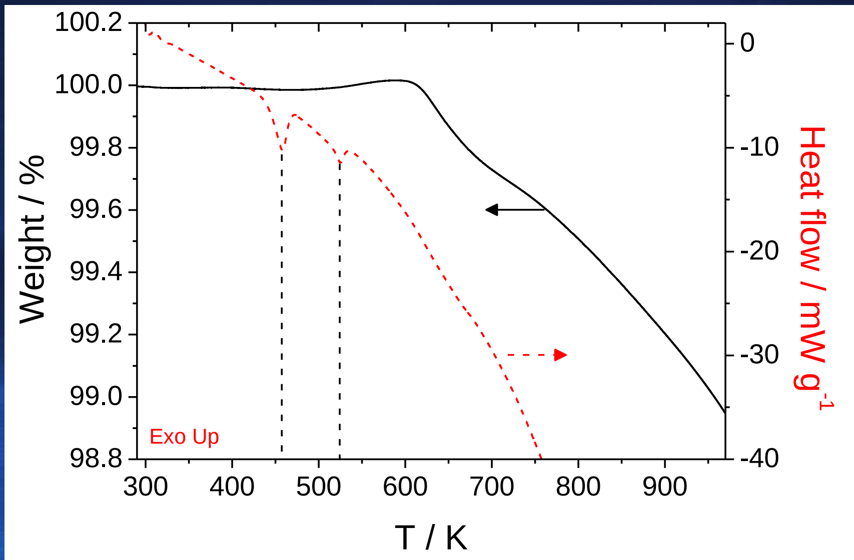


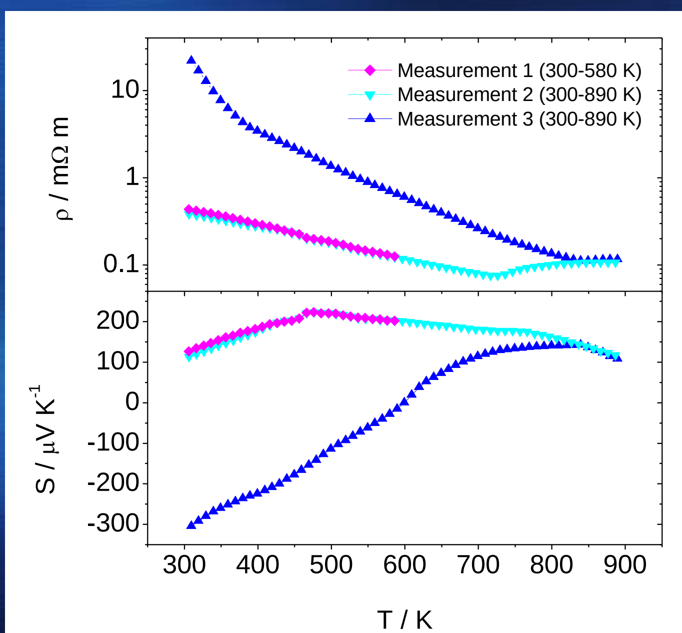
Room-temperature phase
4a × *2a* × *2a*

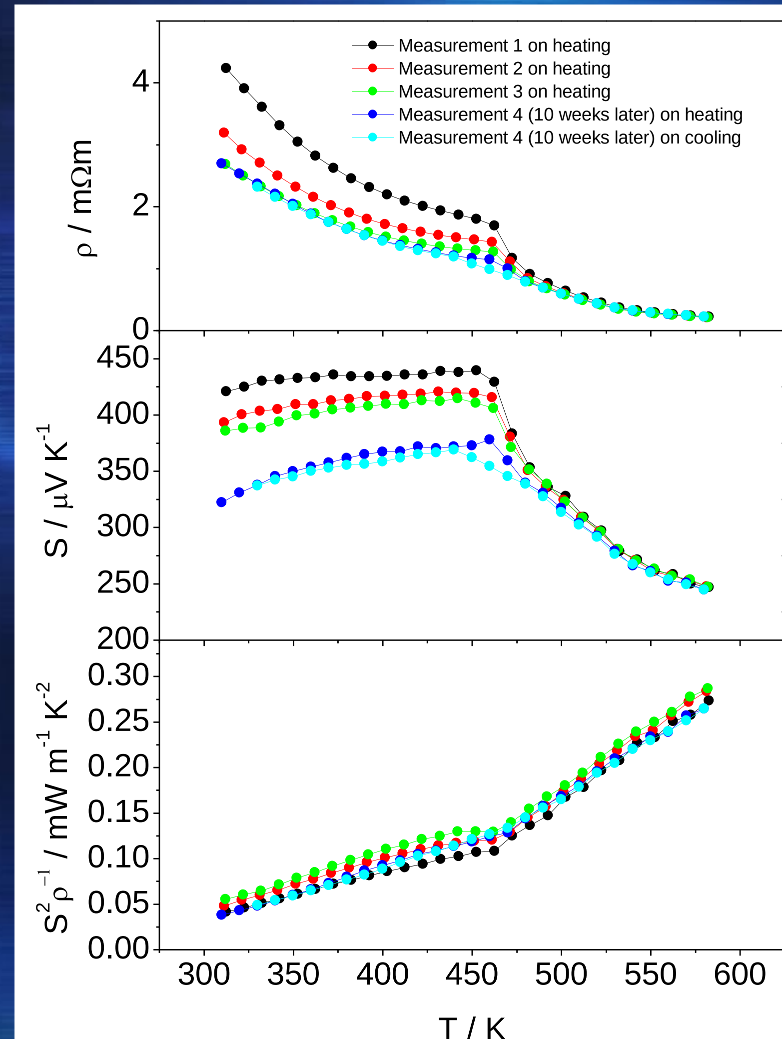
Intermediate phase
