Intrincally low thermal conductivity in $Cu_{12}Sb_4S_{13}$ and $Cu_4Sn_7S_{16}$ complex structures

14th April 2015

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EPSRC Meeting, Loughborough University

Outline

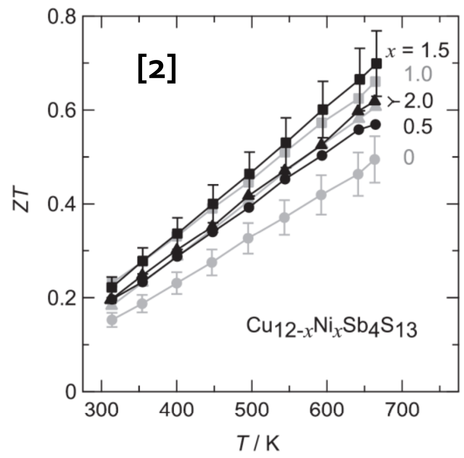
1. Phase stability and TE properties in ternary and Ni-susbtituted $Cu_{12}Sb_4S_{13}$ tetrahedrites

2. Intrinsically Low kappa in $Cu_4Sn_7S_{16}$

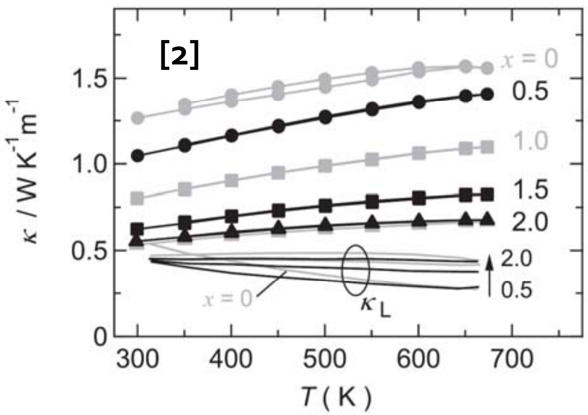
$Cu_{12-x}TM_xSb_4S_{13}$: Thermoelectric properties

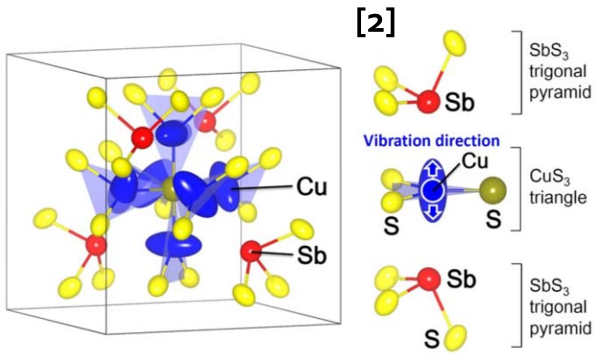
Synthetic tetrahedrites evidence high ZT values:

- **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]



Attractive candidates for TE applications (*p*-type) due to low thermal conductivity





The **very low lattice component** of the thermal conductivity is explained by:

(i) the relatively complex cubic structure

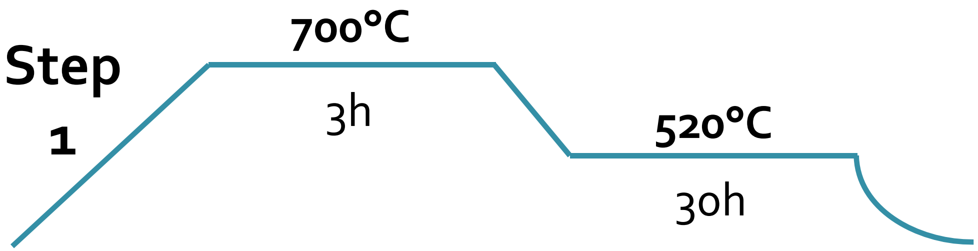
(ii) the dynamical disorder induced by the low-energy vibrational mode of Cu(2) atoms

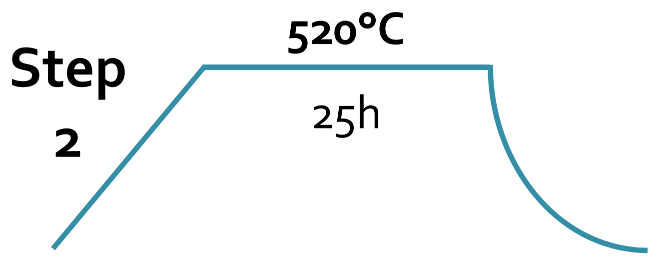
[1] X. Lu et al., Adv. Energy Mater. 3 (2013) 342-348. [2] K. Suekuni *et al.*, J. Appl. Phys. 113 (2013) 043712.

Samples preparation

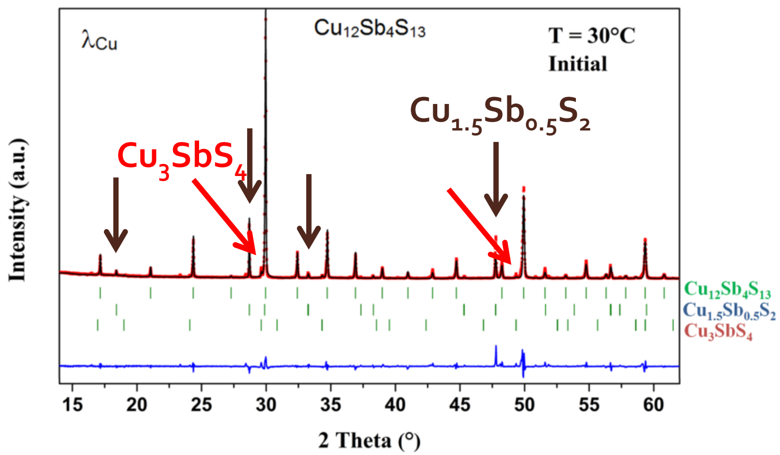
$Cu_{12}Sb_4S_{13}$ and **$Cu_{10.4}Ni_{1.6}Sb_4S_{13}$** samples:

reaction of stoichiometric mixtures of high purity elements in sealed tube

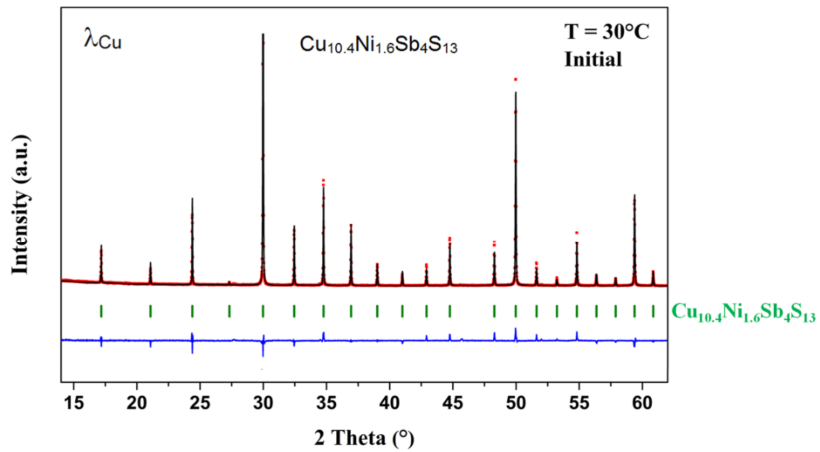




$Cu_{12}Sb_4S_{13}$



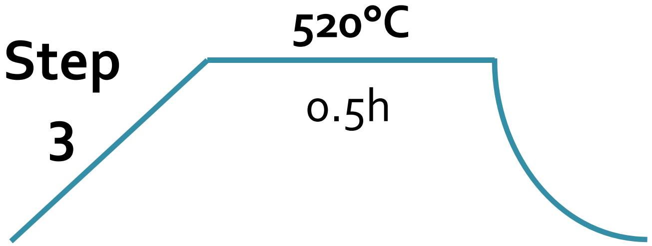
$Cu_{10.4}Ni_{1.6}Sb_4S_{13}$



Important role play by nickel substitution on the purity of tetrahedrite sample

↔ common substitution of Cu atoms by many elements (Fe, Zn, Ag, …) in natural tetrahedrite

