Intrinsically low thermal conductivity in some Cu-based ternary / quaternary sulfides

14th February 2017

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EPSRC Workshop - Manchester

Properties - Performances

Figure of Merit - zT

$$zT = \frac{\alpha^2 T}{\rho\kappa} \quad \Rightarrow \quad z = \frac{\alpha^2}{\rho\kappa}$$

α - Seebeck Coefficient

$$\alpha = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3}$$

ρ – Electrical Resistivity

$$\rho = \frac{1}{ne\mu}$$

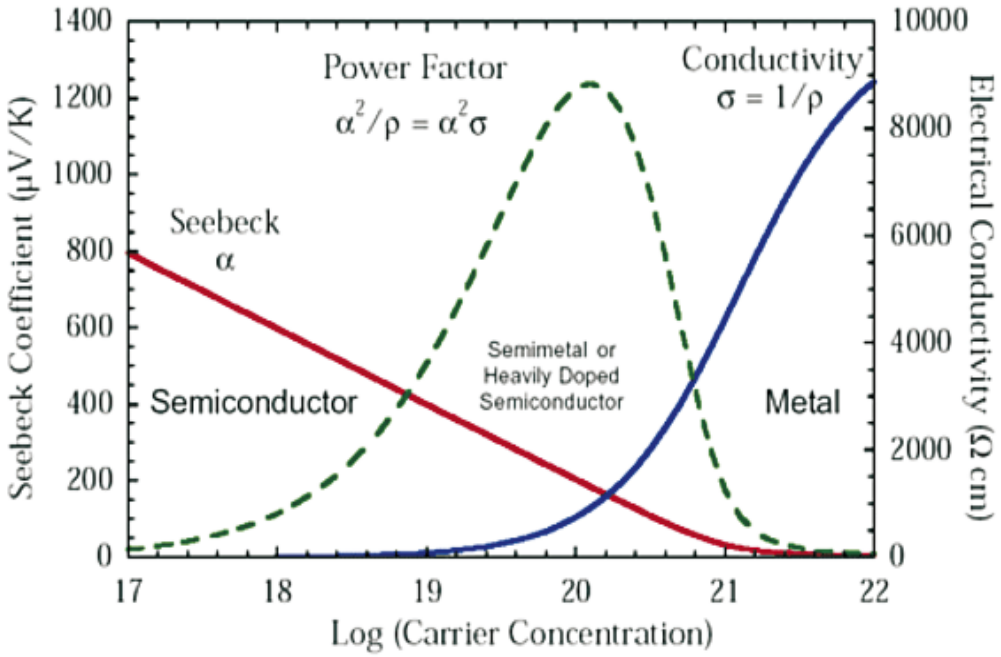
κ - Thermal Conductivity

$$\kappa = \kappa_e + \kappa_l$$

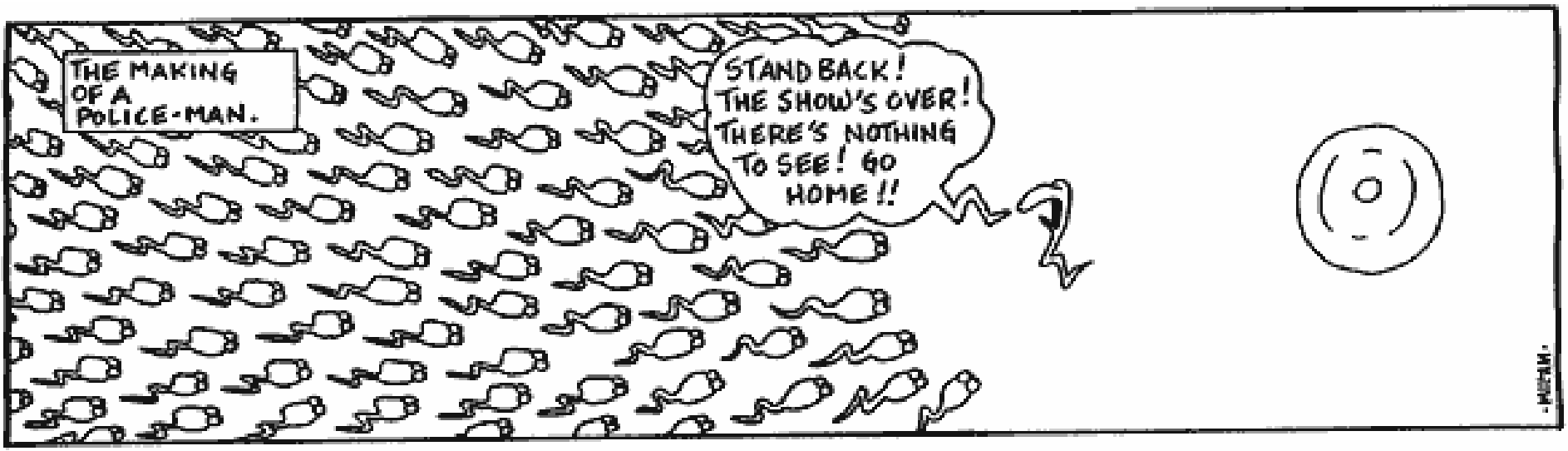
$$\kappa_e = L\sigma T = \frac{1}{ne\mu} LT$$

n – carrier concentration
m* - effective mass of carrier
μ – carrier mobility

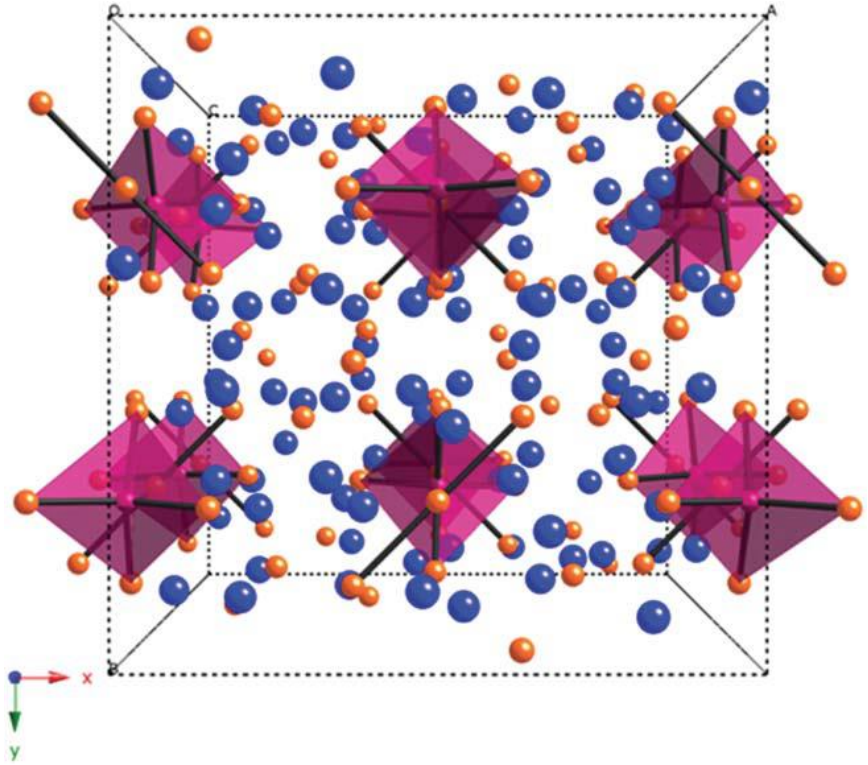
Optimized Carrier Concentration

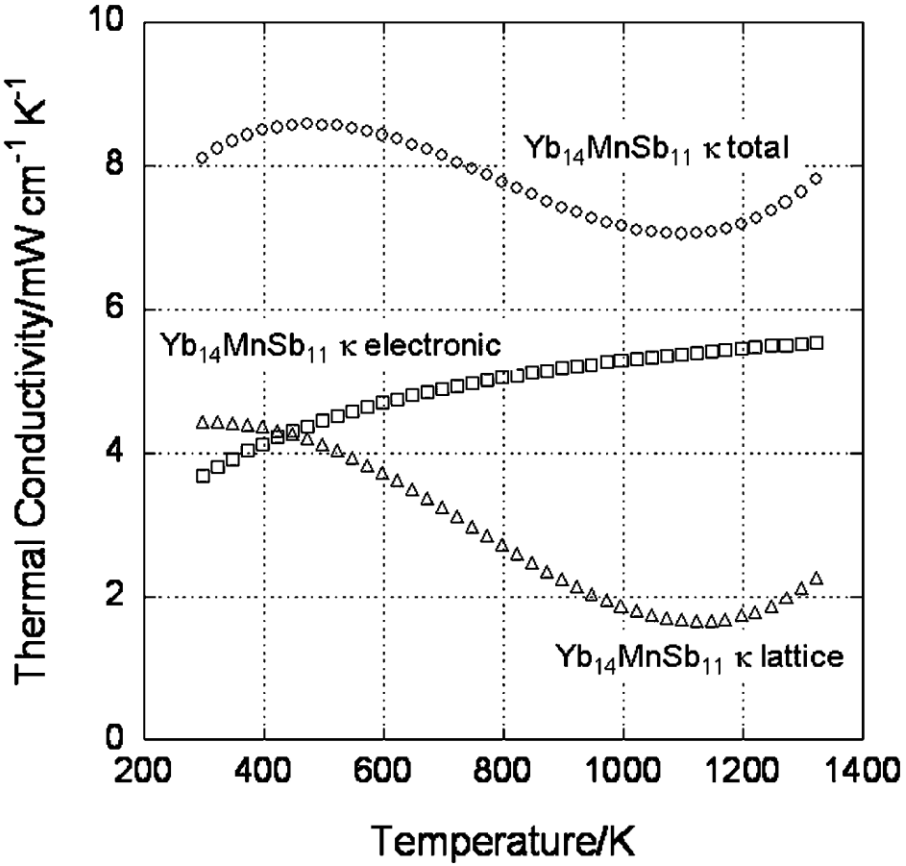


Stopping/Scattering Phonons



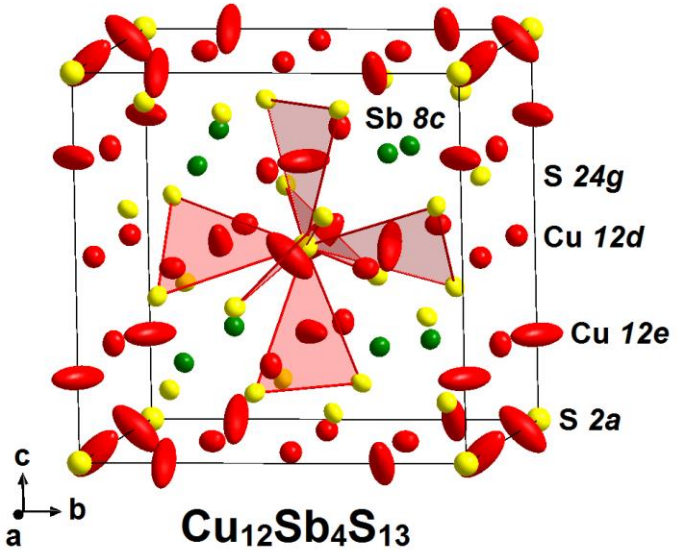
Complex Structures





S. R. Brown et al., Yb14MnSb11. New high efficiency thermoelectric material for power generation, Chem. Mater., 2006, 18, 1873–1877.

$Cu_{12}Sb_4S_{13}$: A complex structure with low κ



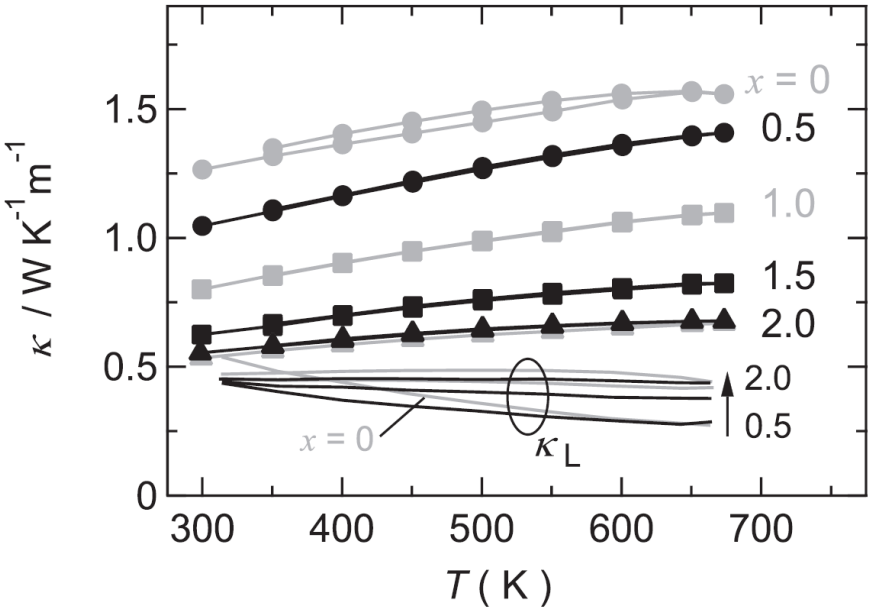
-Large number of elements

-Anharmonic Rattling

-Mass fluctuations

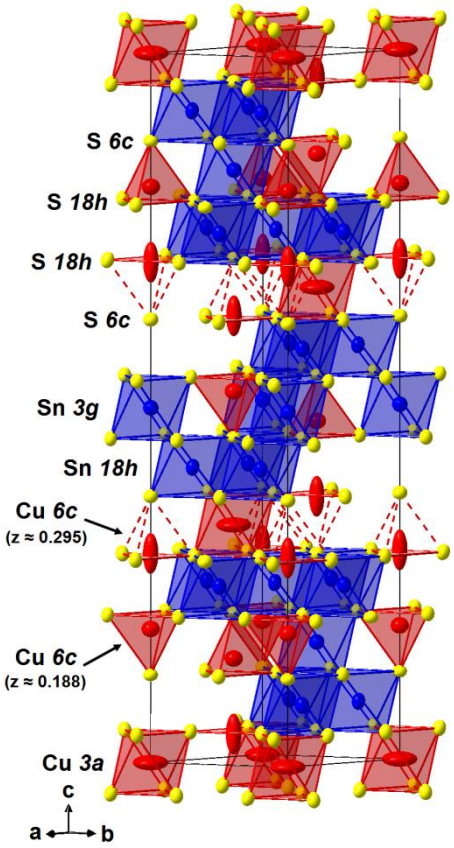
Synthetic tetrahedrites evidence high ∠1 values:

- **0.56** at 673 K for $Cu_{12}Sb_4S_{13}$ [1]
- **0.7** at 673 K for $Cu_{10.5}Zn_{1.5}Sb_4S_{13}$ [1]
- **0.7** at 665 K for $Cu_{10.5}Ni_{1.5}Sb_4S_{13}$ [2]

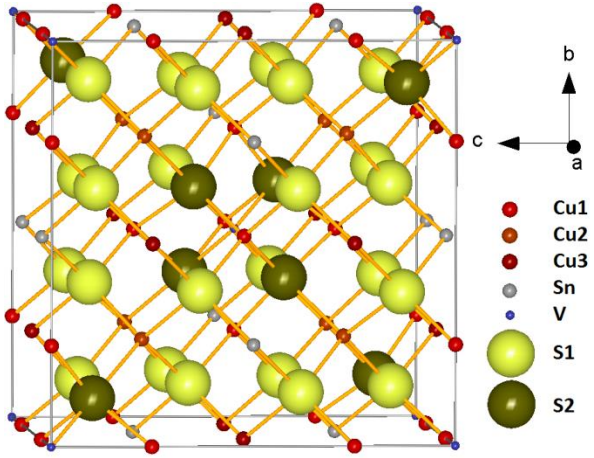


[1] X. Lu et al., Adv. Energy Mater. 3 (2013) 342-348. [2] K. Suekuni *et al.*, J. Appl. Phys. 113 (2013) 043712.

