Thermoelectric Properties of Non-Stoichiometric Bornite

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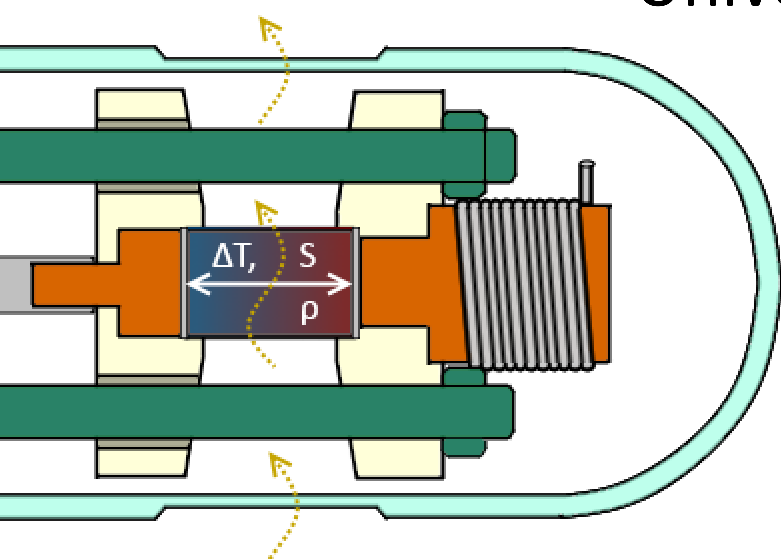
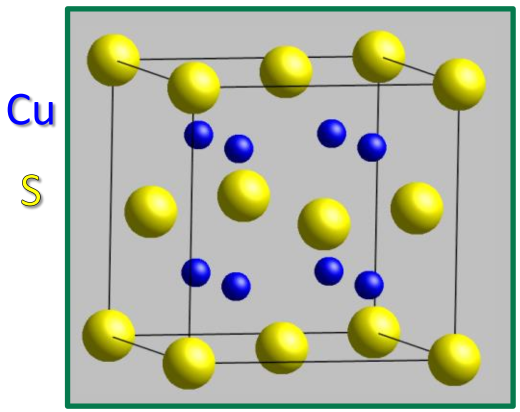


Bornite a Potential Thermoelectric

- State of the art thermoelectrics use rare-earth elements
- New class of thermoelectrics –Phonon Liquid Electron Crystals (PLEC)
  - Conduct electricity like a crystal
  - Exhibit a liquid-like sub lattice



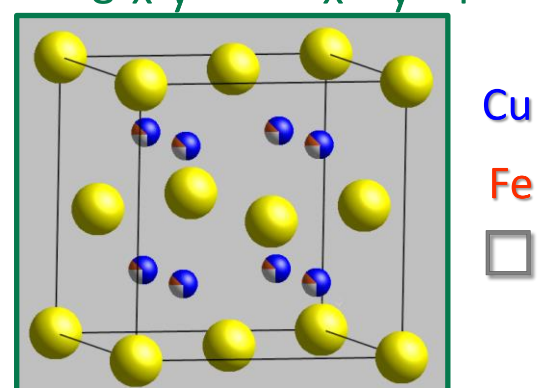
α - $Cu_{2-x}S$ ($M^{+}_{8-x}\square_{x}S_4$)

- Anti-Fluorite structure
- Copper ion conductivity → Ultra-low thermal conductivity
- Very high thermoelectric performance. $ZT_{max}=1.6$

Bornite- Cu_5FeS_4 (M^{+}_{8-x-y} $M^{3+}_{x}\square_{y}S_4$)