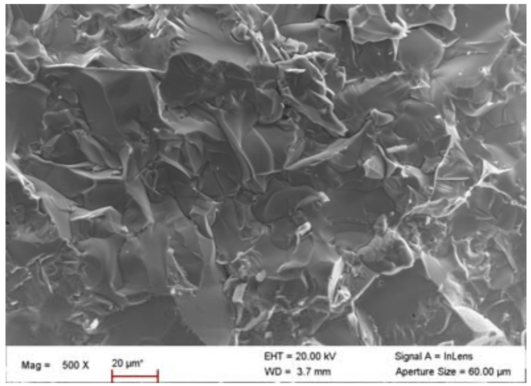
Samples preparation



Spark Plasma Sintering

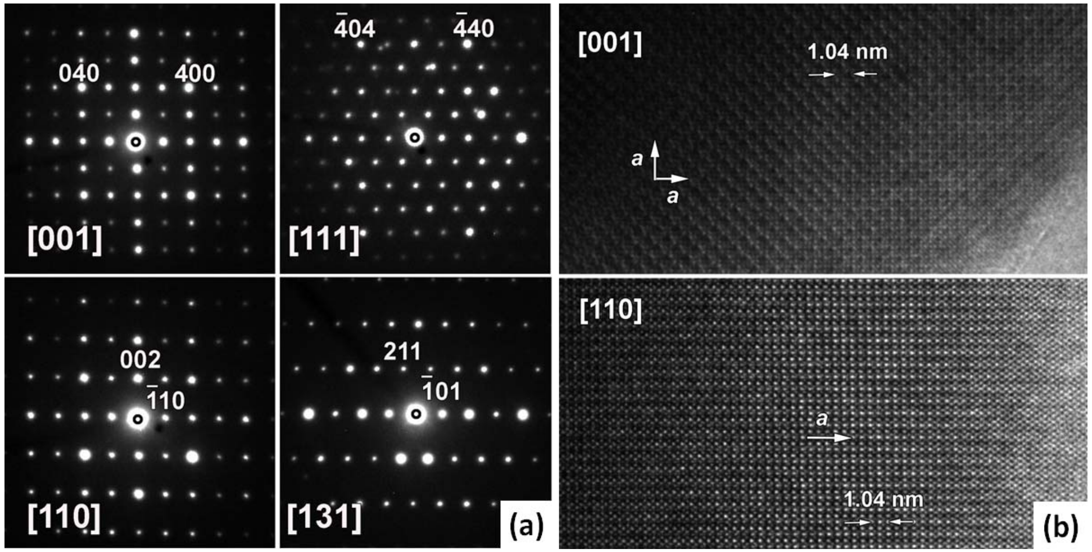
High density pellets (> 98 %) in very short times

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



No cracks suggests good mechanical properties

I-43*m* **a** = 10.4 Å



Absence of stacking defects indicates a well crystallized sample

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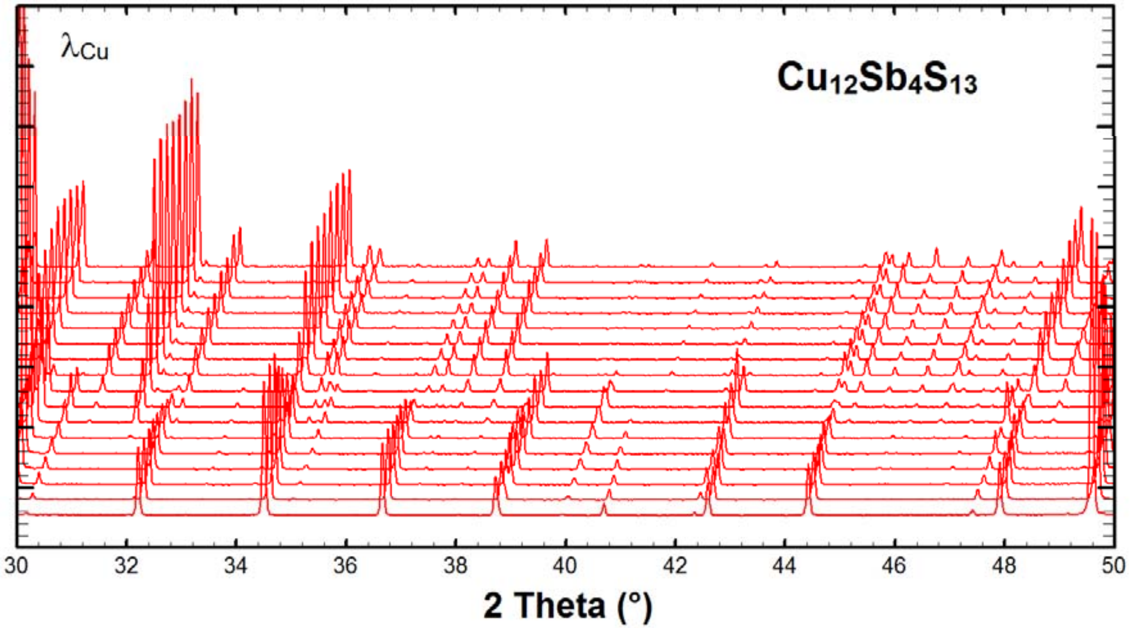
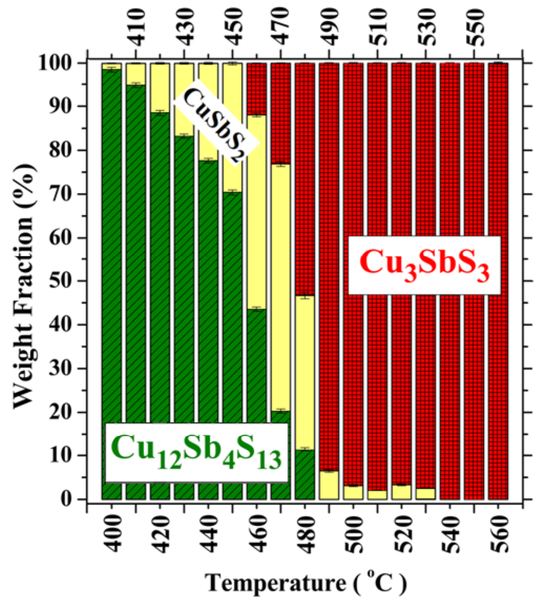
Powder XRD measurements on $Cu_{12}Sb_4S_{13}$



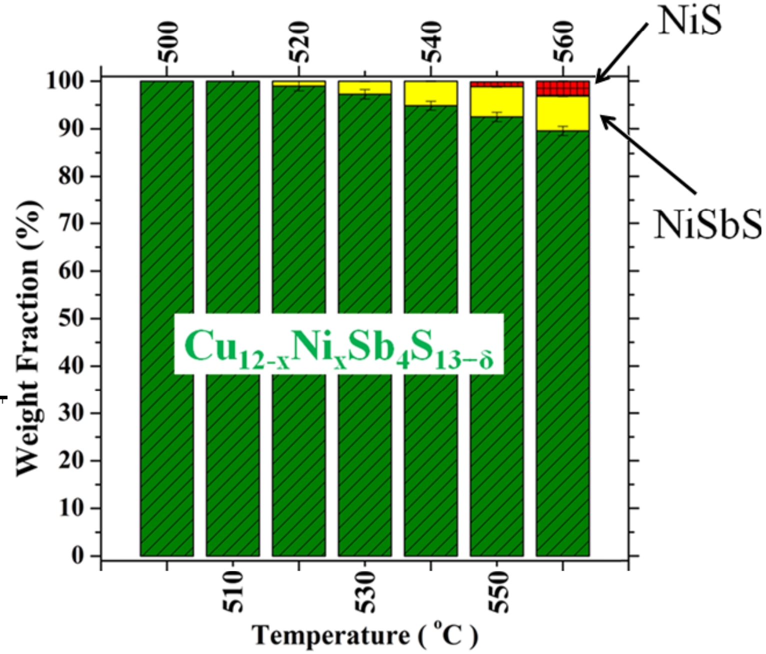
Recording condition:
one pattern every 10°C from
400°C to 560°C
heating rate of 2 °C/min under N_2 flux