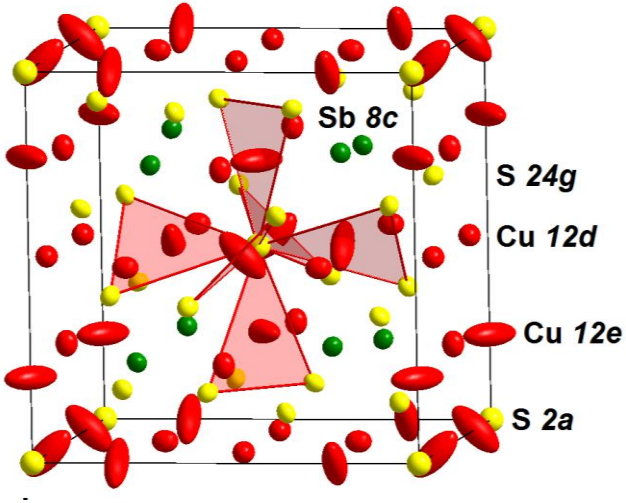
Outline



N-type $Cu_4Sn_7S_{16}$

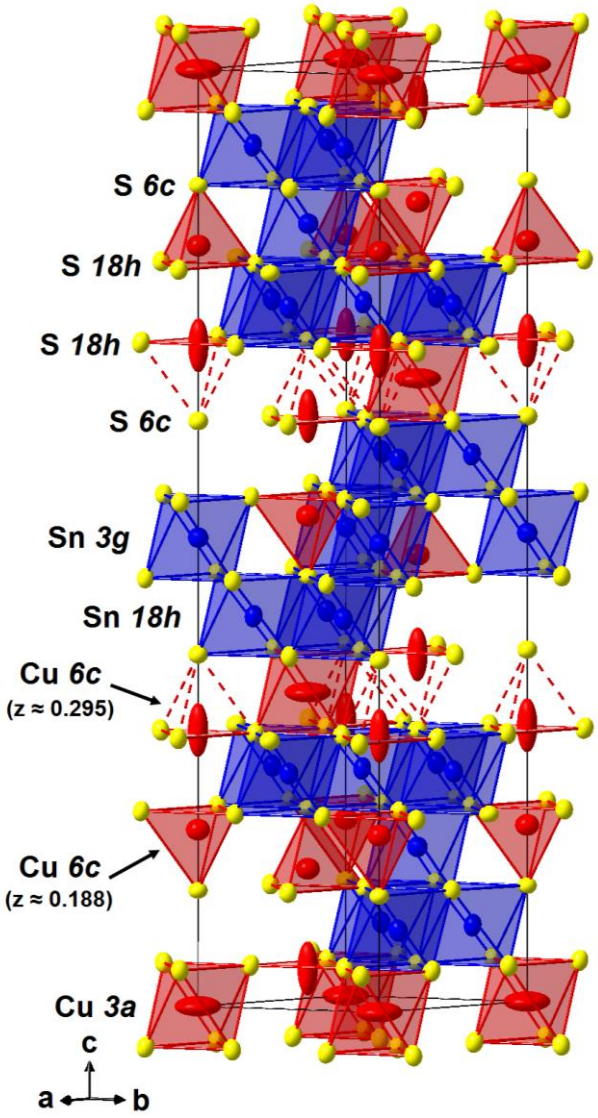


P-type
colusite $Cu_{26}V_2Sn_6S_{32}$



P-type
tetrahedrite $Cu_{12}Sb_4S_{13}$

$Cu_4Sn_7S_{16}$



[1]

Rhombohedral symmetry
Space group R-3m (n°166)
a= 7.372 Å and c = 36.010 Å

- Defect variant of the AB_2X_4 spinel structure
  Tetrahedral sites → 2 non equivalent sites
  Octahedral sites → 3 non equivalent sites

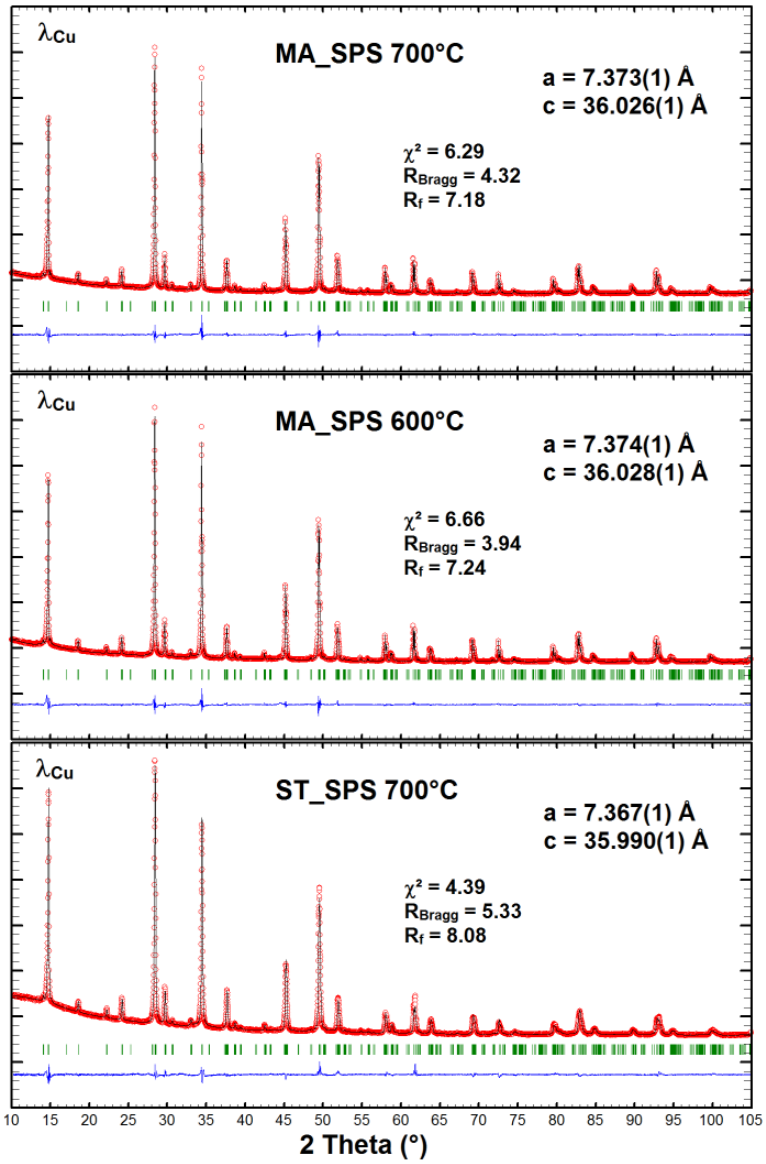
$$(Cu_{0.75}\square_{0.25})(Sn_{1.75}Cu_{0.25})S_4$$

[1] Khanafer, M.; Rivet, J.; Flahaut, J. Bulletin de la Société Chimique de France, 1974, 12, 2670-2676.

$Cu_4Sn_7S_{16}$

- Powder Synthesis
  - -Sealed tube Synthesis (ST)
  - - Mechanical Alloying (MA)

- SPS Sintering (600-700°C/50 MPa)



Similar structural parameters, except:

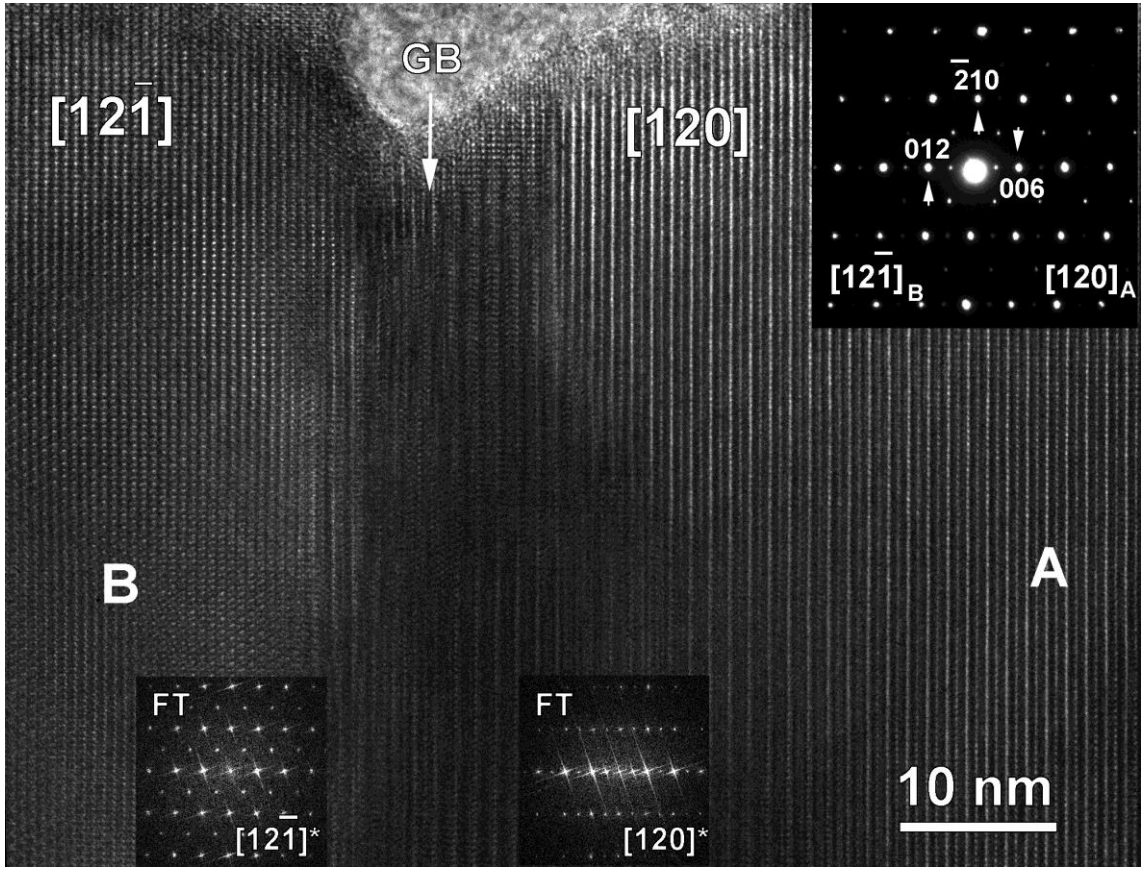
-Cell parameters (ST) < (MA)
(wide non-stochiometry range)

- Lower cristallinity in ST samples
  - →Composition inhomogeneity
  - → Structural defects

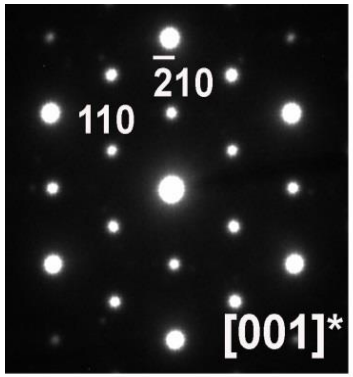
C. Bourges, et al. , Acta Mater. (2015)

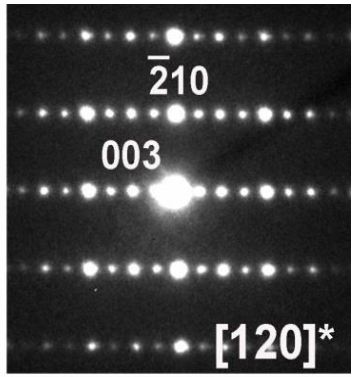
$Cu_4Sn_7S_{16}$

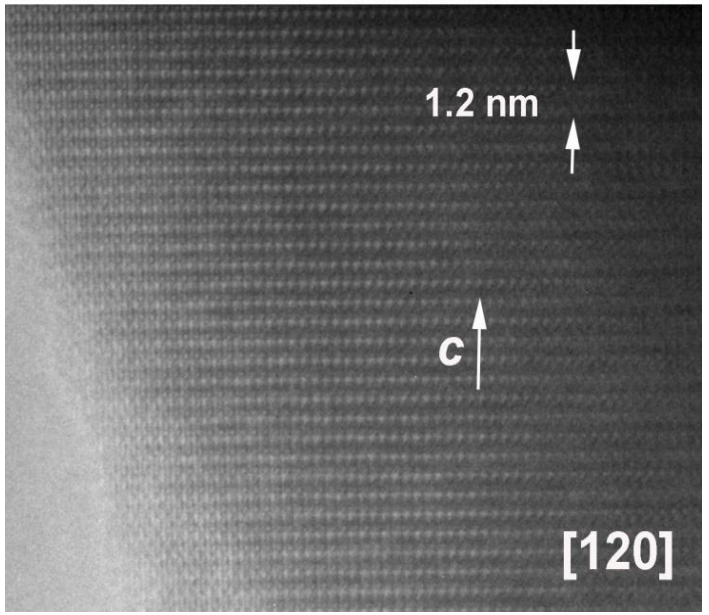
(ST)



(MA)



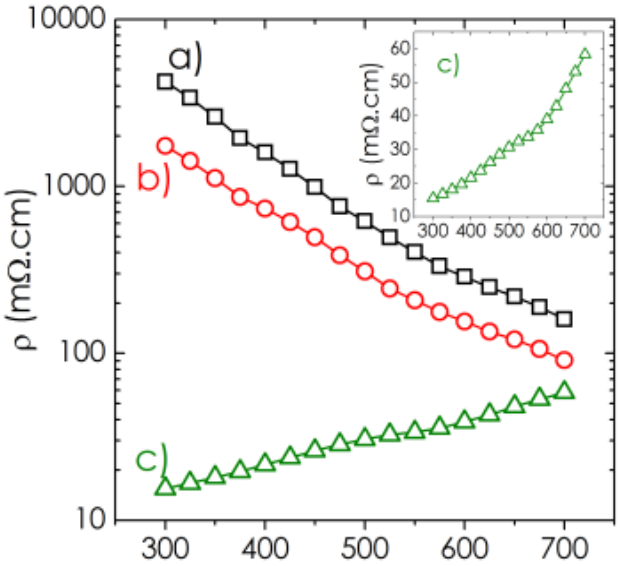


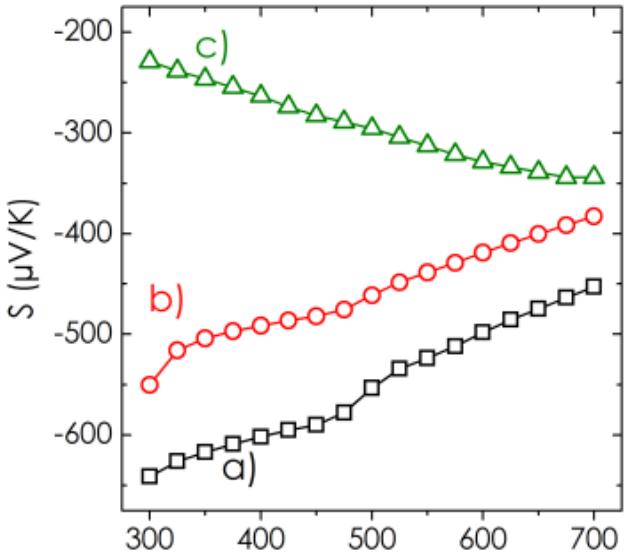


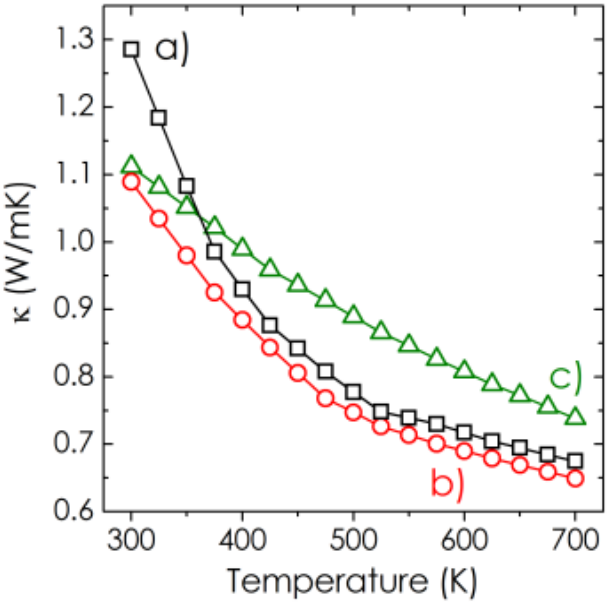
-Anisotropic cristallites

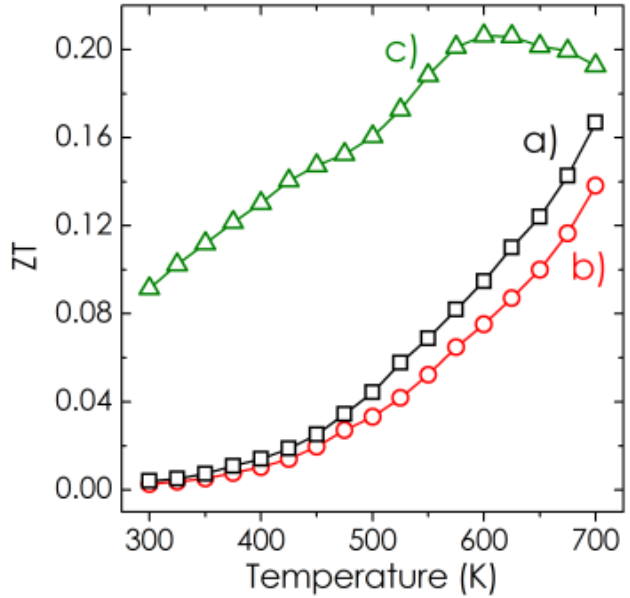
-Grain Boundaries: Twinning, Intergrowths