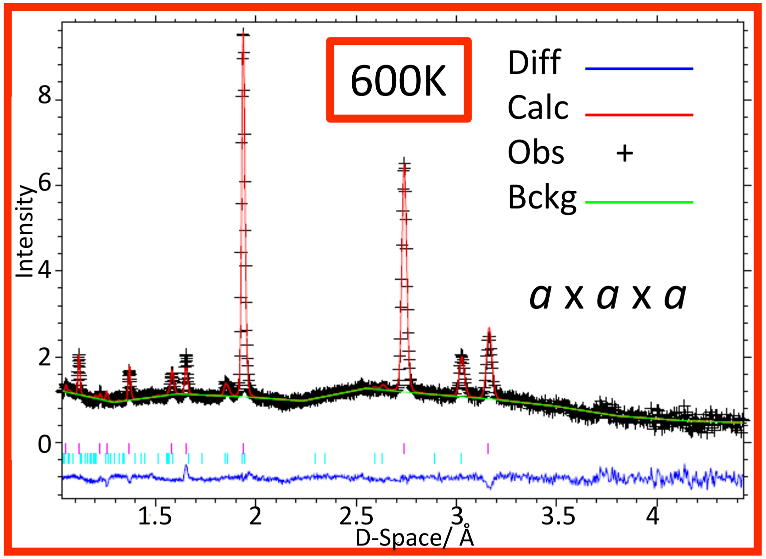
- Anti-Fluorite related structure at high temperature
- Copper ion mobility → Ultra-low thermal conductivity
- Poor electronic properties → Low $ZT_{max}\approx 0.4$