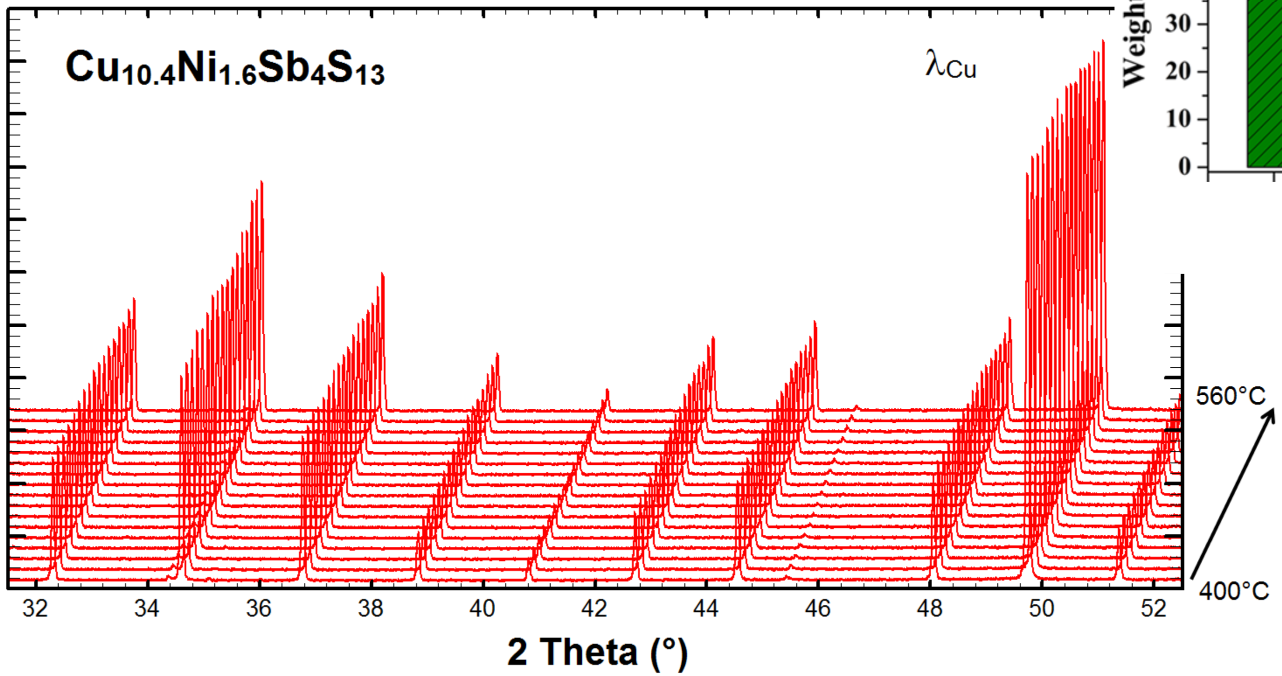


1. Tetrahedrite phase decomposes between 410°C and 480°C
2. Chalcostibite $CuSbS_2$ phase exists at intermediated temperatures (410°C - 490°C)
3. Skinnerite Cu_3SbS_3 phase appears at 460°C

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

Powder XRD measurements on $Cu_{10.4}Ni_{1.6}Sb_4S_{13}$





With similar thermal process

$Cu_{10.4}Ni_{1.6}Sb_4S_{13}$ is stable up to 560°C

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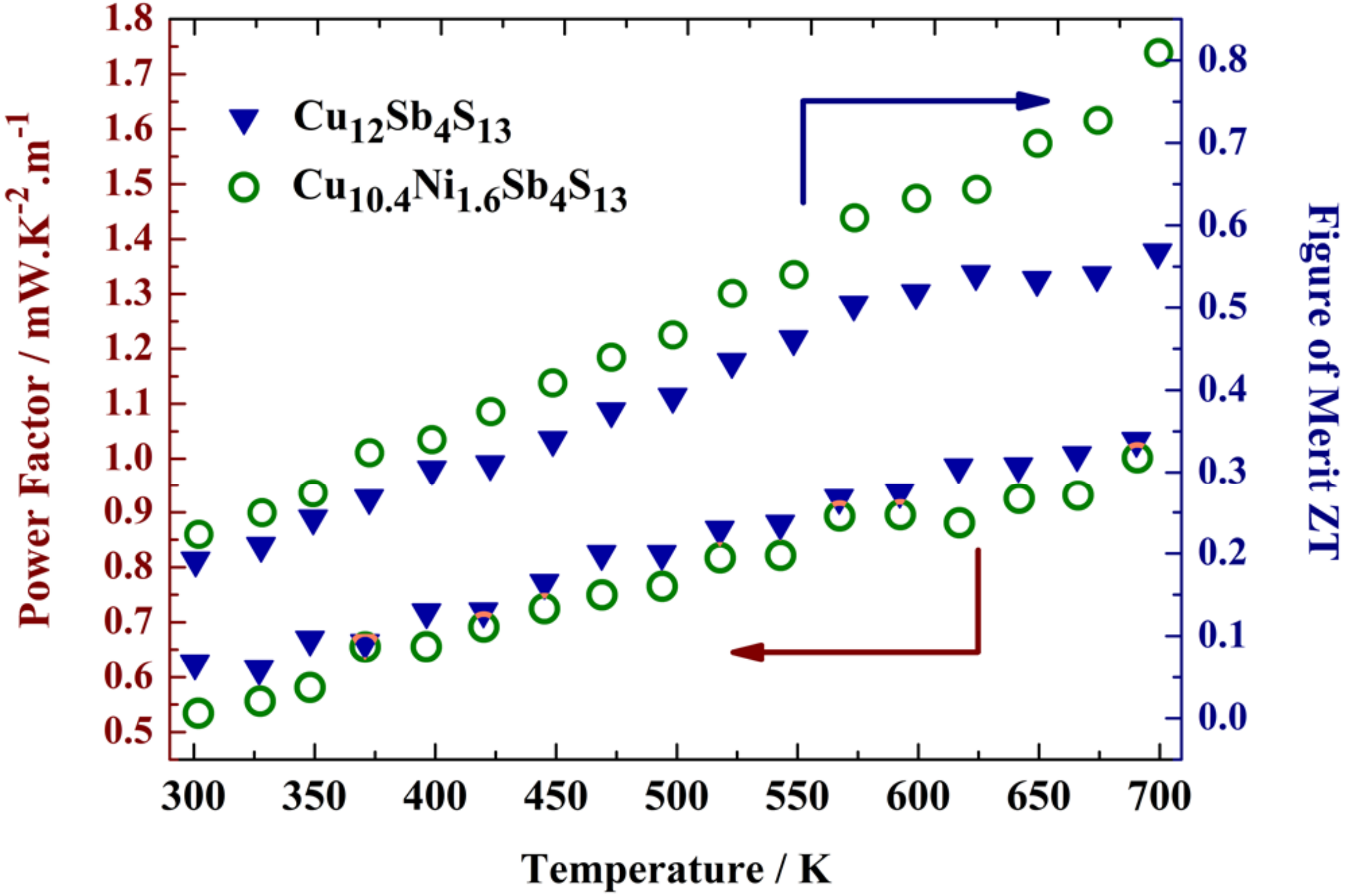
Thermoelectric properties