$Cu_4Sn_7S_{16}$









Mechanical alloying

a) 700°C and **b) 600°C**

Sealed tubes

c) 700°C

-Metallic behavior in ST

Sulfur vacancies

Vacancy occupation

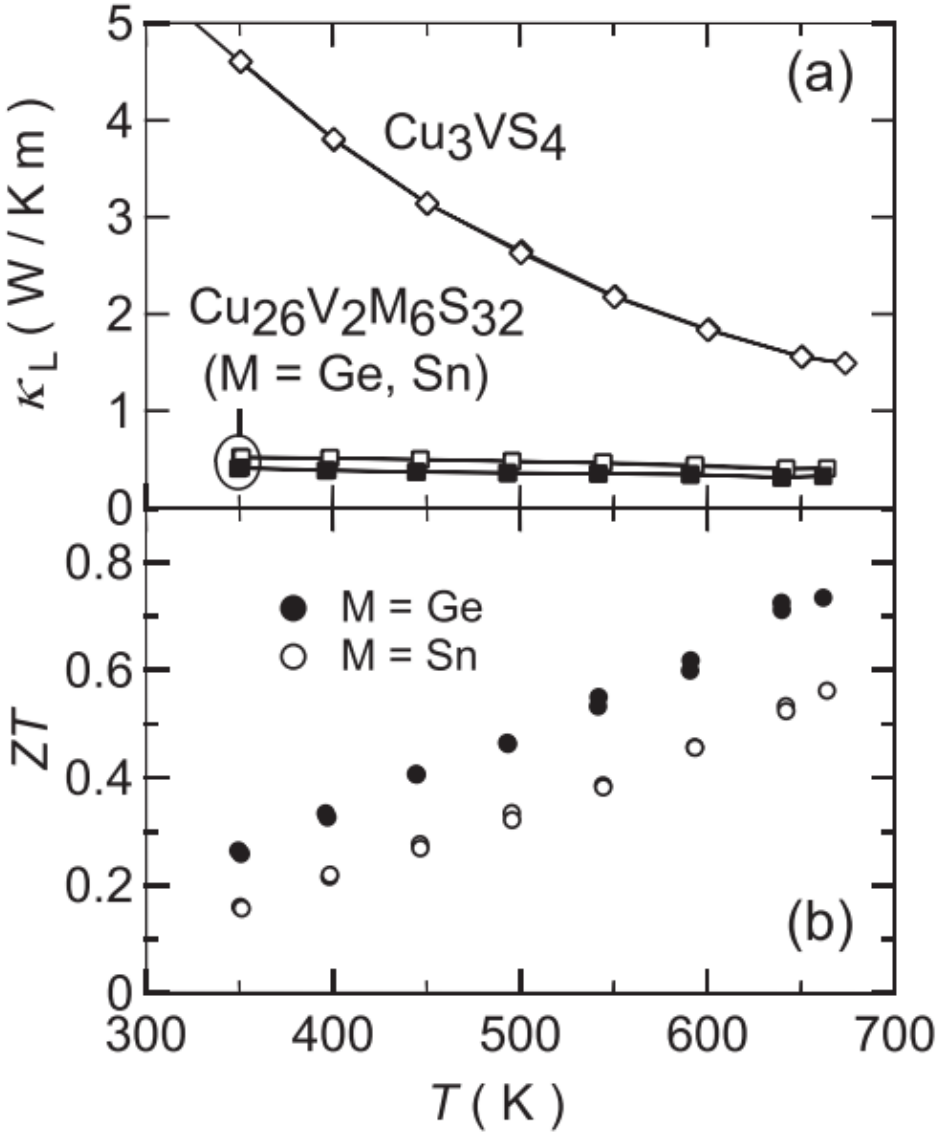
-Low thermal conductivty

-ZT=0.2 @600K

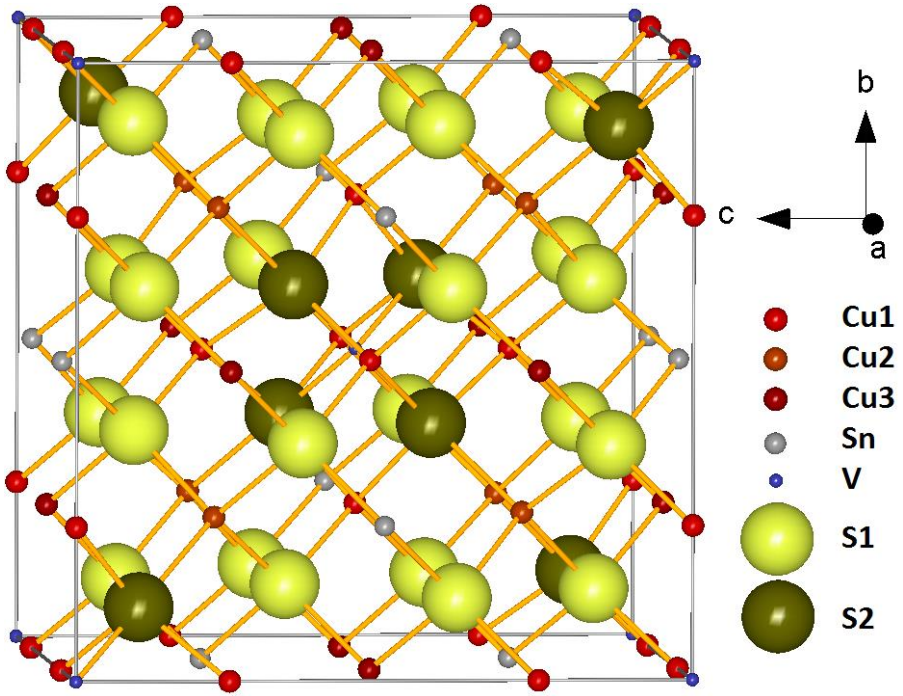
C. Bourges, et al. , Acta Mater. (2015)

Colusite : $Cu_{26}V_2Sn_6S_{32}$

Suekuni et al. APL 2014



Cubic symmetry
Space group P-4 3 n (n°218)
a ≈ 10.7 Å
66 atoms per unit cell



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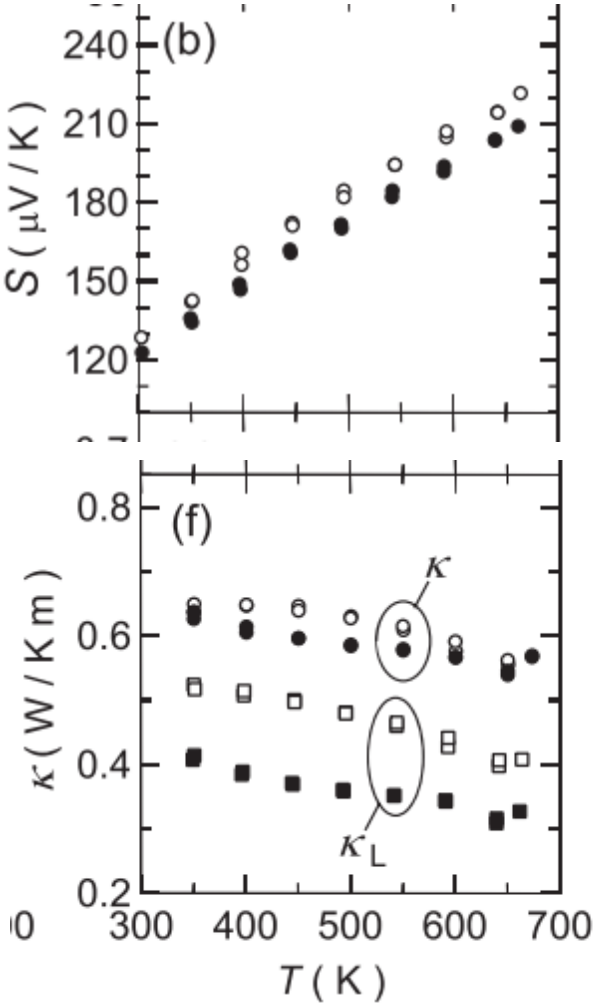
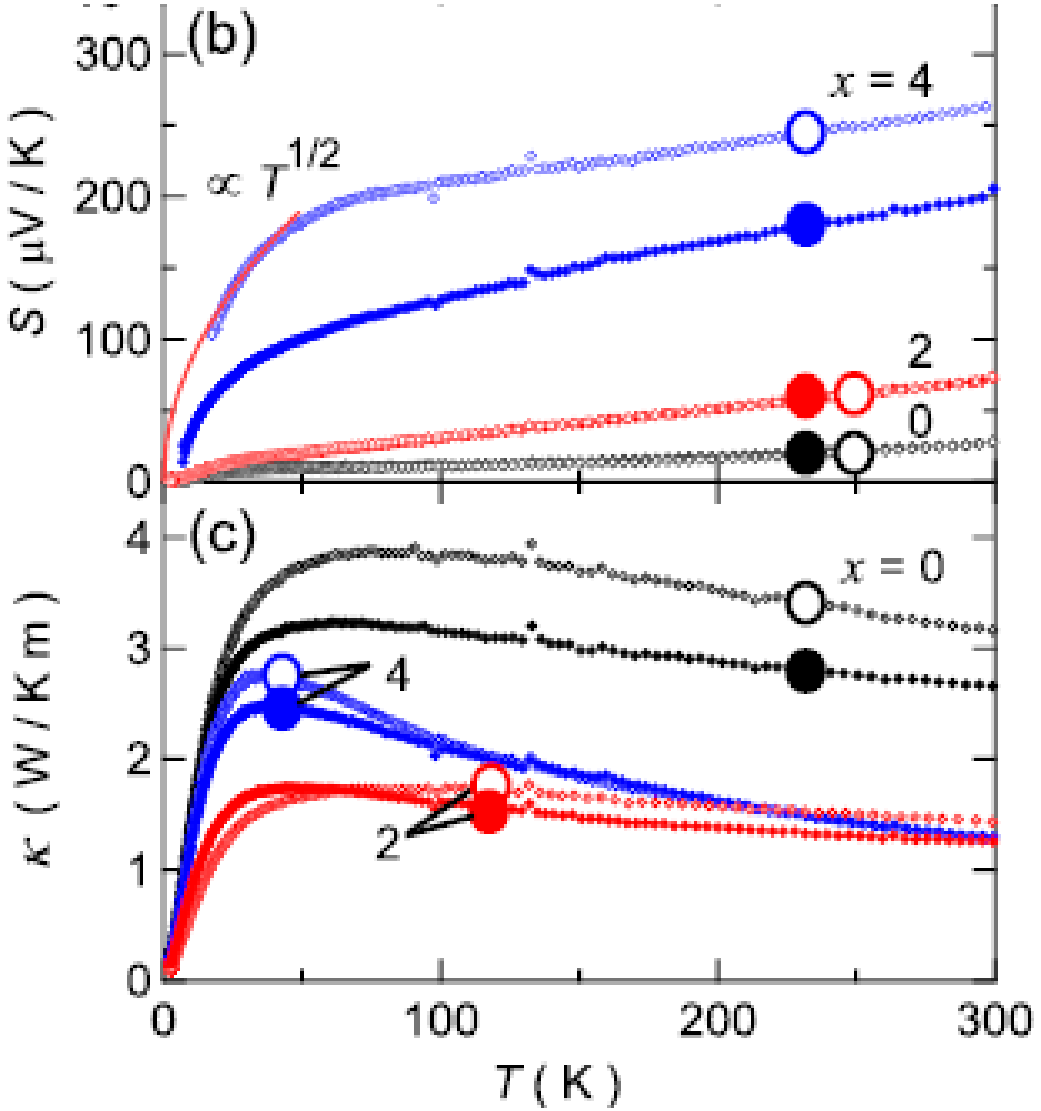
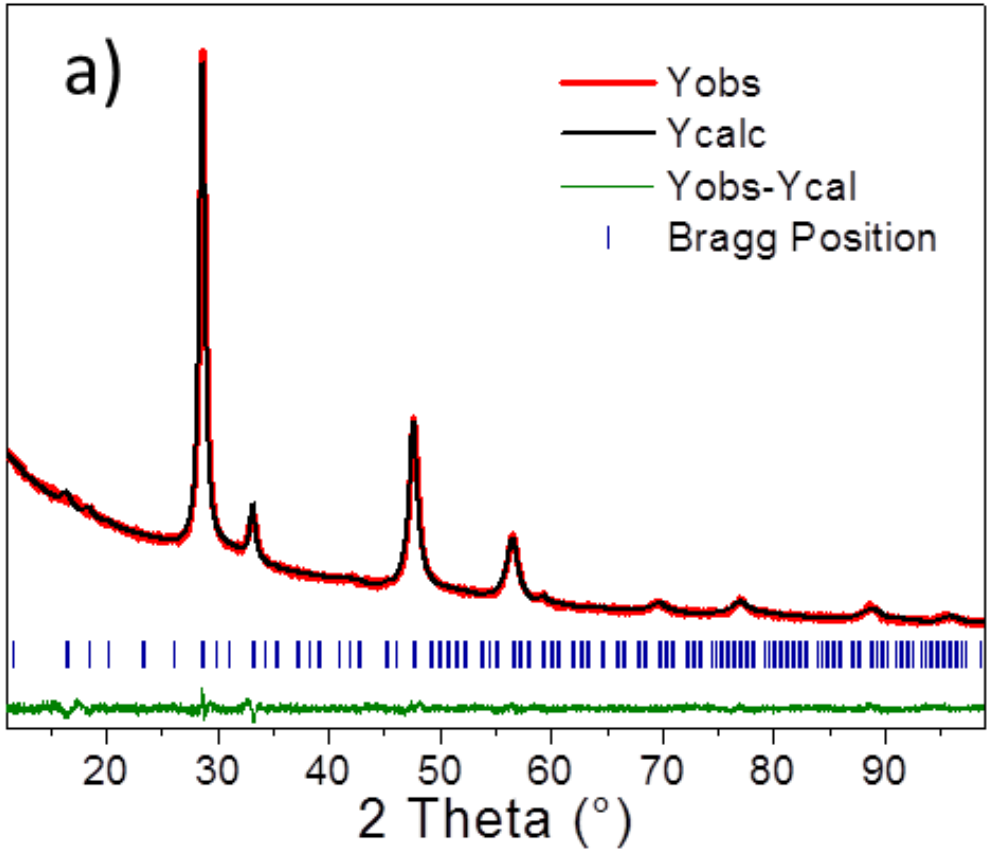