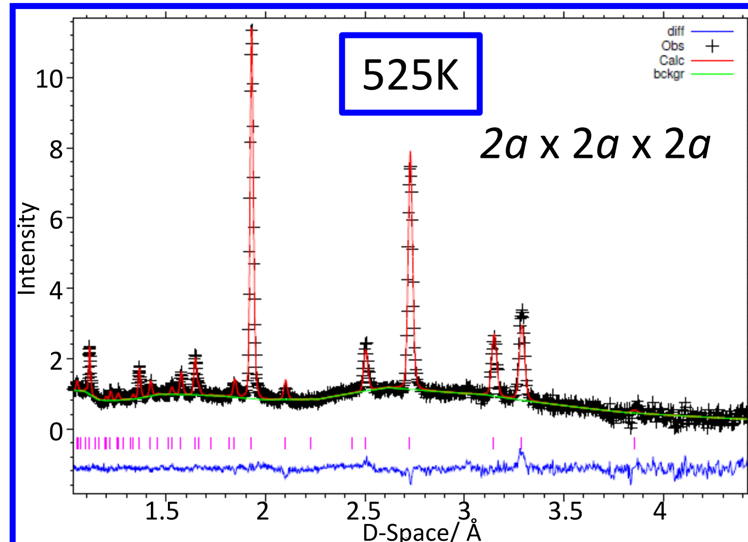
- Shows a number of phase transitions

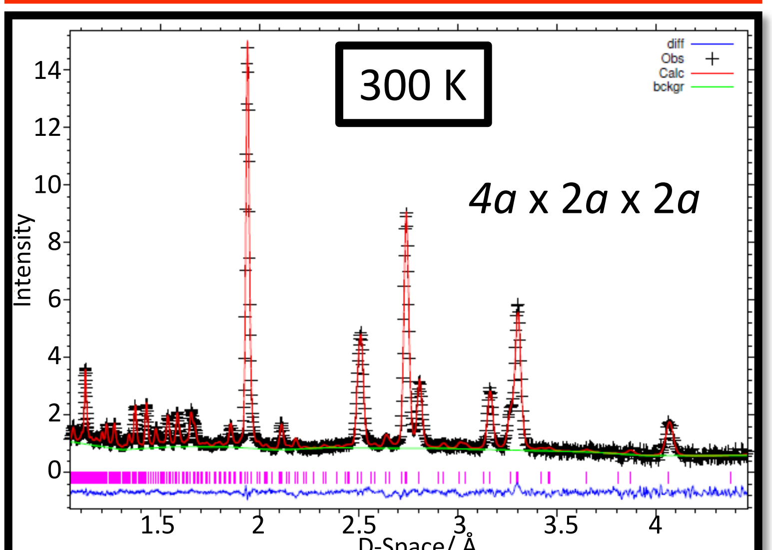


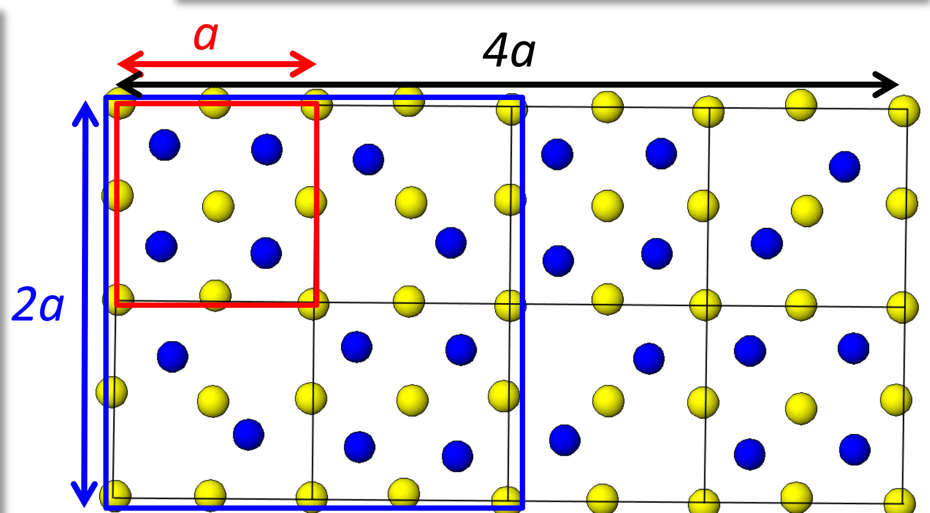
High Temperature Phase

Phase Transitions in Cu_5FeS_4









Limit on Solid Solution Behaviour

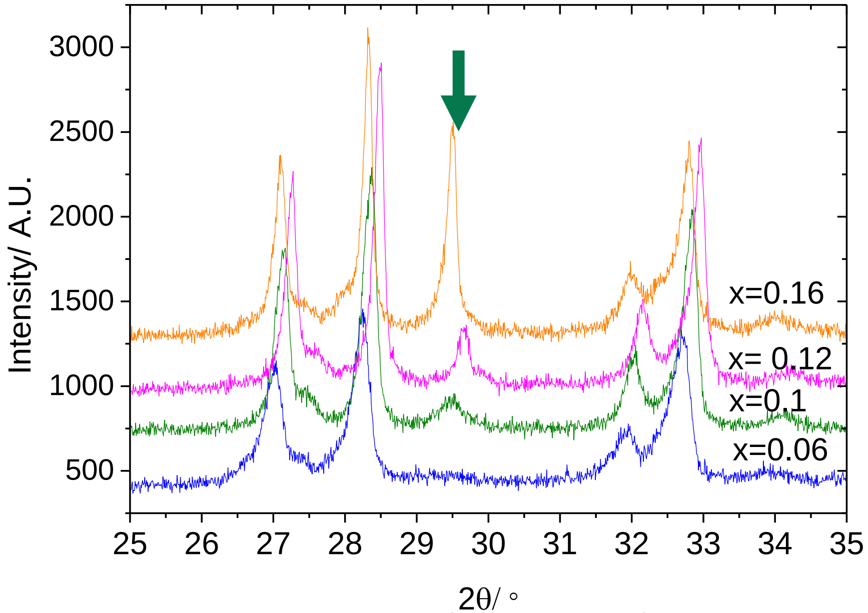
$Cu_{5-x}FeS_4$

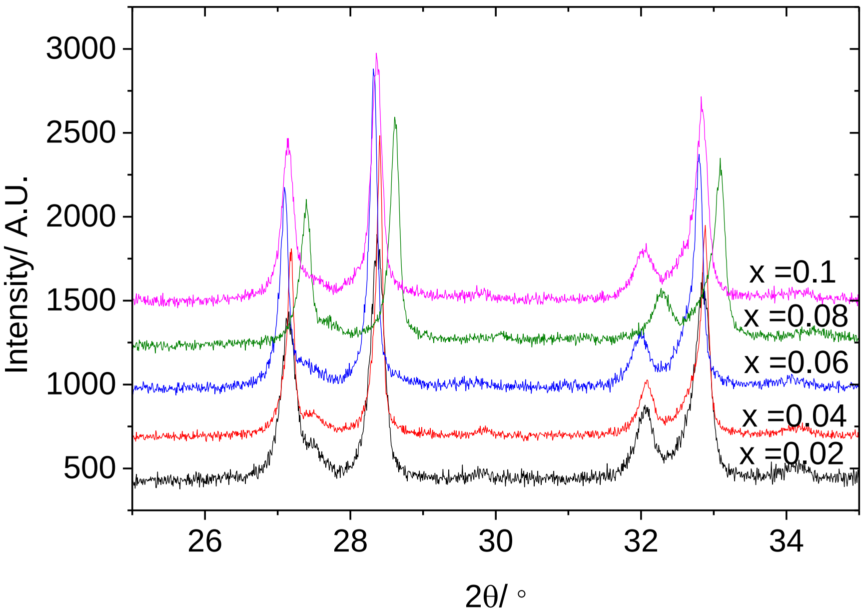
- Copper Deficiency

$Cu_{5+x}Fe_{1-x}S_4$

- Copper on Iron site substitution

- All samples made by ball milling then hot pressing
- Powder X-ray diffraction Data of the 2 series