ZT = 0.8 at 700 K for $Cu_{10.4}Ni_{1.6}Sb_4S_{13}$

Confirmation of the benefit role of nickel substitution on TE properties

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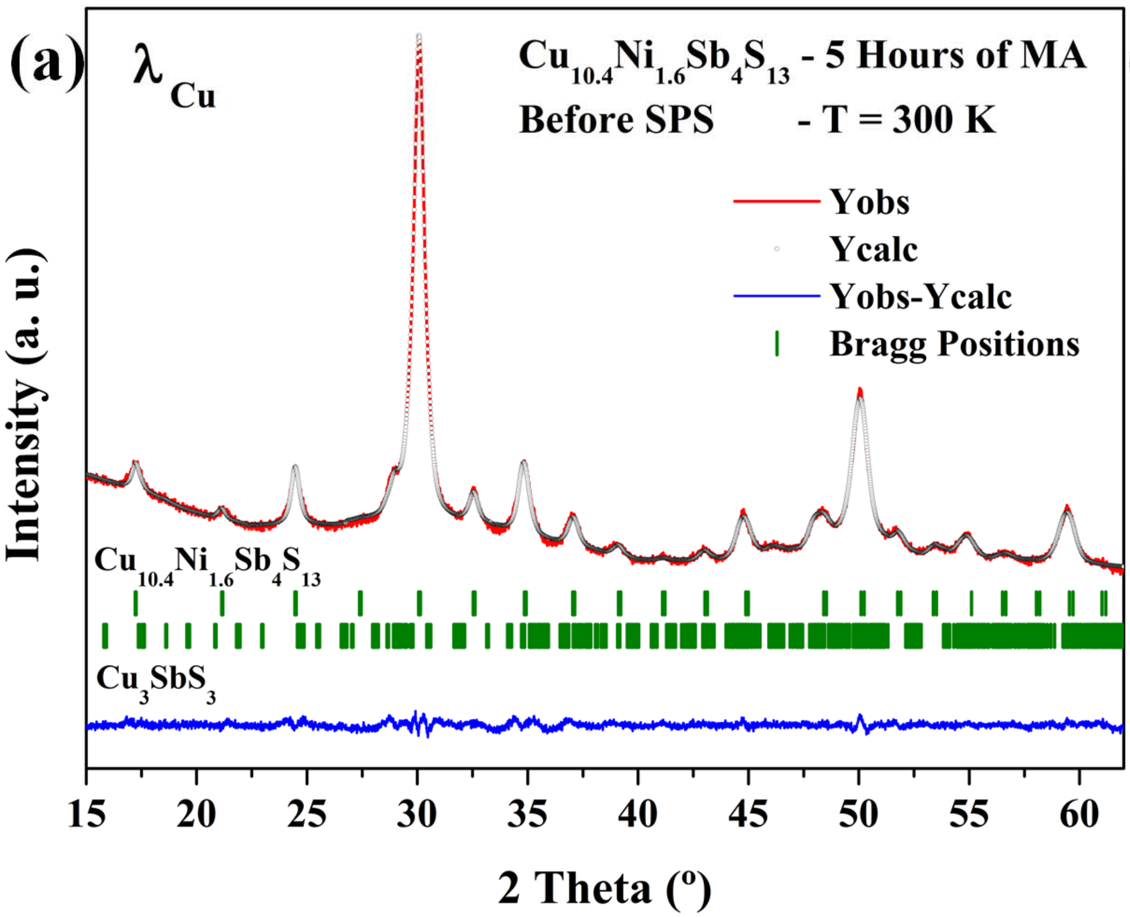
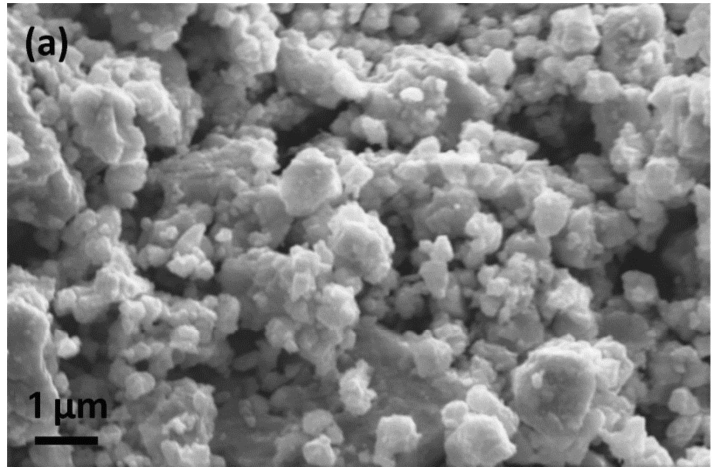
Up-scaling Perspectives