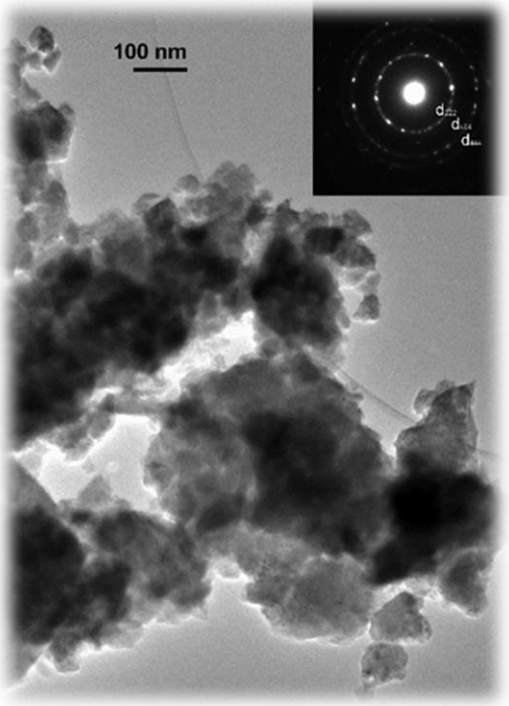
Suekuni et al. JAP 2014



Mechanical Alloying

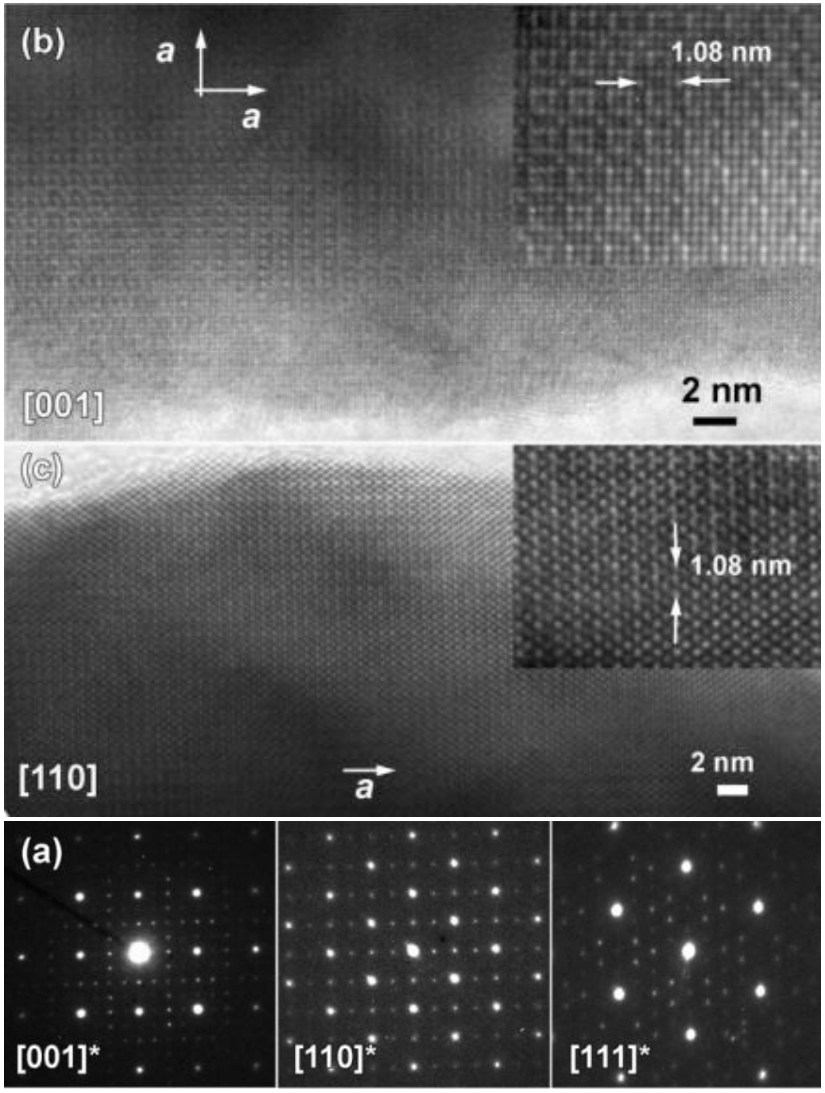
Homogeneity & reproducibility

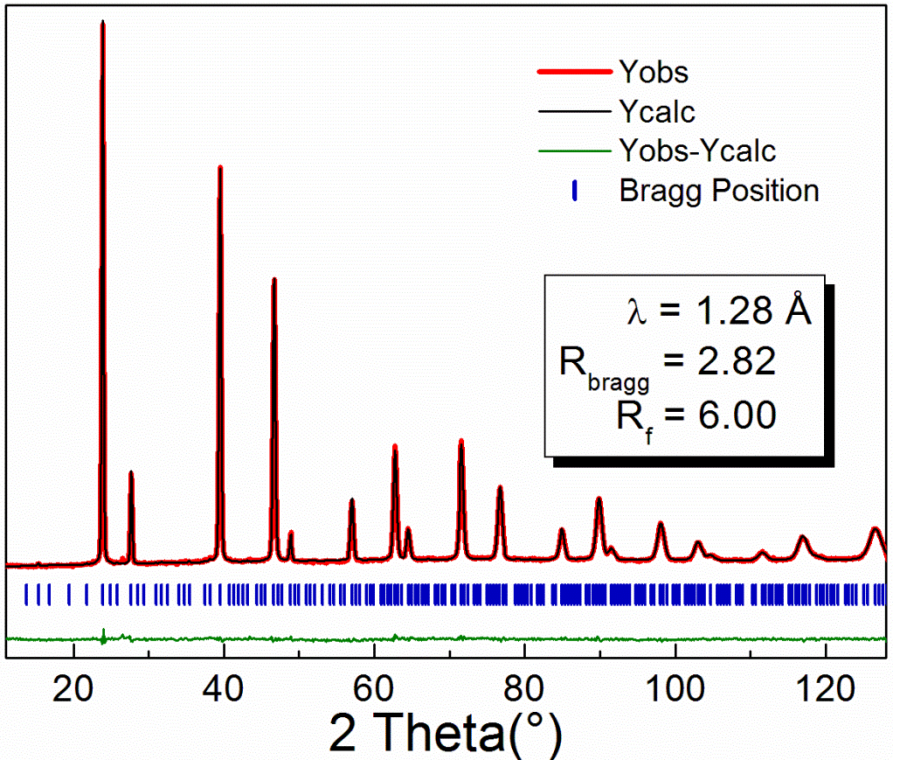




C. Bourgès et al., J. Mater. Chem. C (2016)

Bulk $Cu_{26-x}Zn_xV_2Sn_6S_{32}$





C. Bourgès et al., J. Mater. Chem. C (2016)

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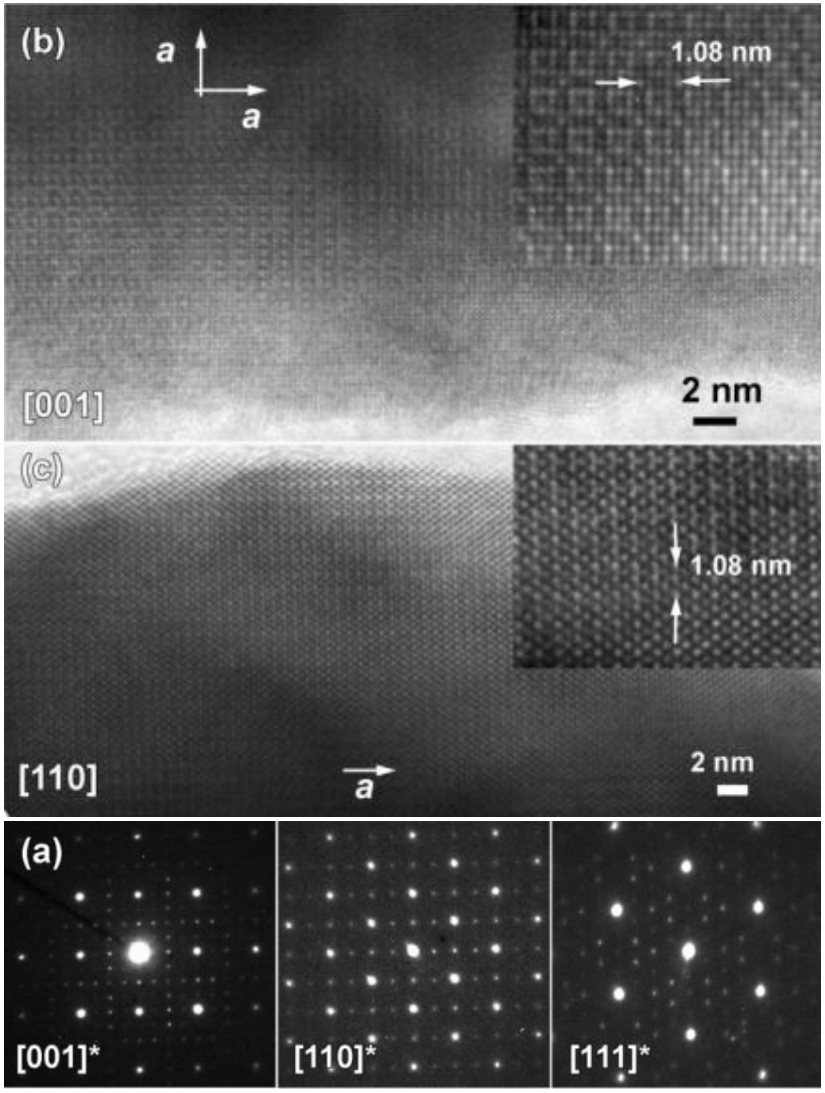
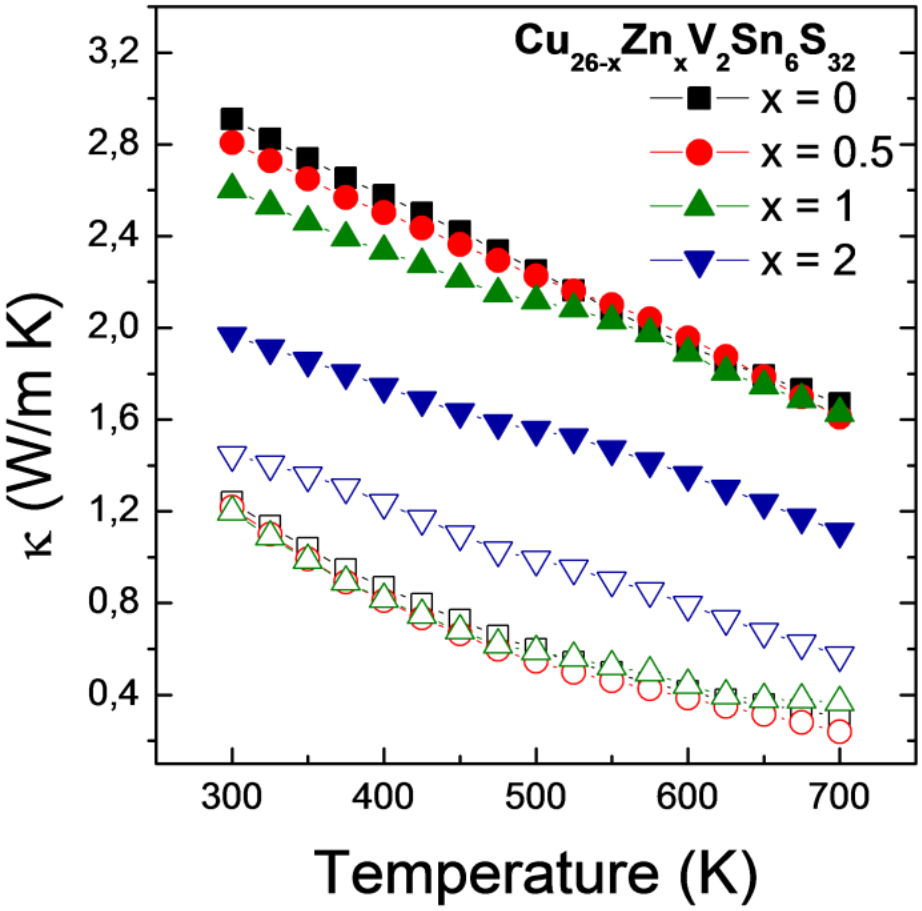




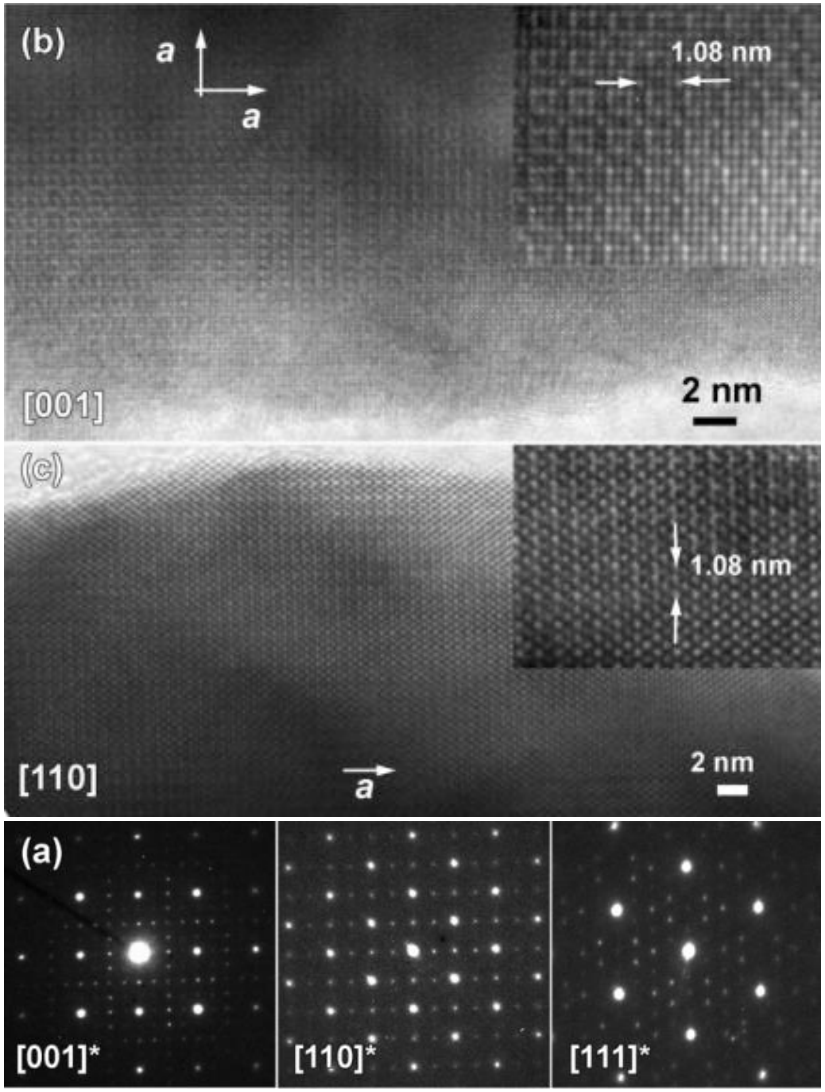
Controlled stoichiometry

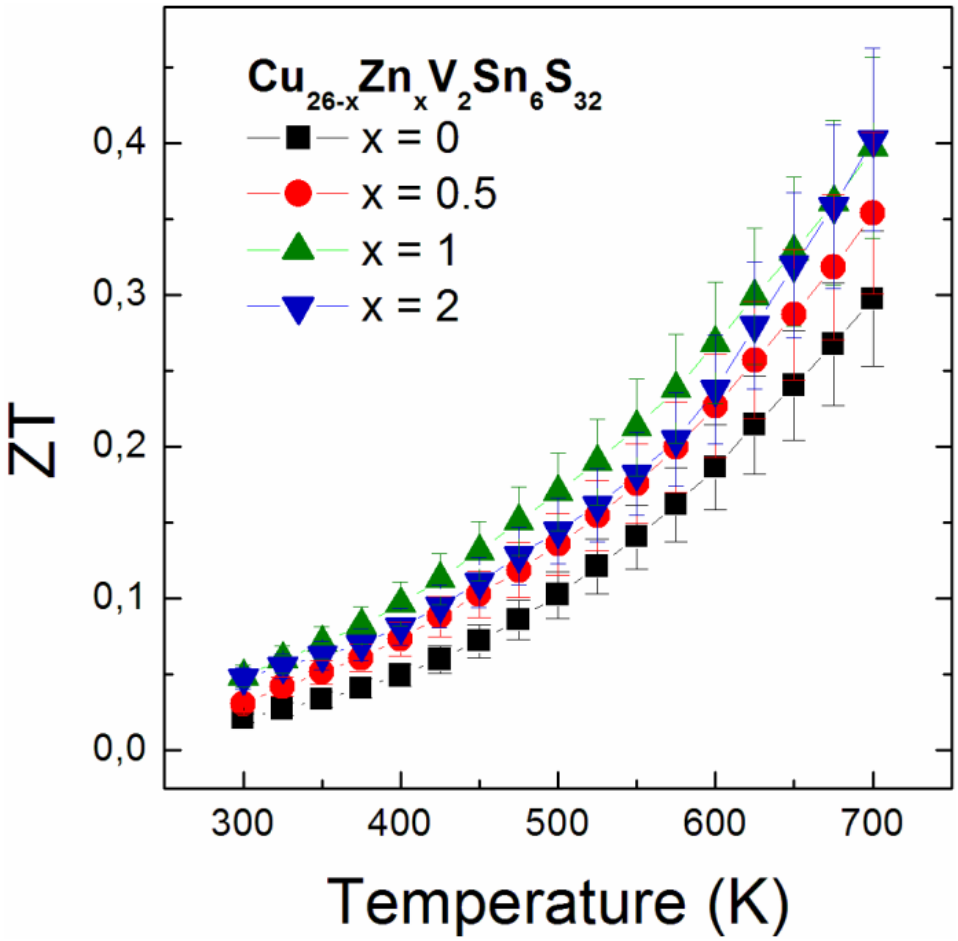
Large kappa (metallic behavior)