2a × *2a* × *2a*

High-temperature phase
a × *a* × *a*

Thermoelectric properties of bornite

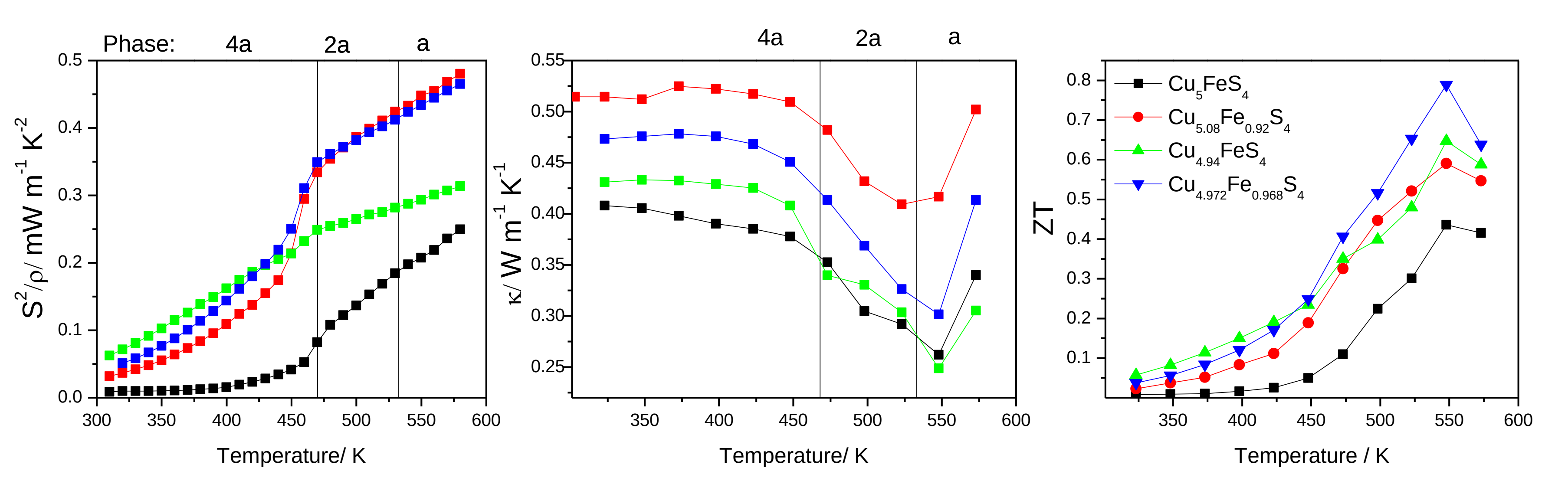






Guelou *et al. J. Mater. Chem. C*, 2015, **3**, 10624.