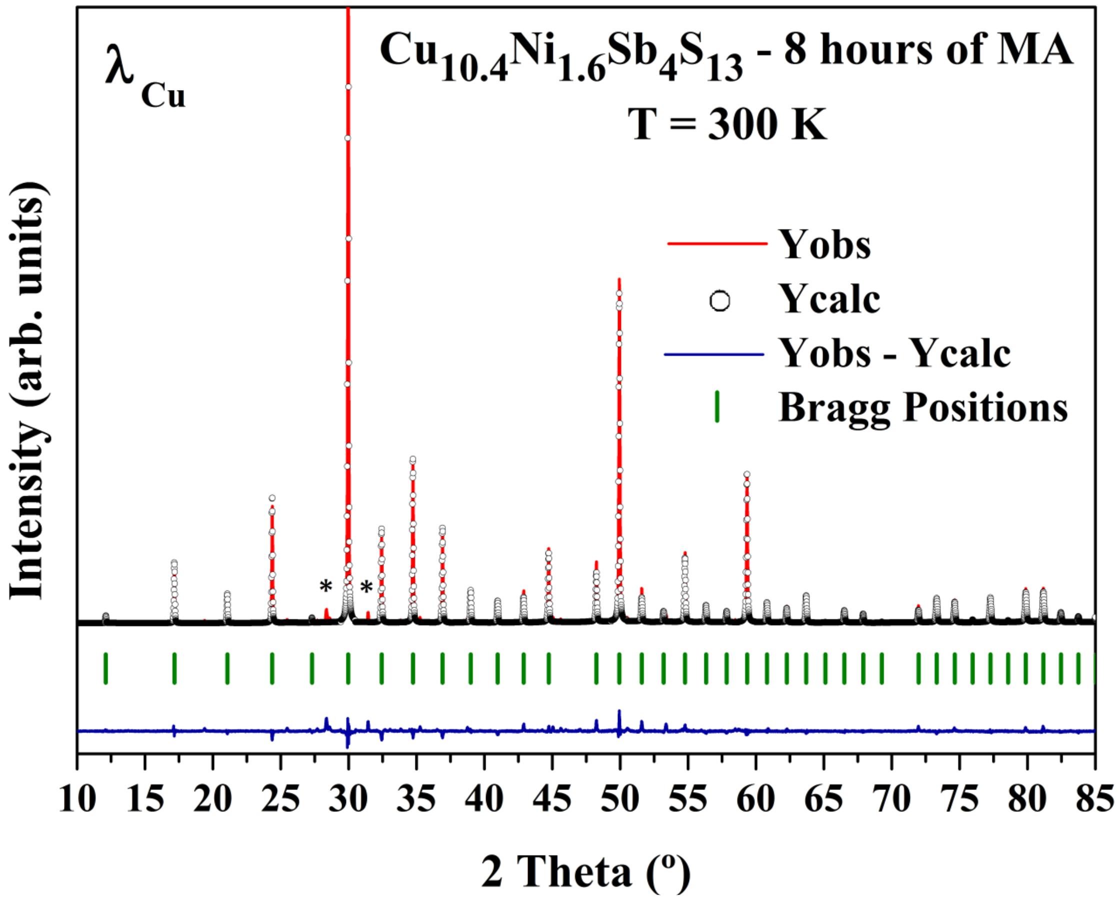
Mechanical Alloying from pure elements

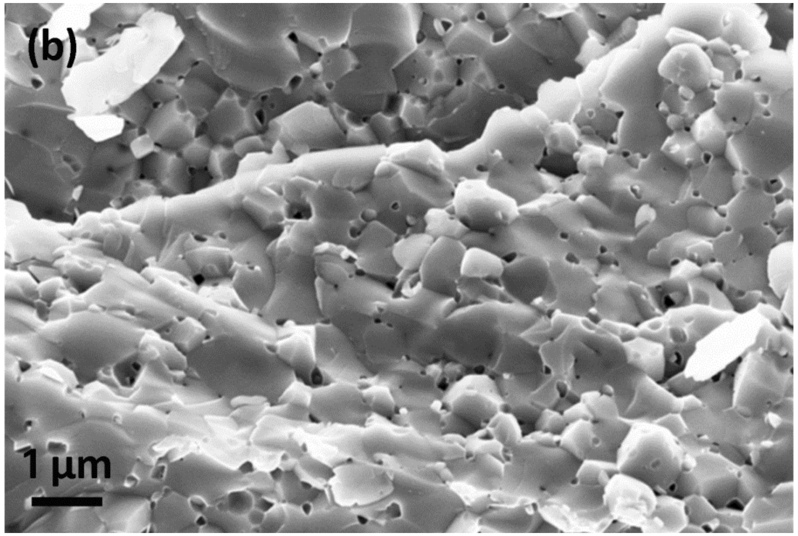




T. Barbier et al. (JACerS submitted)

Mechanical Alloying
from pure elements





AFTER SPS

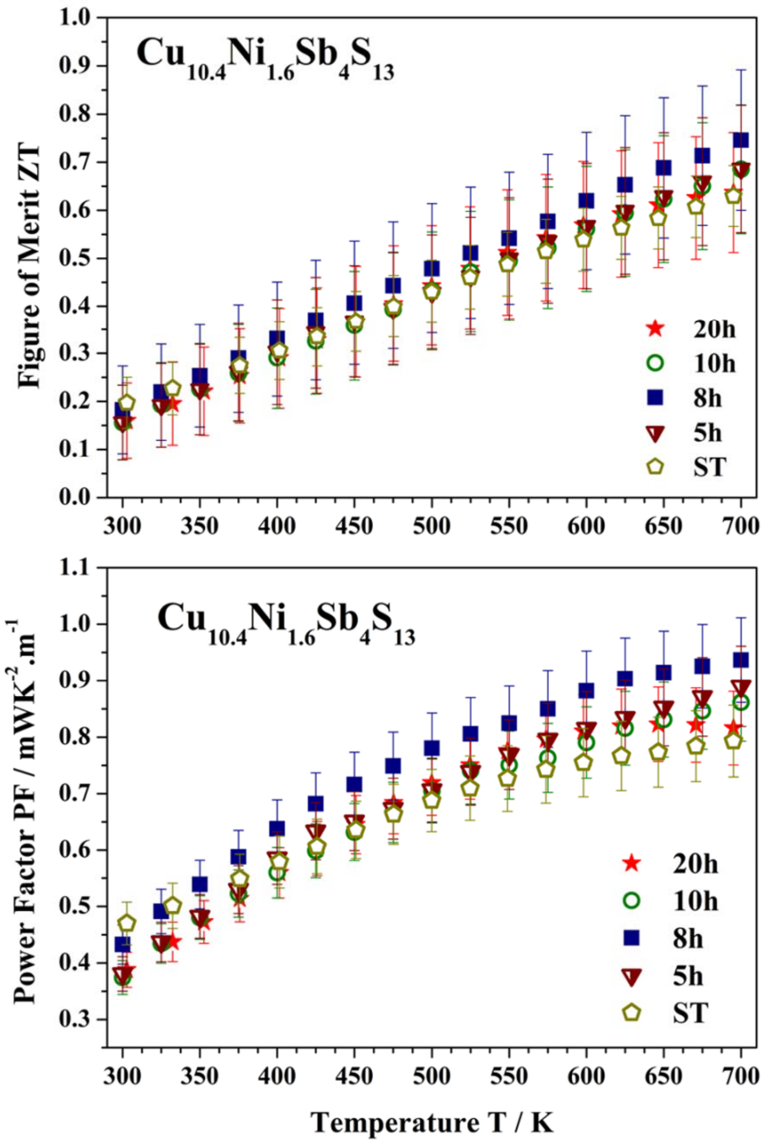
T. Barbier et al. (JACerS submitted)

Up-scaling Perspectives

Mechanical Alloying from pure elements

ZT near 0.8 at 700K

Comparable values than conventional samples



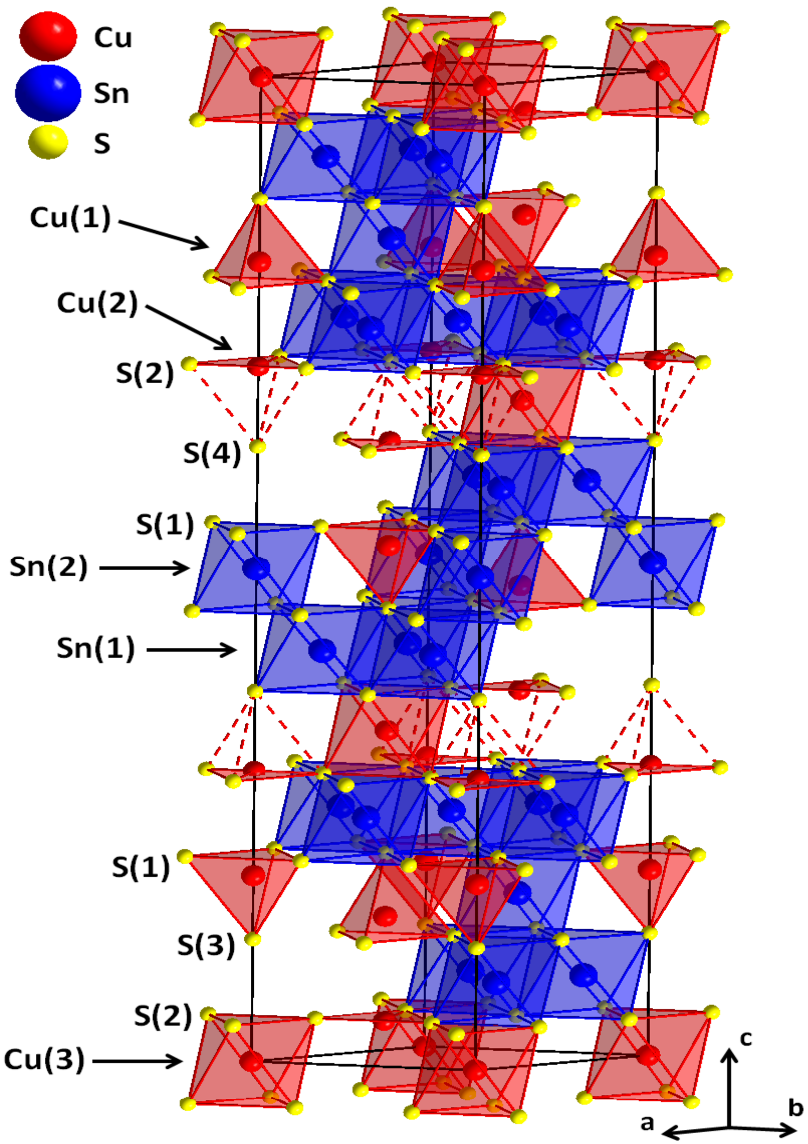
T. Barbier et al. (JACerS submitted)