$Cu_{22}^{+}Cu_4^{2+}V_2^{5+}Sn_6^{4+}S_{32}^{2-}$

C. Bourgès et al., J. Mater. Chem. C (2016)

Bulk $Cu_{26-x}Zn_xV_2Sn_6S_{32}$

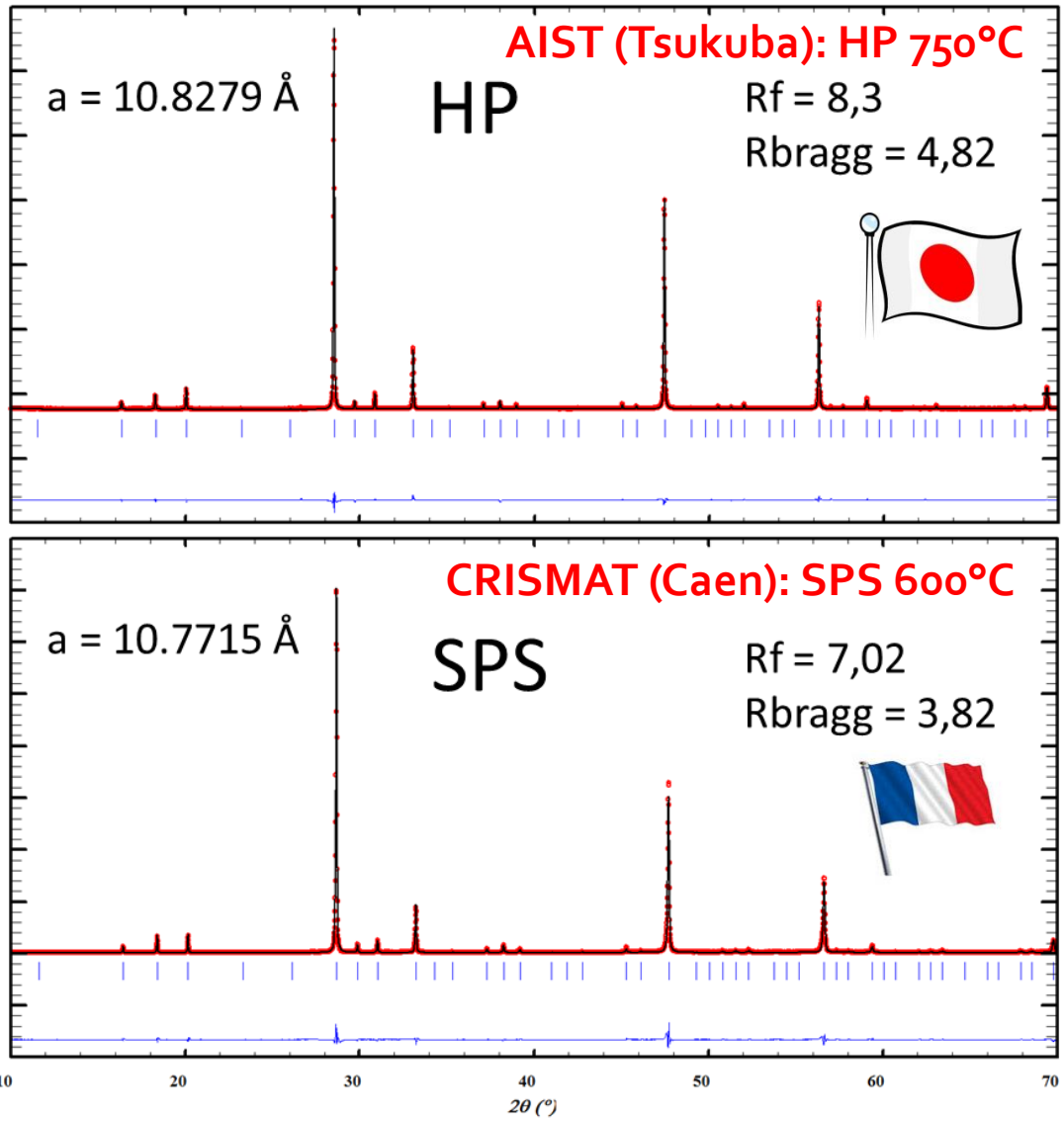




ZT = 0.4@700K for x = 1

C. Bourgès et al., J. Mater. Chem. C (2016)

French MA Powder densified in Japan & France



High cristallinity & purity.

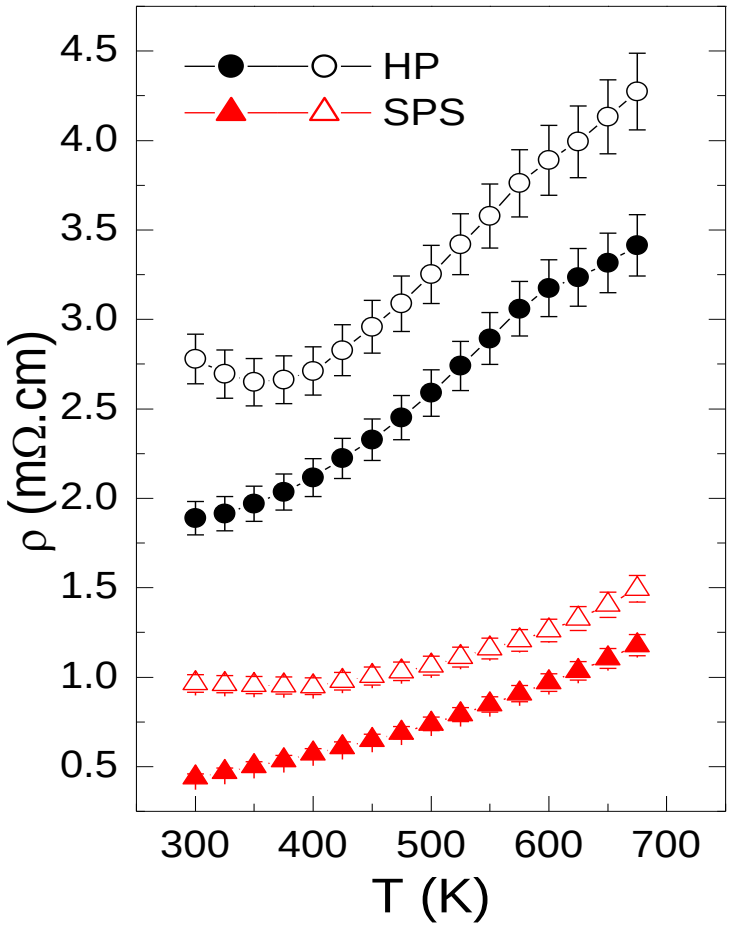
But XRD data and EDS analyses suggest :

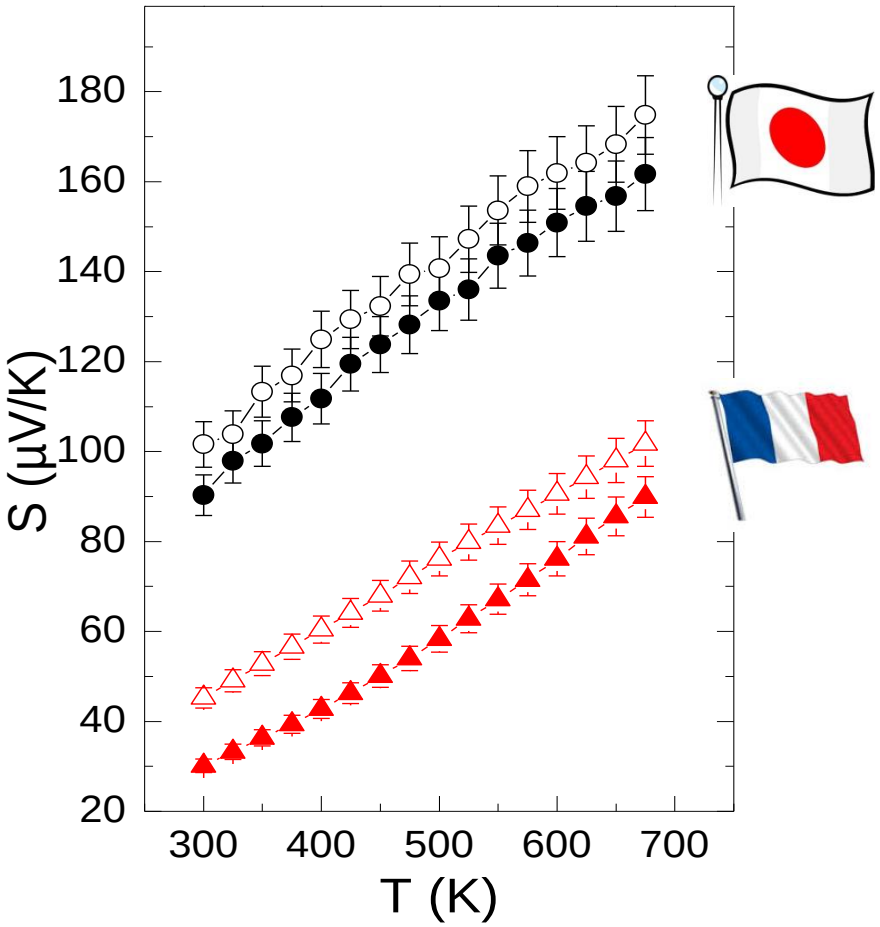
-Sulfur deficiency

-Cu excess

High resolution neutron diffraction is required.

Transport Properties

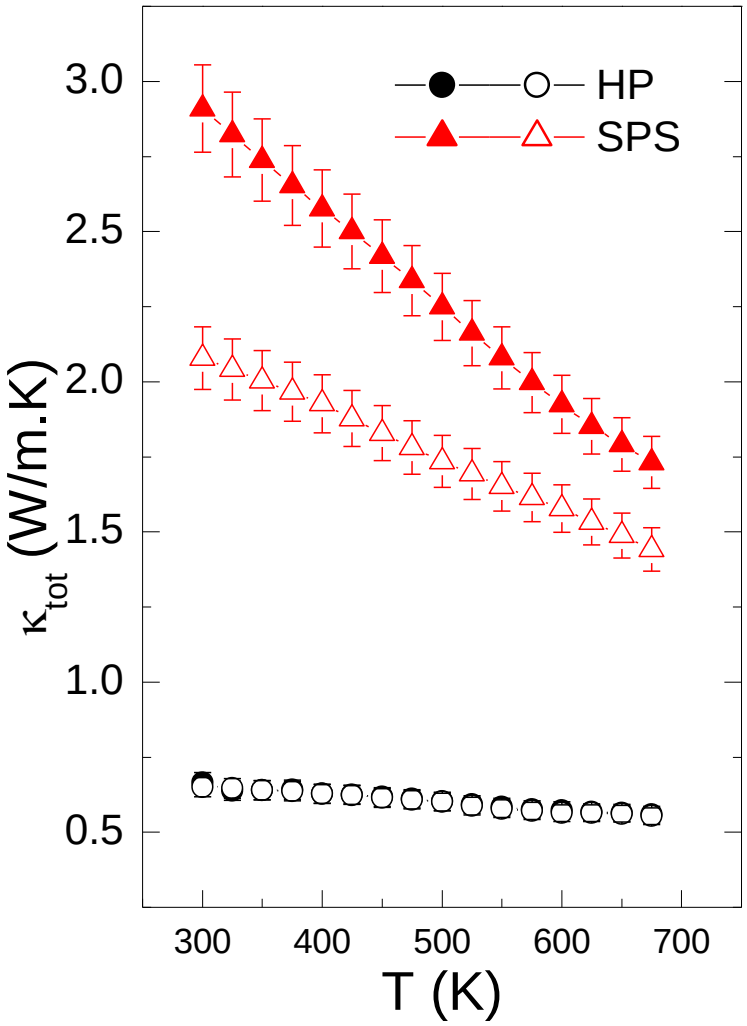


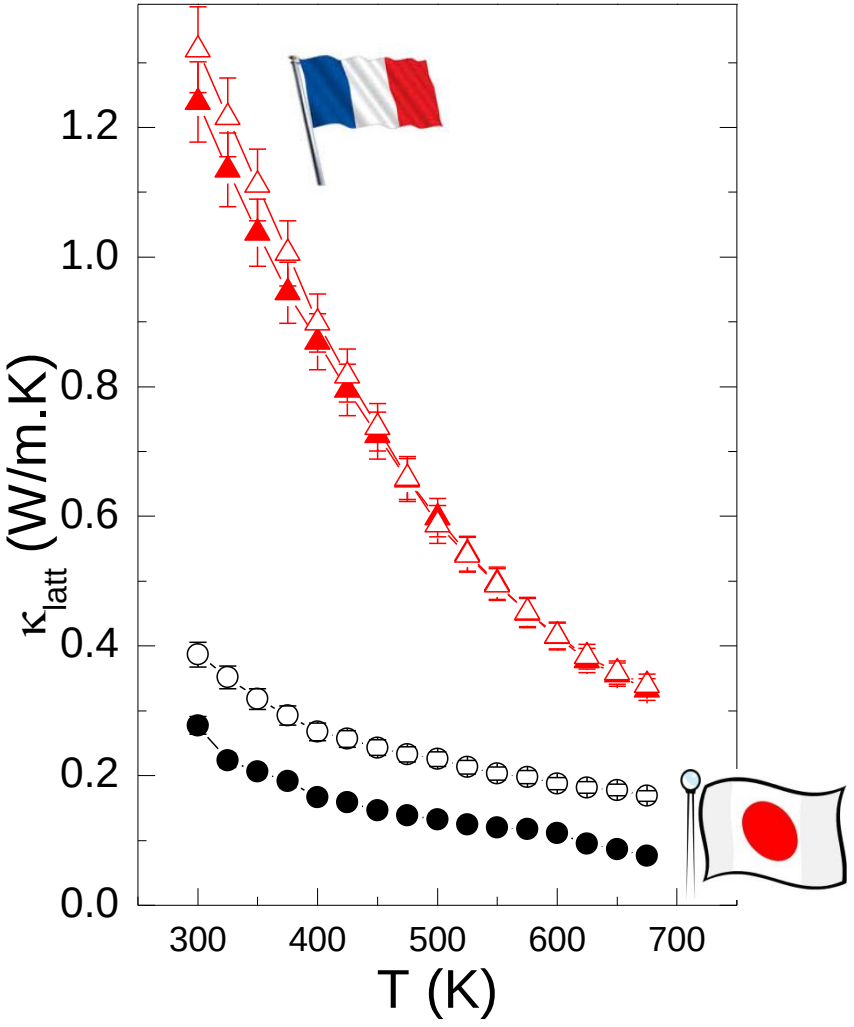


-Sulfur deficiency ➔ Electron doping in Japanese HP sample.