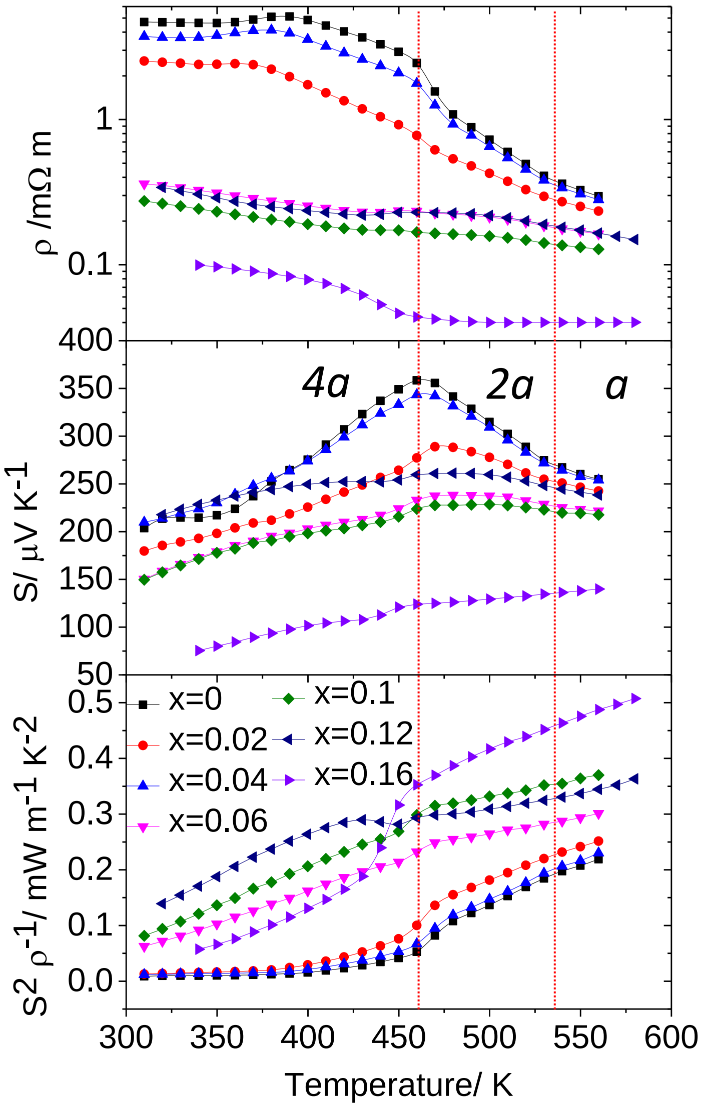


- Chalcopyrite ($CuFeS_2$) impurity forming at higher x

- All show a single phase

$Cu_{5-x}FeS_4$

Cu Deficiency – Electronic Transport Properties



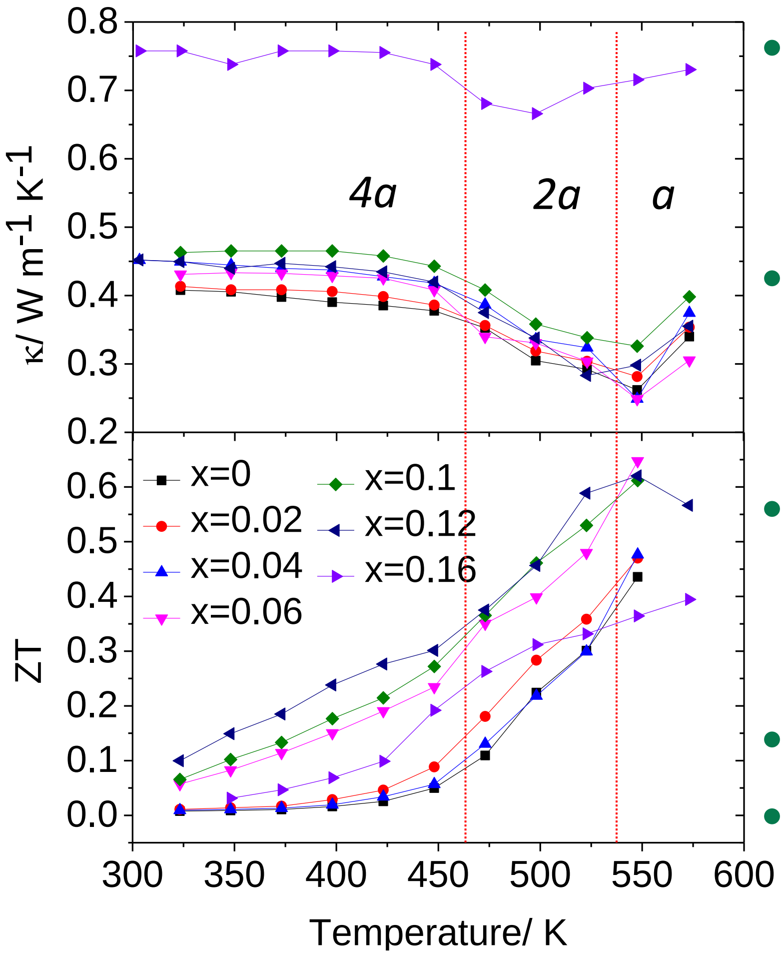
- Resistivity decreases across the series
- Reduced by a factor 10 when x=0.16
- Behaves as a semi-conductor through entire composition range