Outline

1. Phase stability and TE properties in ternary and Ni-susbtituted $Cu_{12}Sb_4S_{13}$ tetrahedrites

2. **Intrinsically Low kappa in $Cu_4Sn_7S_{16}$**

Crystal structure of $Cu_4Sn_7S_{16}$



[1]

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

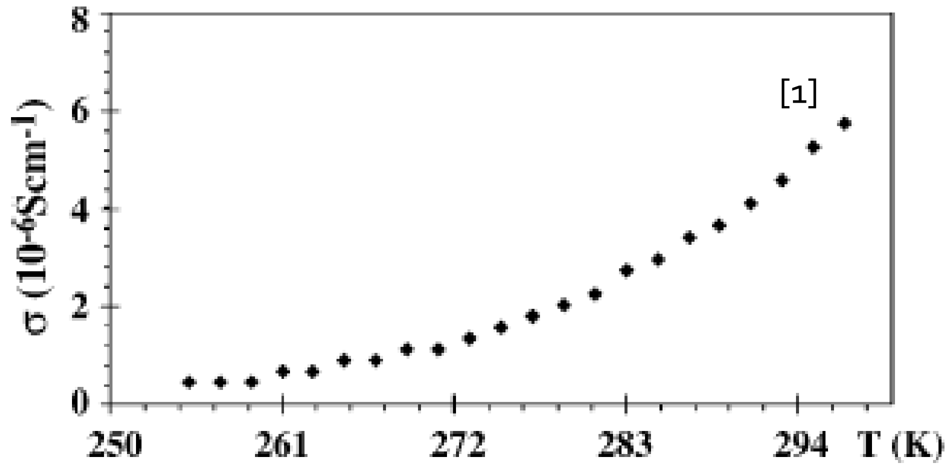
- Defect variant of the AB_2X_4 spinel structure
  Tetrahedral sites → 2 non equivalent sites
  Octahedral sites → 3 non equivalent sites

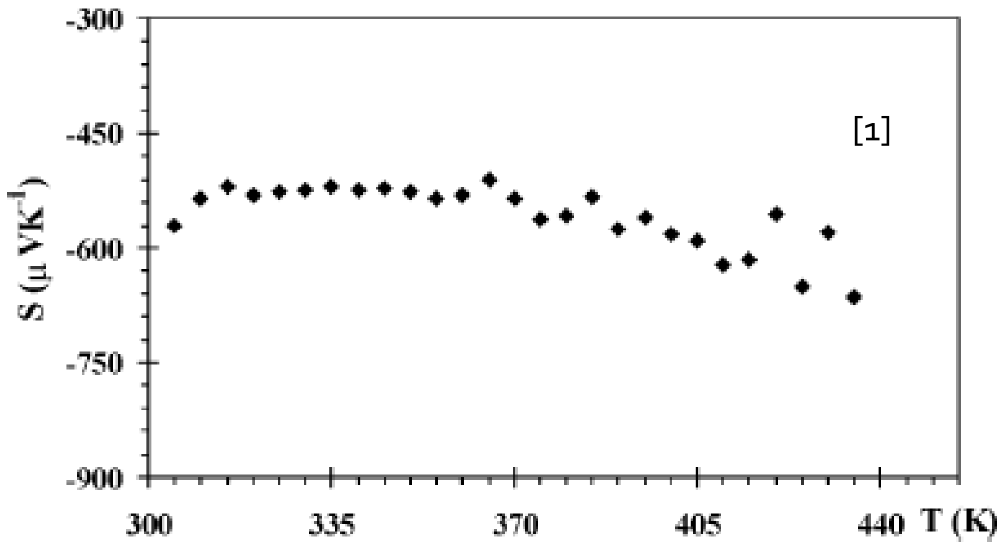
$$(Cu_{0.75}\square_{0.25})(Sn_{1.75}Cu_{0.25})S_4$$

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

Electrical Properties of $Cu_4Sn_7S_{16}$

- Poor Semiconductor ($\sigma=10^{-6}$ Scm^{-1})
- High DOS at Fermi level (Gap 0.8-1.27 eV)
  $\rightarrow$Large Seebeck coefficient
- Low density (compacted powders)
- Low cost and abundant elements





. Temperature dependence of the Seebeck coefficient of $Cu_4Sn_7S_{16}$.

[1] J.P.F. Jemetio, P. Zhou, H. Kleinke, Journal of Alloys and Compounds (2006)

Synthesis of $Cu_4Sn_7S_{16}$

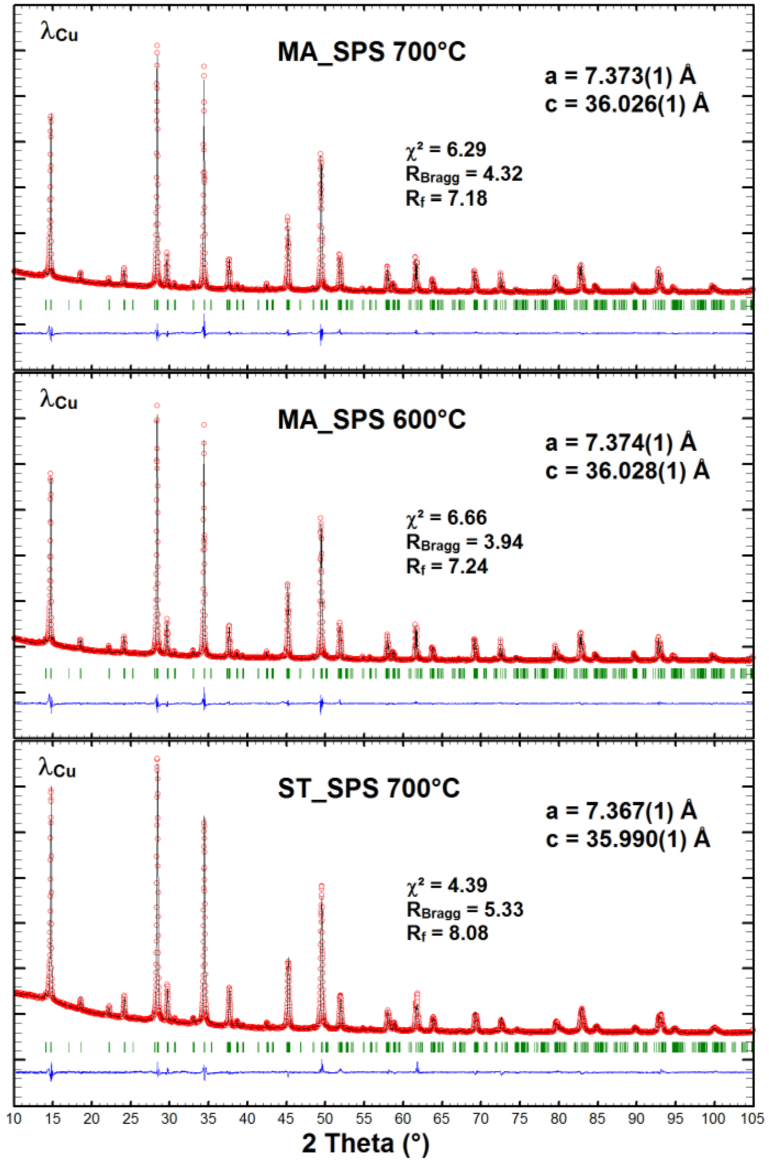
- Powder Synthesis
  - -Sealed tube Synthesis (ST)
  - - Mechanical Alloying (MA)