-Cationic occupancy

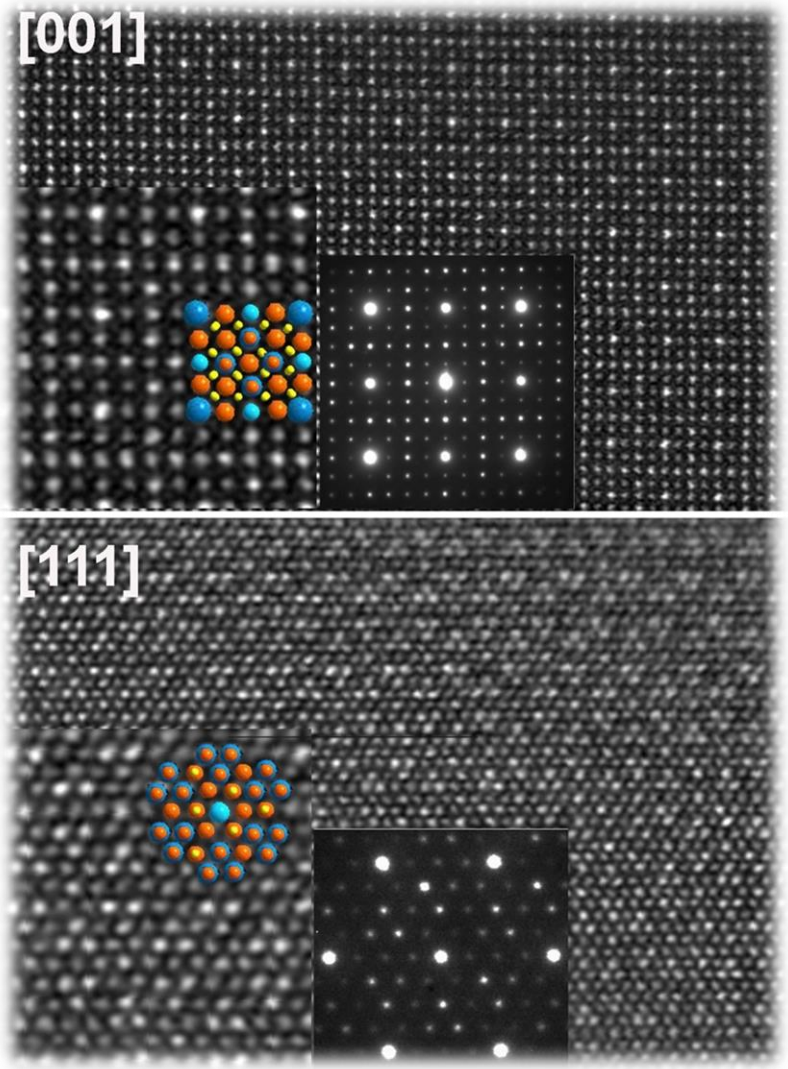
Transport Properties

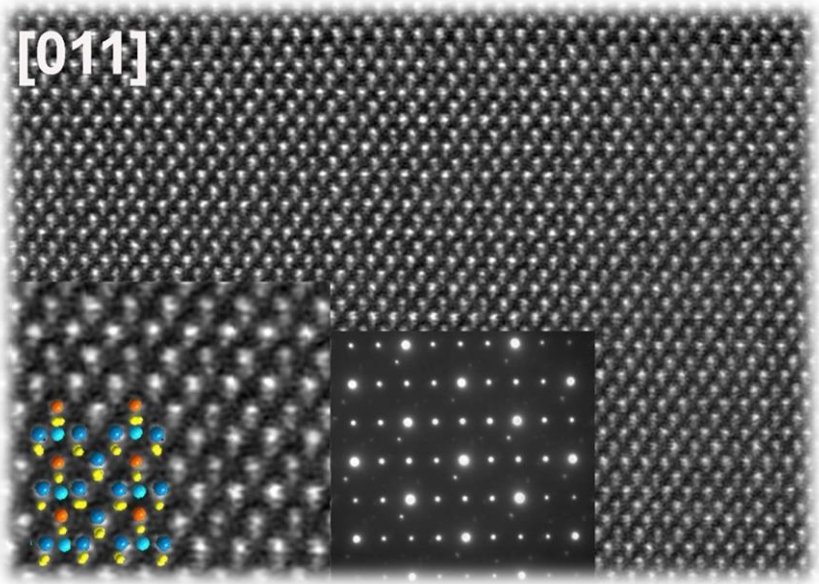




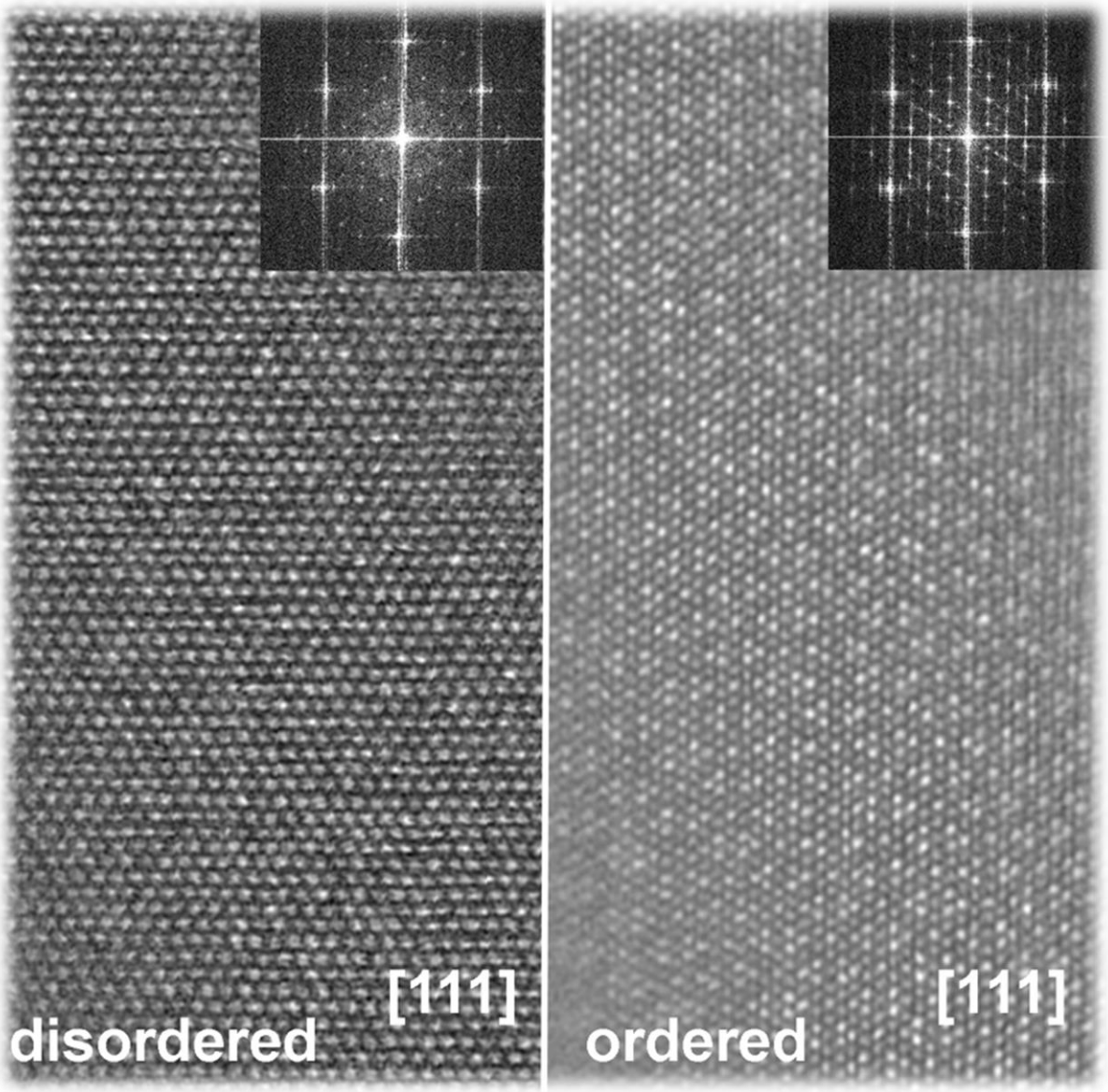
➔ Structural/point defects?

French colusite is well ordered!!!!



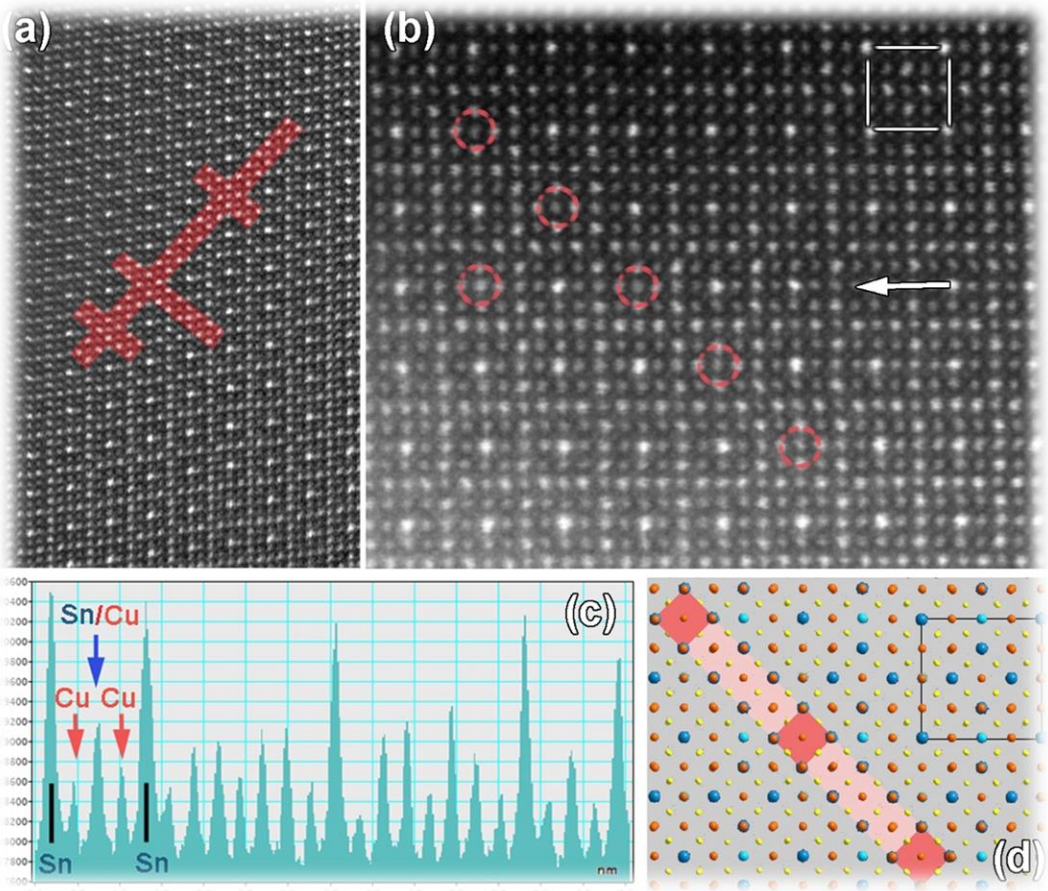


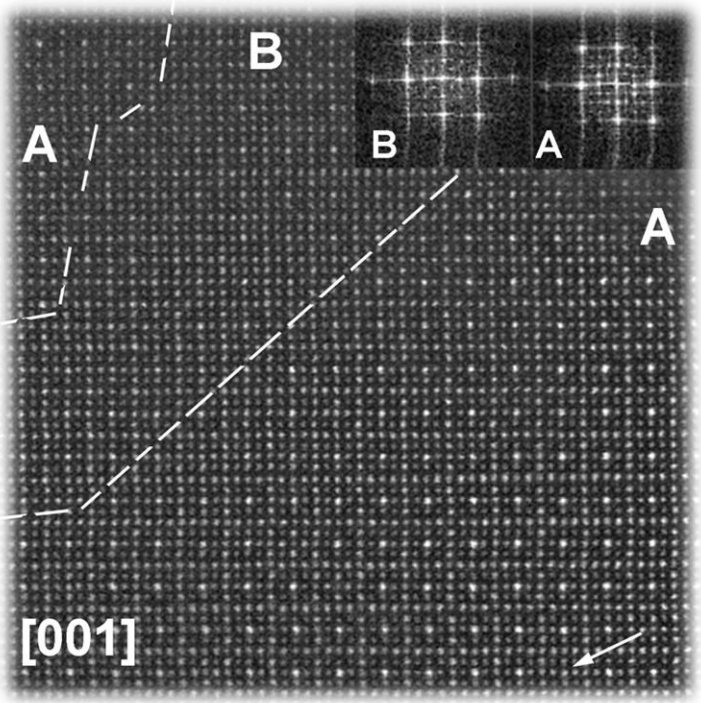
Japanese colusite is disordered



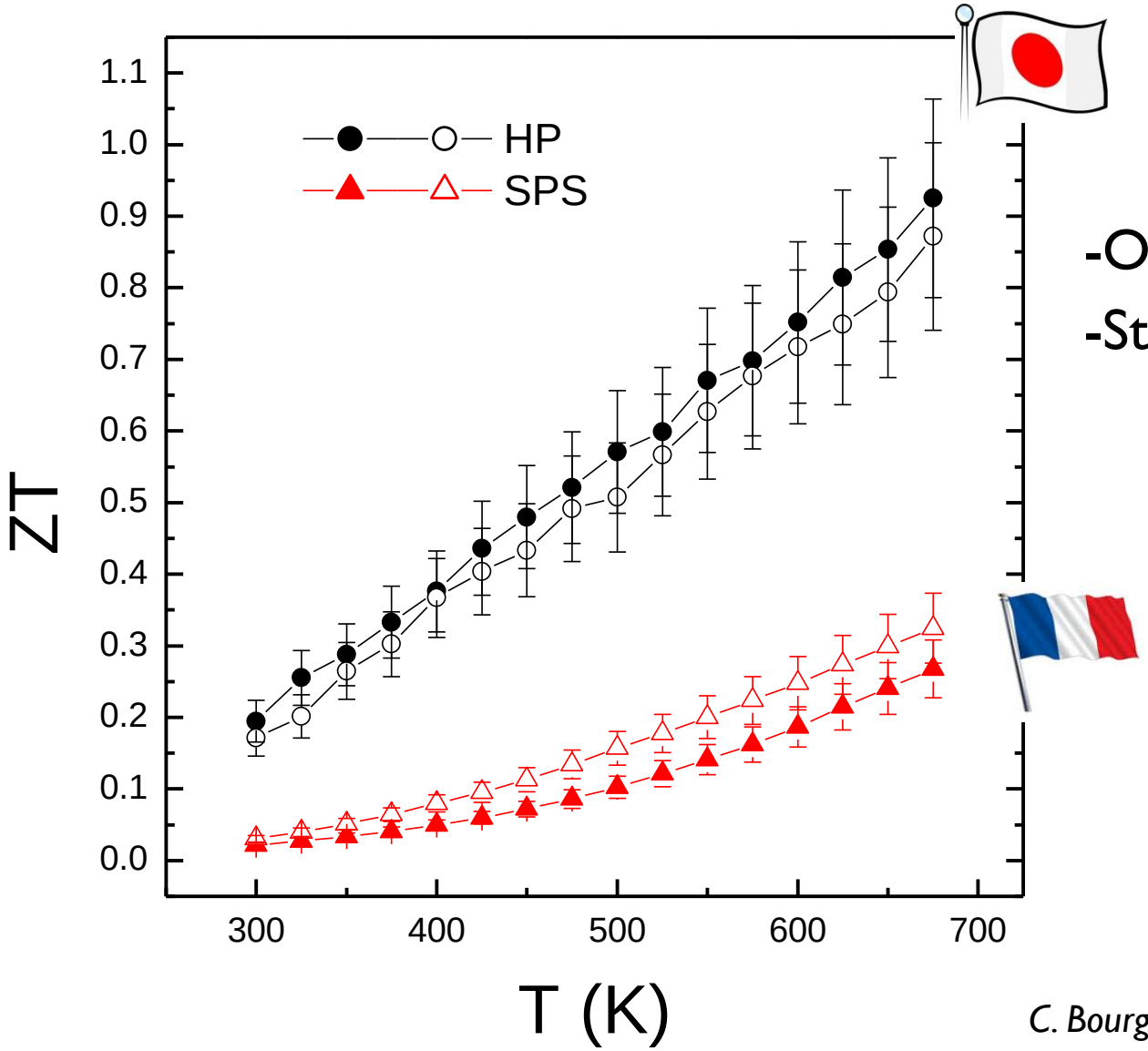
Point defects

➔ Cu/Sn mixed occupancy





Transport Properties

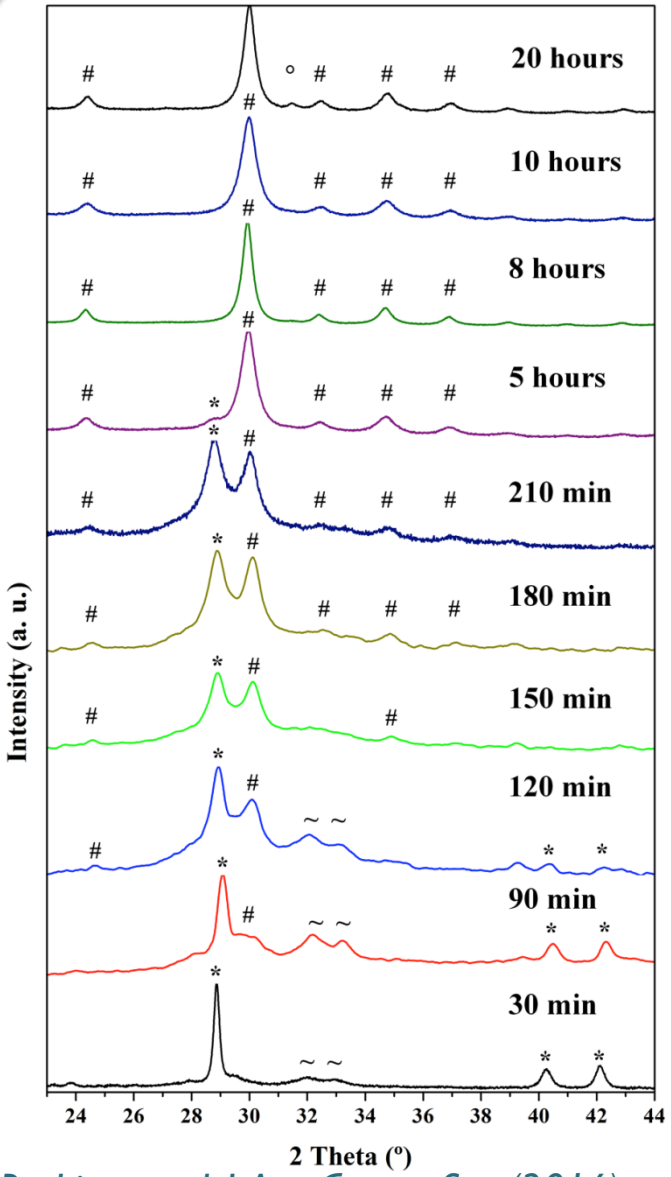


-Optimized carrier conc.