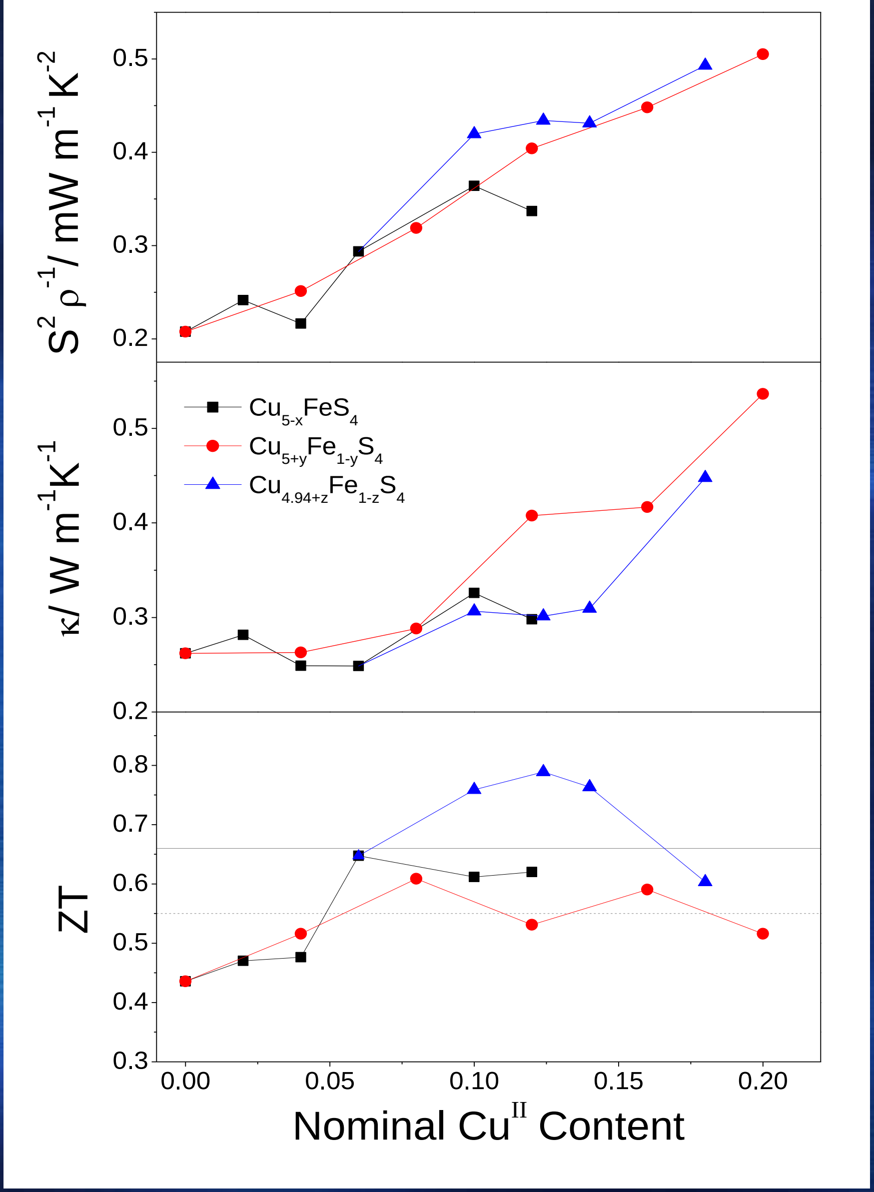
Optimising ZT of bornite



Cu_5FeS_4	Cu+Fe=6, Parent Phase	Low S^2/ρ, Low κ
$Cu_{5-x}FeS_4$	Cu+Fe<6, Iron Rich	Improved S^2/ρ, Low κ
$Cu_{5+x}Fe_{1-x}S_4$	Cu+Fe=6, Copper Rich	Great S^2/ρ, Increased κ
$Cu_{4.94+x}Fe_{1-x}S_4$	Cu+Fe=5.94, Copper Rich	Great S^2/ρ, Low κ