- 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

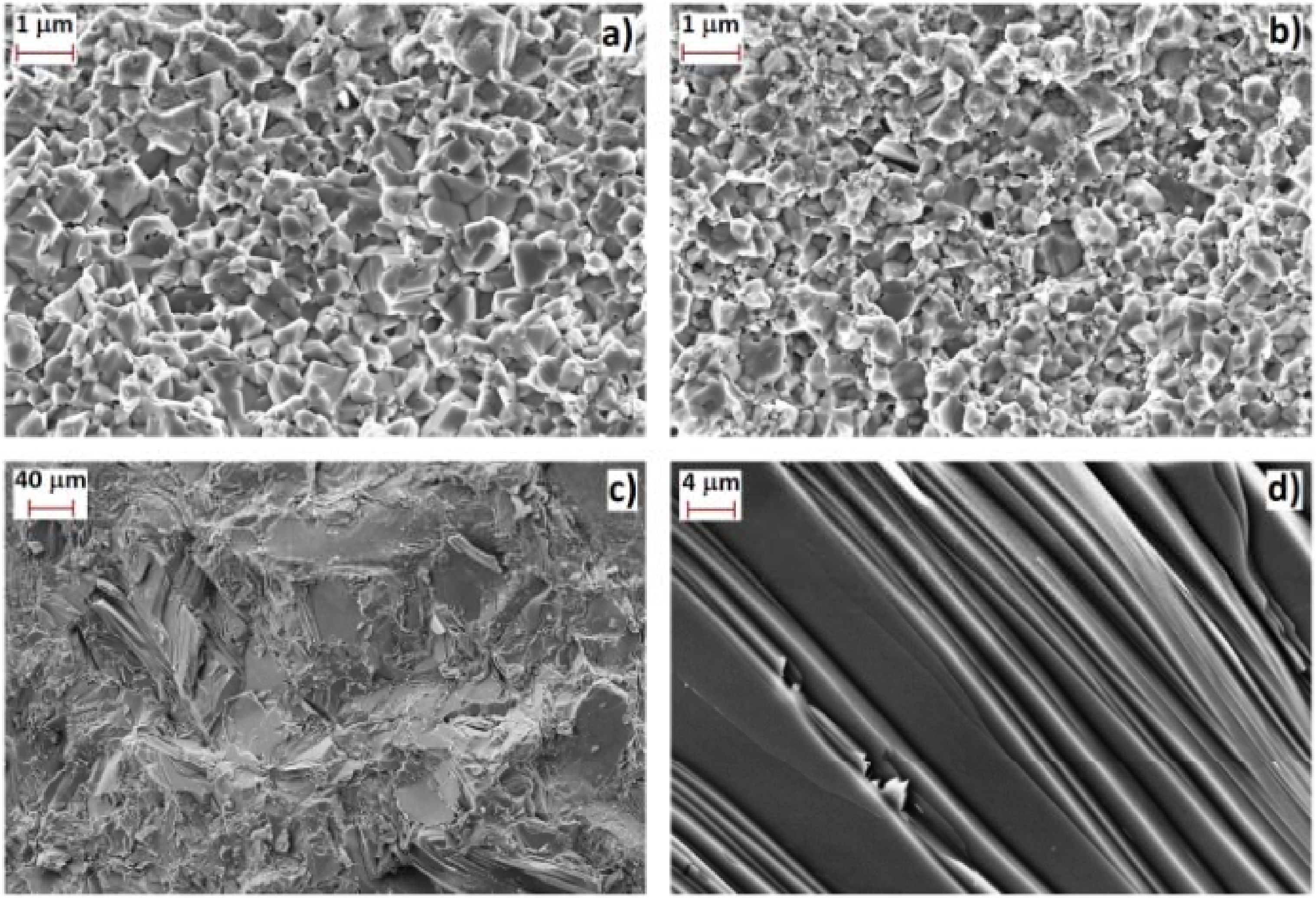


C. Bourges, P. Lemoine, O. Lebedev, E. Guilmeau, Acta Materialia (submitted)

Microstructure

(MA)

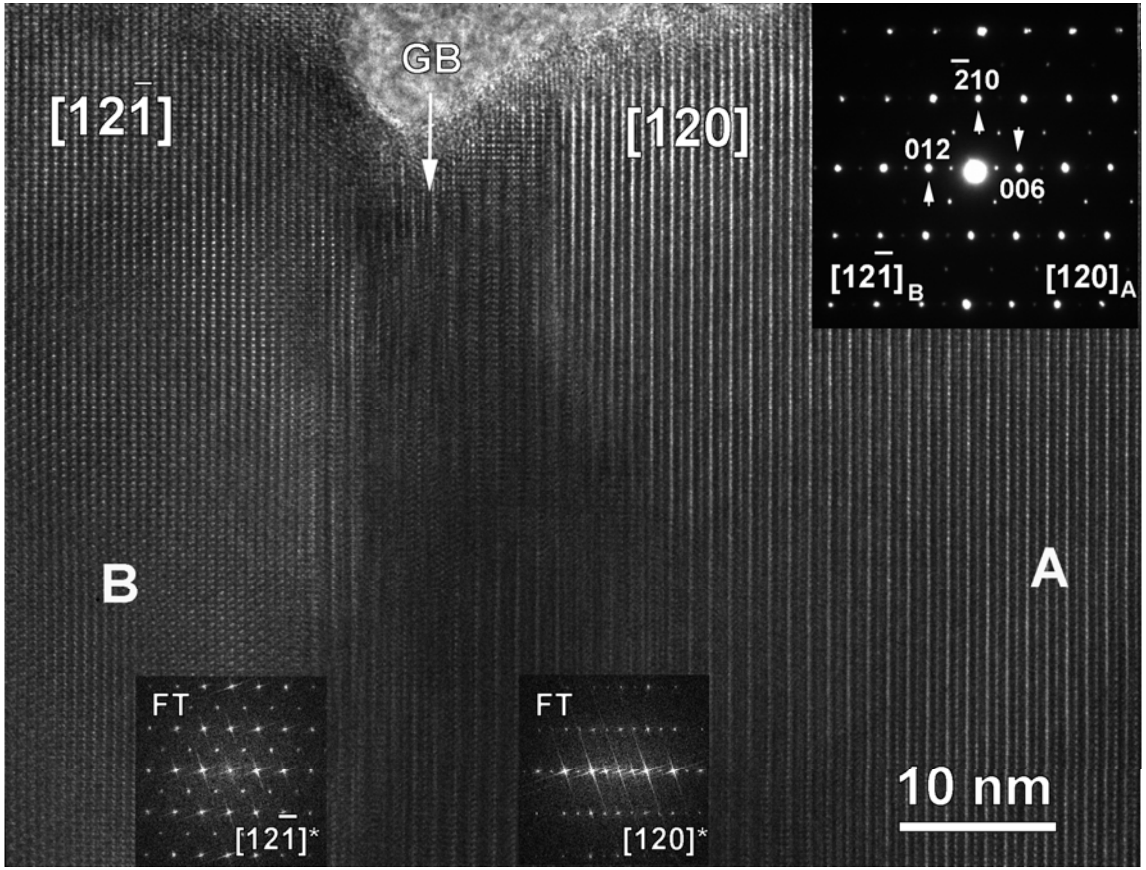
(ST)