- |S| decreases with increasing Cu deficiency
- p-type conduction throughout series
- Anomalies in properties arising from 4a→2a phase transitions

- Increased power factor across the series -from P.F.≈0.2 to P.F≈0.5 mW m^{-1} K^{-2}

$Cu_{5-x}FeS_4$

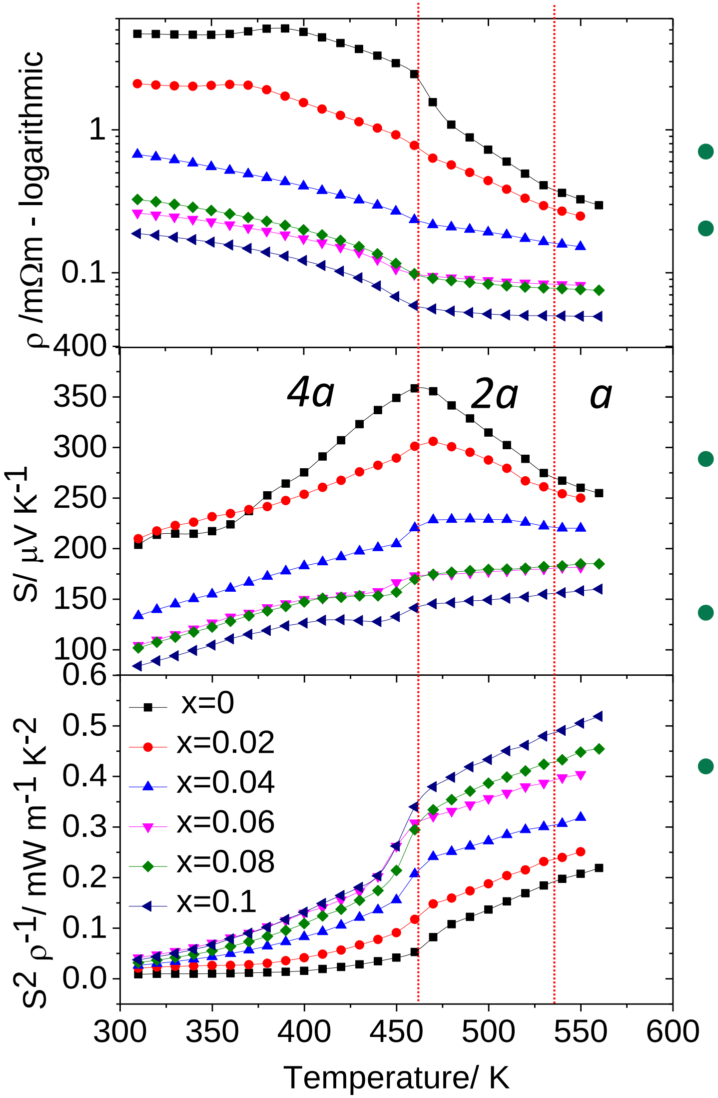
Cu Deficiency – Thermal Transport properties