S. Long *et. al.*, *Chem. Mater.*, 2018, **30**, 456

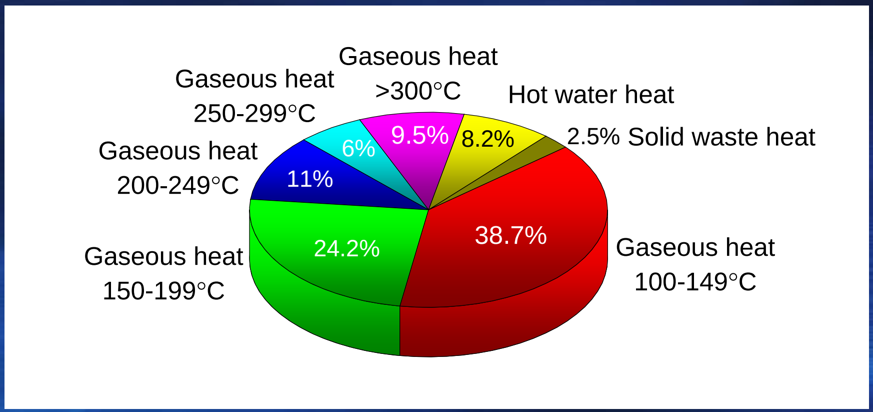
Optimising ZT of bornite



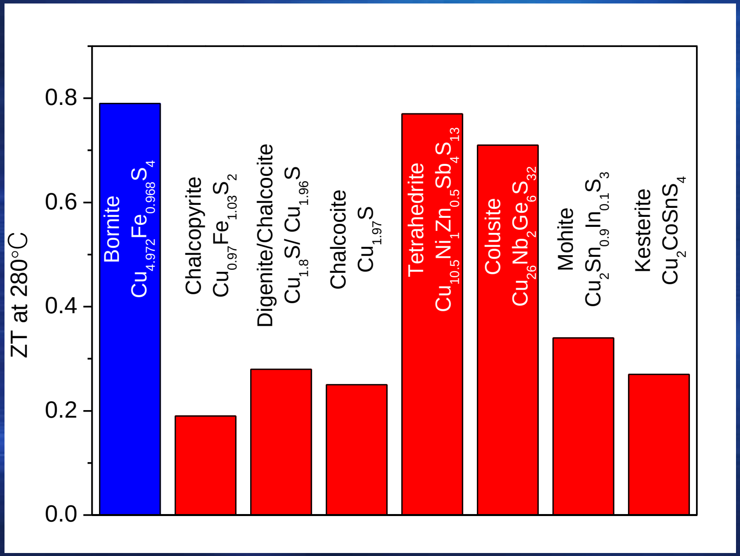
- Cu_5FeS_4 contains Cu(I) and Fe(III)
- Nominal Cu(II) content gives hole concentration.
- Substitution of Fe by Cu has greater impact on the nominal Cu(II) content than Cu deficiency.
- A critical level of vacancies (ca. 1%) is required in order to achieve a high ZT.

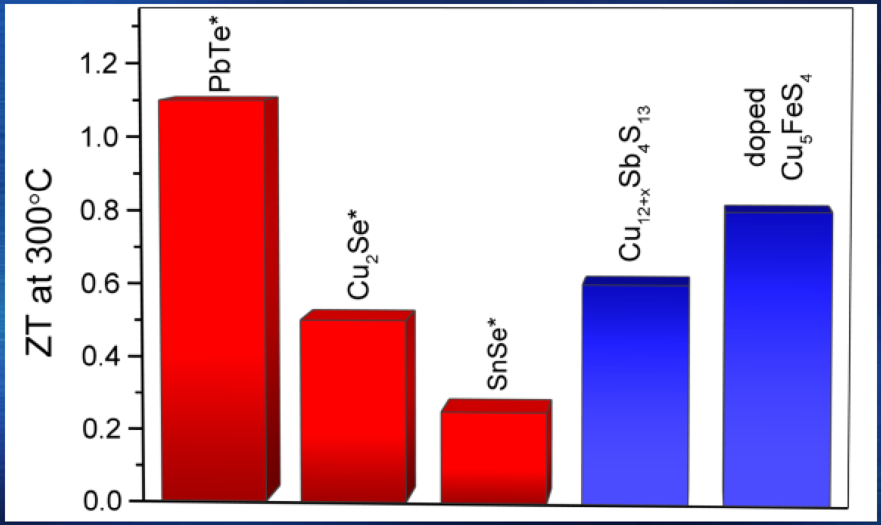
Comparison with existing materials

Waste heat recovery



Copper-containing sulfide minerals





Bornite, together with tetrahedrites and colusites, are promising p-type materials for applications at temperatures below 300°C.

*_Nature_, 2012, **489**, 414 ; 2014, **508**,373; _Nature Materials_, 2012, **11**,422.

Conclusions so far…

- In copper-rich tetrahedrites, low thermal conductivity is related to copper ionic mobility. These materials are likely to be phonon liquid electron crystals (PLEC).
- There is no evidence of PLEC behaviour in stoichiometric tetrahedrites ($Cu_{12-x}TM_xSb_4S_{13}$). Weak copper bonding results in low-energy vibrational modes.
- Bornite is a promising p-type thermoelectric material.
- In bornite, deviations from the ideal Cu_5FeS_4 stoichiometry result in significant enhancements in ZT.

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SEVENTH FRAMEWORK PROGRAMME

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