-Structural disordering

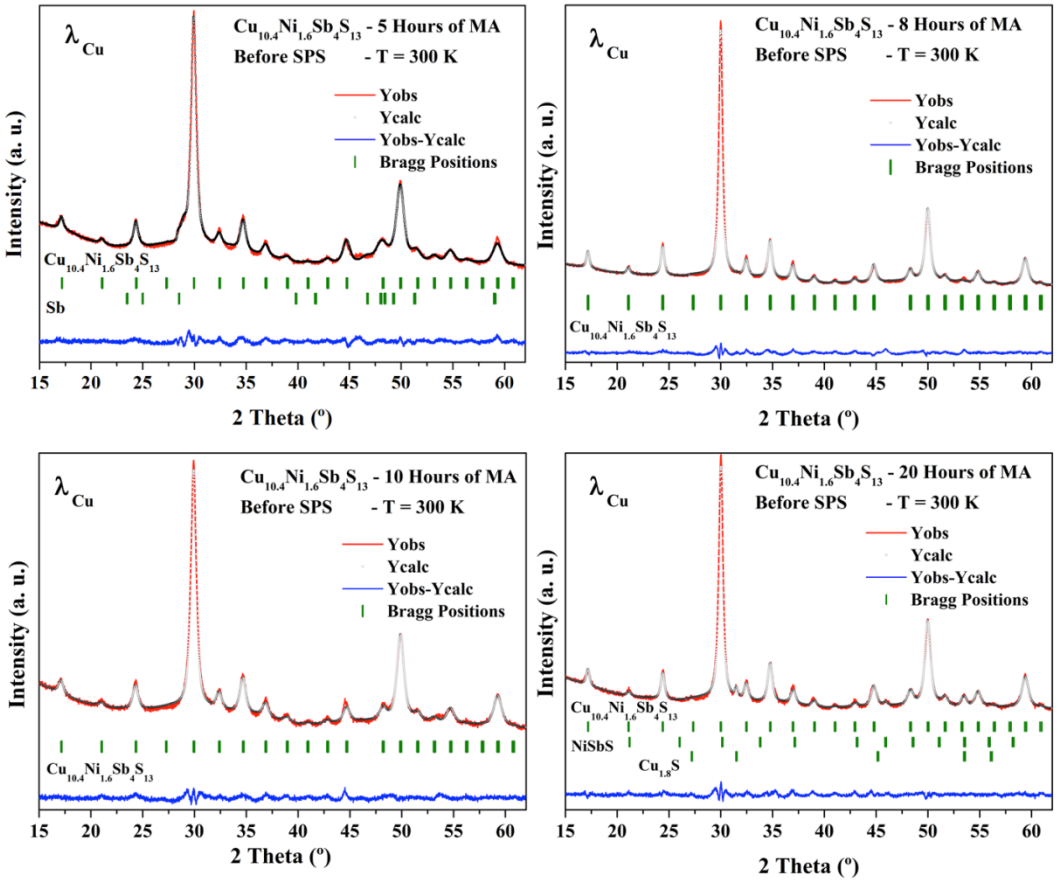
C. Bourgès et al., soon submitted (2017)

Mechanical Alloying of $Cu_{10.4}Ni_{1.6}Sb_4S_{13}$



Reaction of stoichiometric mixtures from the elements

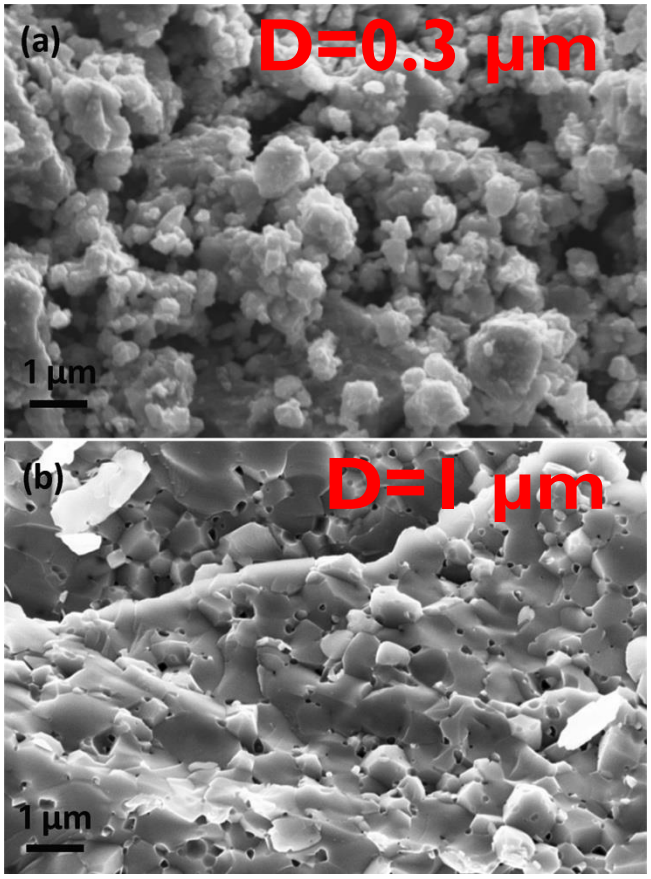
WC jars & balls, 600 rpm

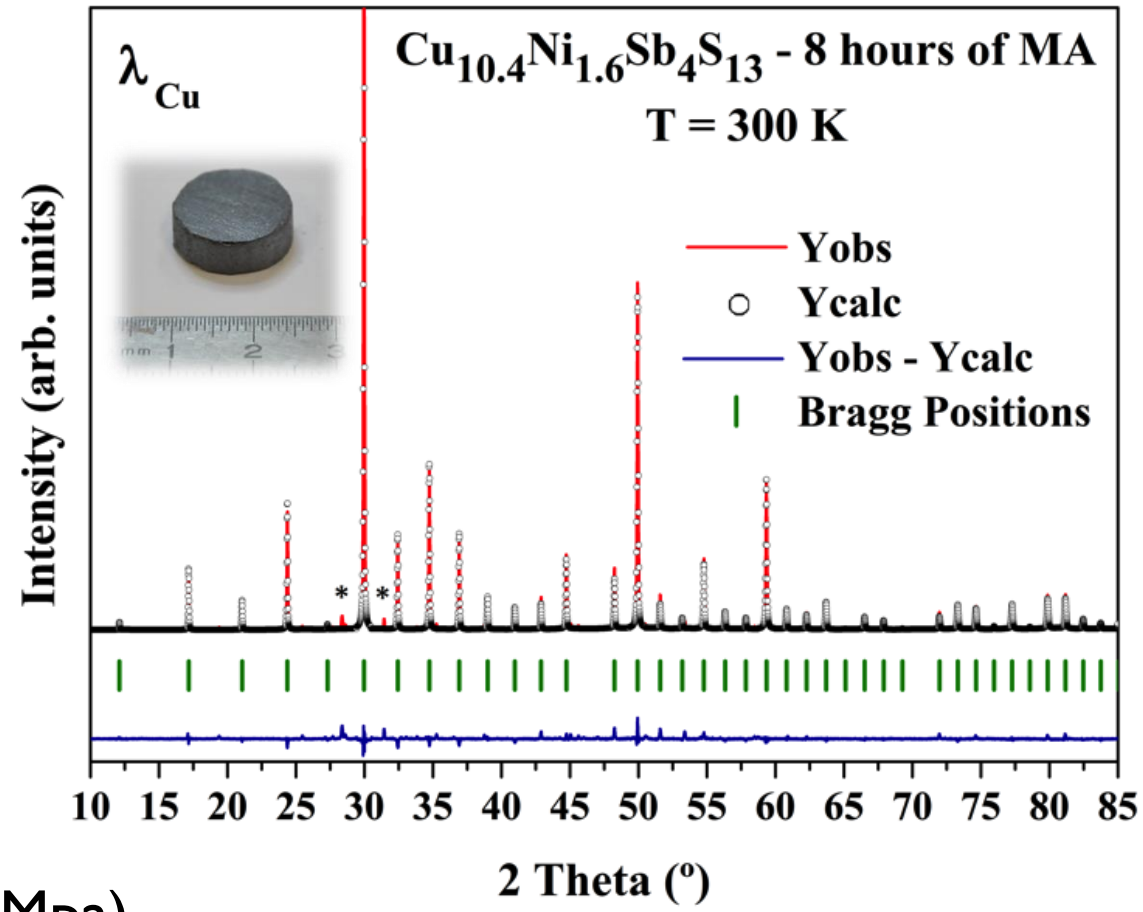


T. Barbier et al. J. Am. Ceram. Soc (2016)

Mechanical Alloying of $Cu_{10.4}Ni_{1.6}Sb_4S_{13}$

As ball-milled





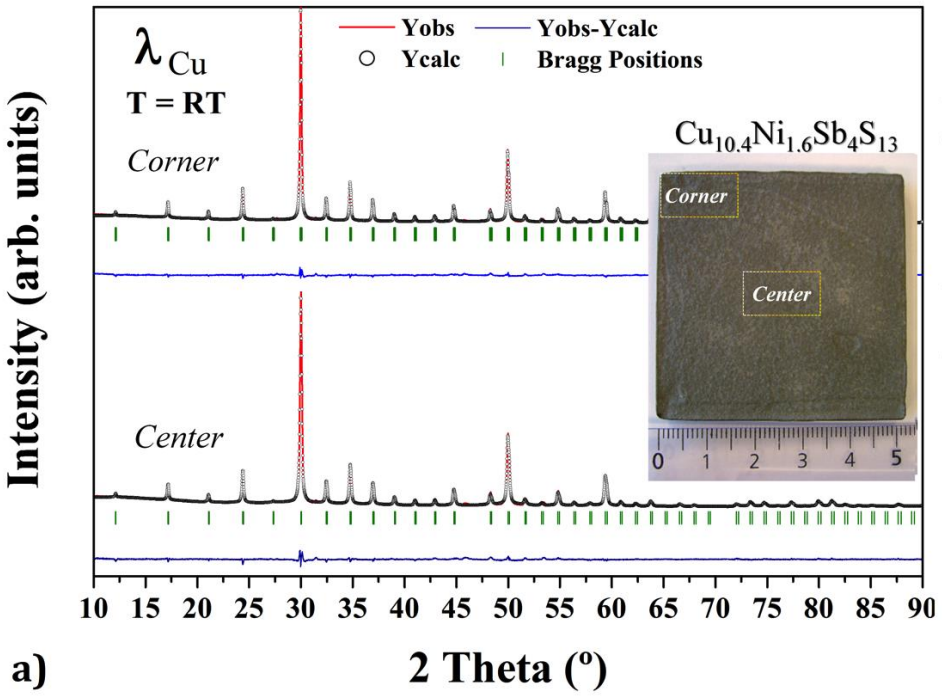
After SPS (480°C/30 min/60 Mpa)
density>95%

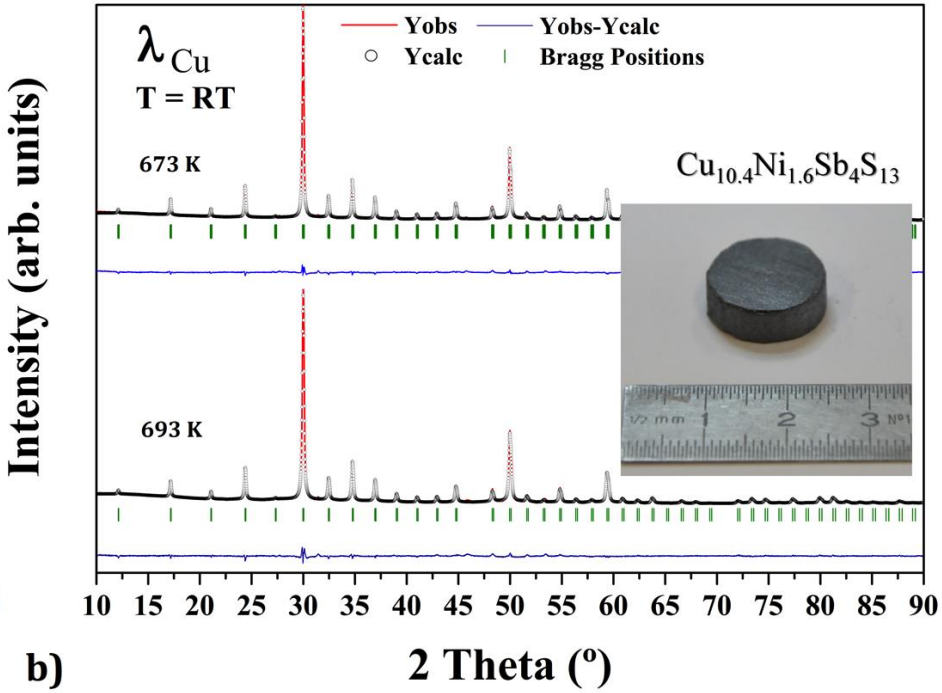
T. Barbier et al. J. Am. Ceram. Soc (2016)