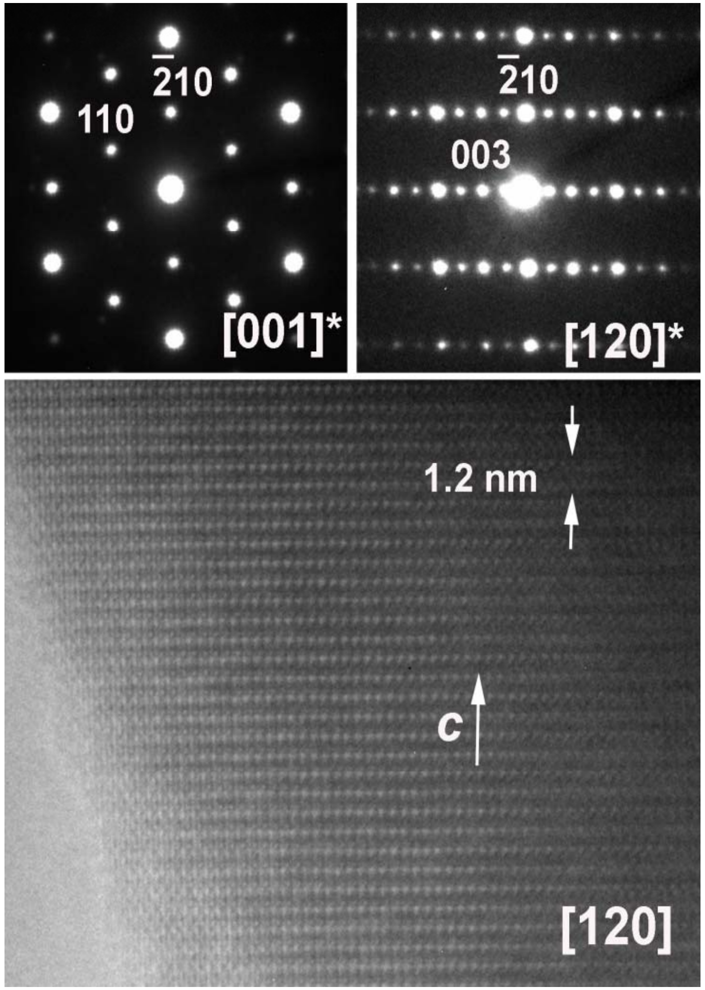
C. Bourges, P. Lemoine, O. Lebedev, E. Guilmeau, Acta Materialia (submitted)

TEM

(ST)



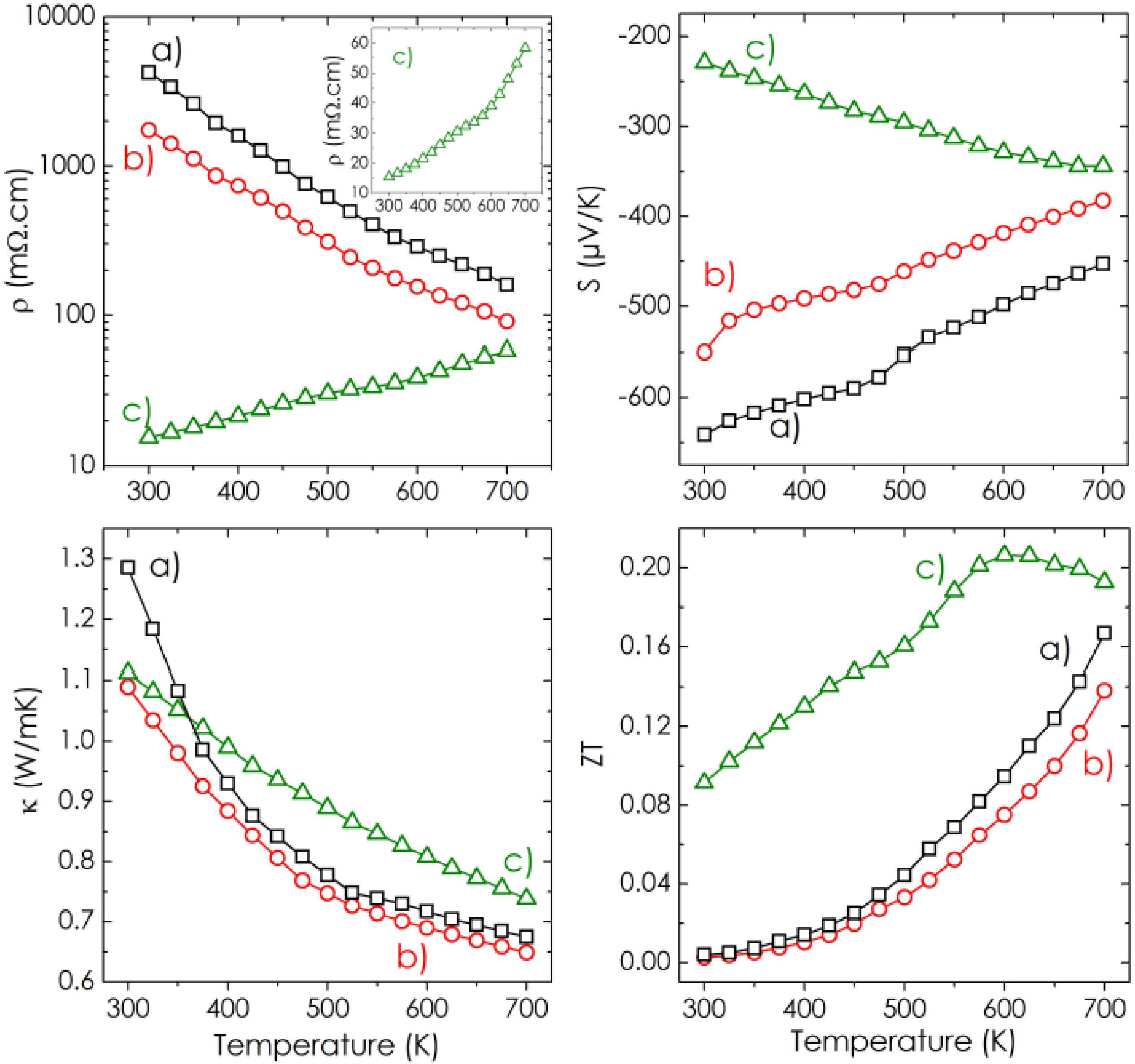
(MA)



-Anisotropic cristallites
-Grain Boundaries: Twinning, Intergrowths

C. Bourges, P. Lemoine, O. Lebedev, E. Guilmeau, Acta Materialia (submitted)

TE Properties



<u>Mechanical alloying</u>

a) 700°C and **b) 600°C**

<u>Sealed tubes</u>

c) 700°C

-Metallic behavior in ST

Tweed and intergrowth Strc.

Local composition, coord.

S vacancies, Cu occupancy

-Low thermal conductivty

-ZT=0.2 @600K

C. Bourges, P. Lemoine, O. Lebedev, E. Guilmeau, Acta Materialia (submitted)

Conclusion

$Cu_{12}Sb_4S_{13}$

✓ **Significant and benefit role of nickel substitution on:**

- the thermoelectric properties
- the purity of the sample
- the stability of the phase

✓ **Maximum operating temperature:**

- 400°C (673 K) for $Cu_{12}Sb_4S_{13}$
- 510°C (783 K) for $Cu_{10.4}Ni_{1.6}Sb_4S_{13}$

✓ **Mechanical alloying provides up-scaling routes to tetrahedrites**

- ZT=0.7-0.8 @ 700K

Conclusion

$Cu_4Sn_7S_{16}$

✓ **Synthesis conditions modifies electrical properties:**

- Metallic behavior in ST samples (first time)
- Inhomogeneity, structural defects (twinnings, Intergrowth)

✓ **Intrinsically low thermal conductivity (<1 W/mK):**

- Complex structure
- Origin?? (Cu(2) sites in triangular coordination (tetrahedrite))

✓ ***Low kappa achieved by taking advantage of the complex structure in this Cu-Sn-S ternary compound, opens the route to the discovery of other complex thermoelectric materials.***

Acknowledgements

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