Up-scaled SPS Process

$Cu_{10.4}Ni_{1.6}Sb_4S_{13}$

T. Barbier et al. J. All. Comp. (2015)





T. Barbier et al. RSC Advances (2016)

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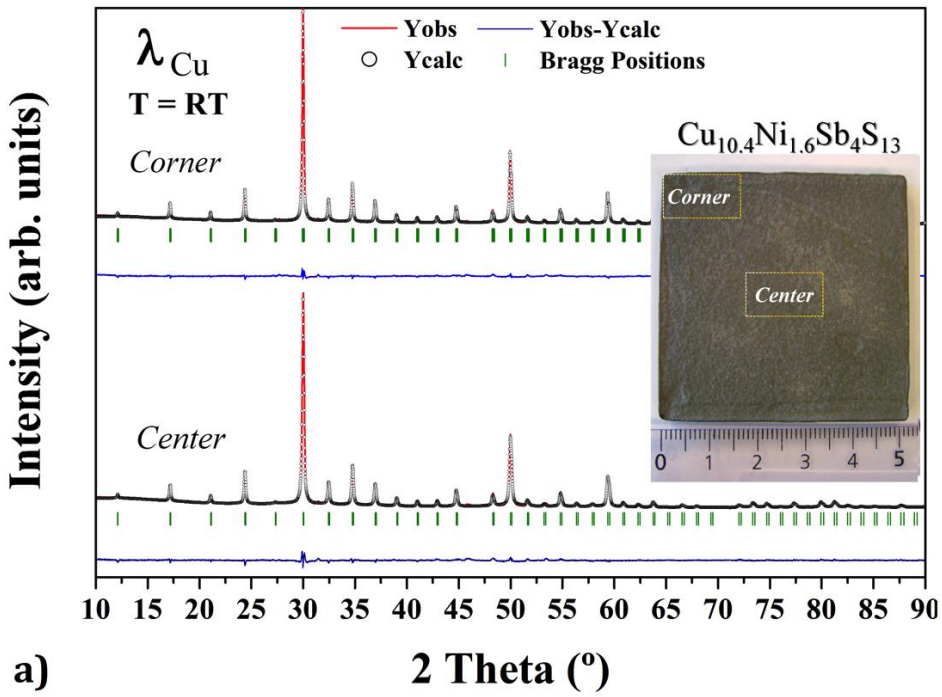
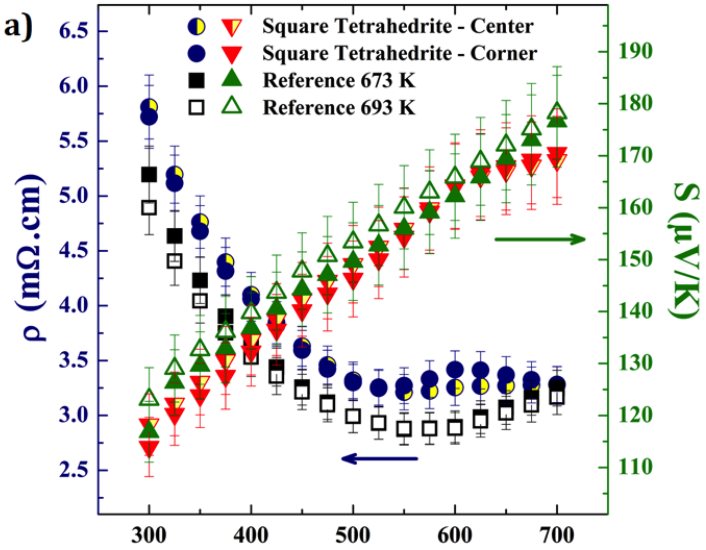
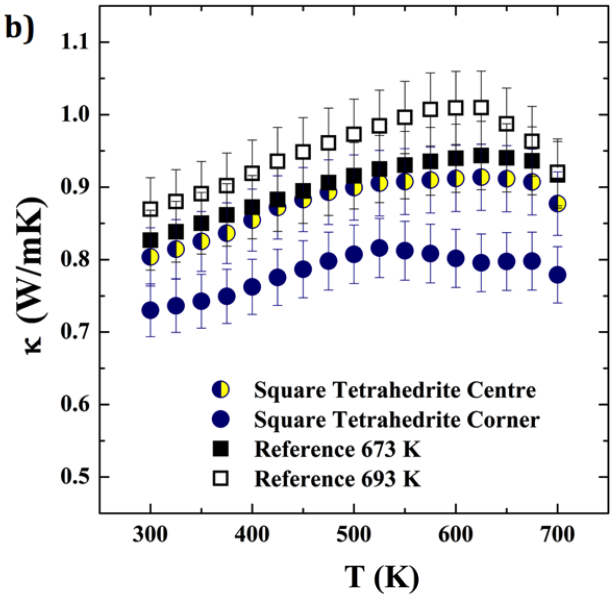


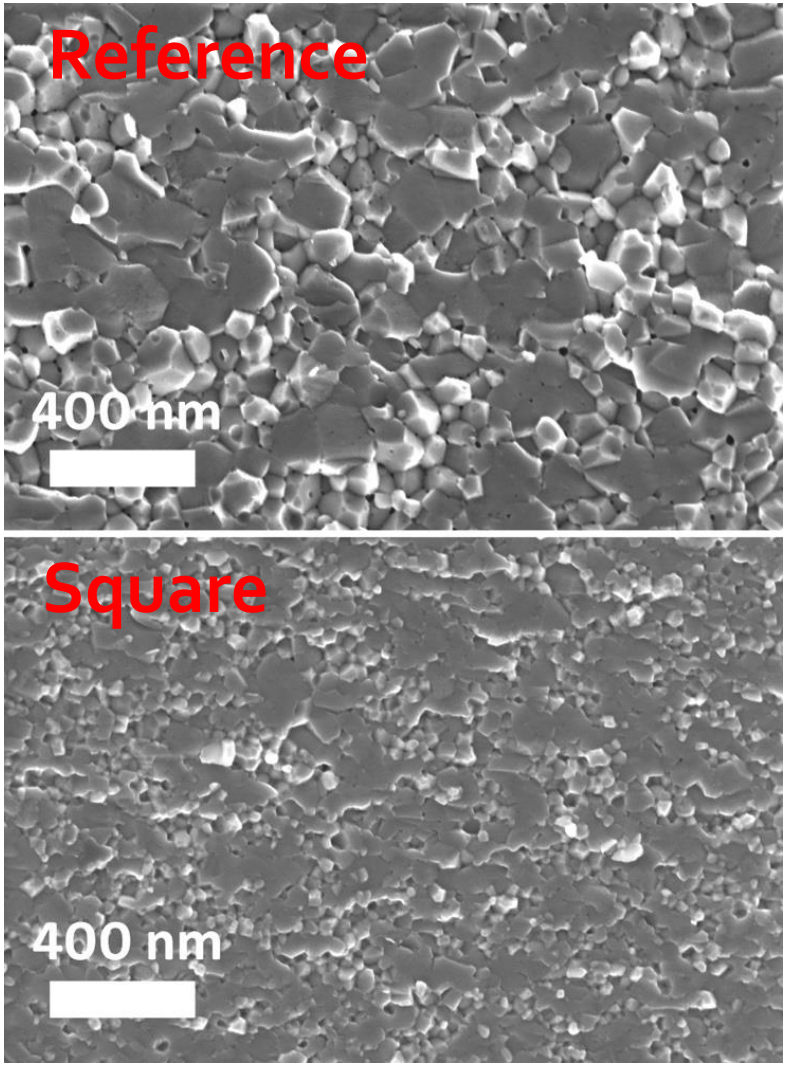
T. Barbier et al. RSC Advances (2016)

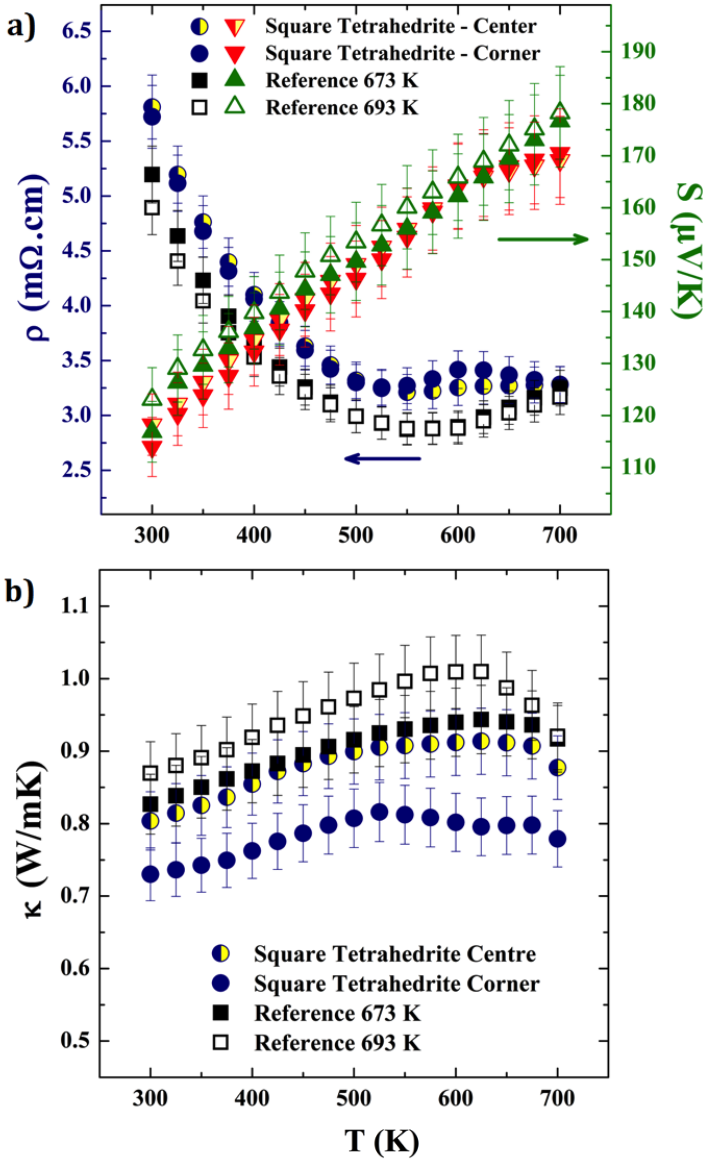




Up-scaled SPS Process

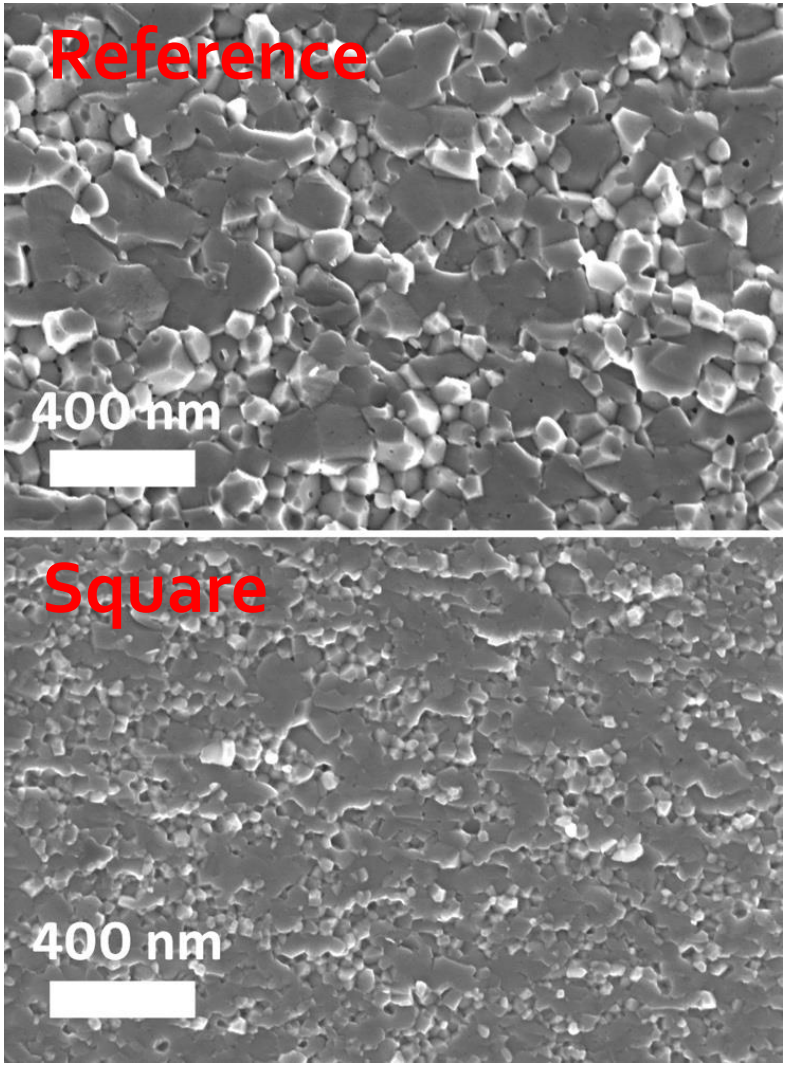
$Cu_{10.4}Ni_{1.6}Sb_4S_{13}$

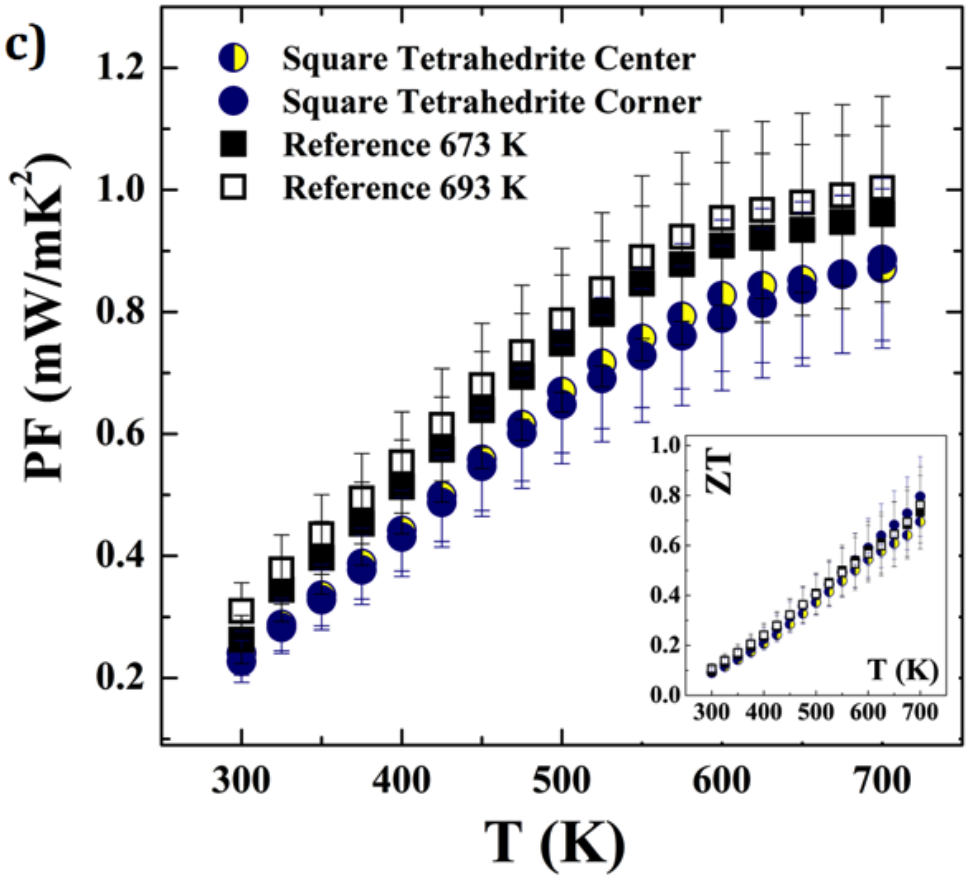




Up-scaled SPS Process

$Cu_{10.4}Ni_{1.6}Sb_4S_{13}$





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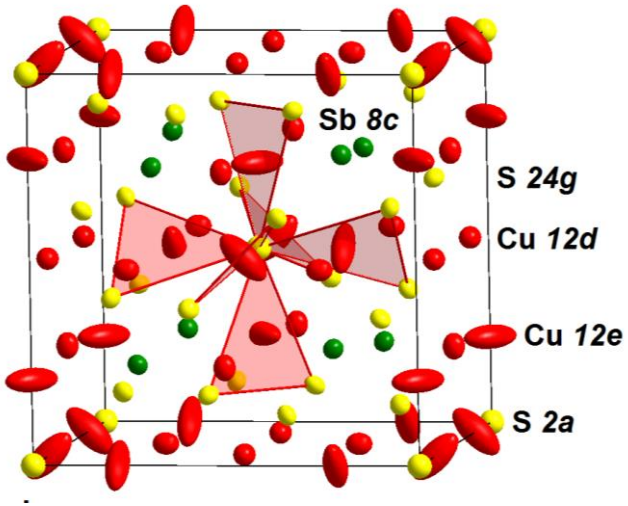
Ternary/Quaternary Sulfides

-N-type metallic $Cu_4Sn_7S_{16}$
(ZT=0.2, Acta Mater. 2015)

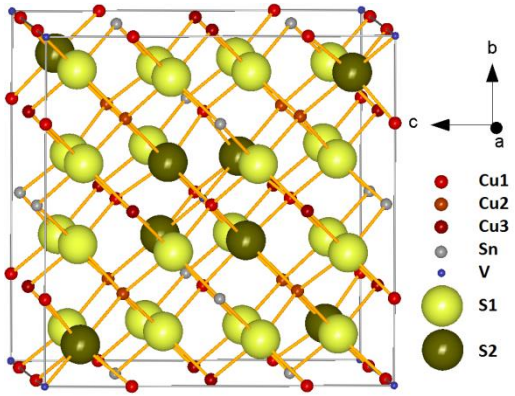


-Metallic $Cu_{26}V_2Sn_6S_{32}$ colusite
(ZT=0.4, J. Mater. Chem. C 2016)
(ZT=0.9, soon submitted)

-Metallic $Cu_{12}Sb_4S_{13}$ tetrahedrite
(ZT=0.8, J. All. Comp. 2015, RSC Adv. 2016, JACerS 2016)

-Semicond. $Cu_8Fe_3Sn_2S_{12}$ Stannoidite
(ZT=0.4, soon submitted)

-Semicond. $Cu_5FeS_{4-x}Se_x$ bornite
(ZT=0.6, Dalton Trans. 2017)



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