- x=0.16 shows highest *κ*
  -BUT contains chalcopyrite (κ=6 W m^{-1} K^{-1}) impurity
- κ_{total} for samples where x≤0.12 show little sensitivity to copper content
- Wiedemann-Franz law suggests reduced $\kappa_{lattice}$ values when x≤0.12
- ZT>0.6 between 0.06≤x≤0.12
- ZT_{max}=0.65 for x= 0.06
  - ZT_{max} at 550 K / 277 ^{o}C

$Cu_{5+x}Fe_{1-x}S_4$

Cu Substitution – Electronic Transport Properties



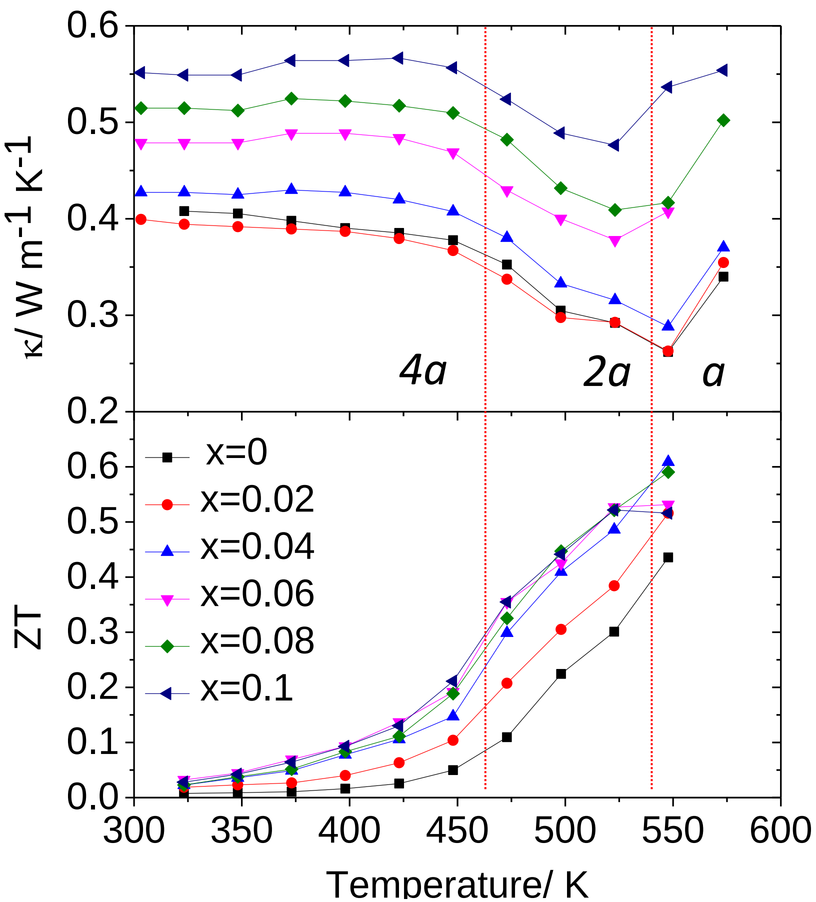
- Significant reductions in resistivity
- Samples where x≥0.6 show ρ=0.1 mΩ m in *2a* and *a* phases

- Seebeck coefficients lower than Cu deficient Series
- p-type conduction

- Progressive increases in the P.F. with copper substitution

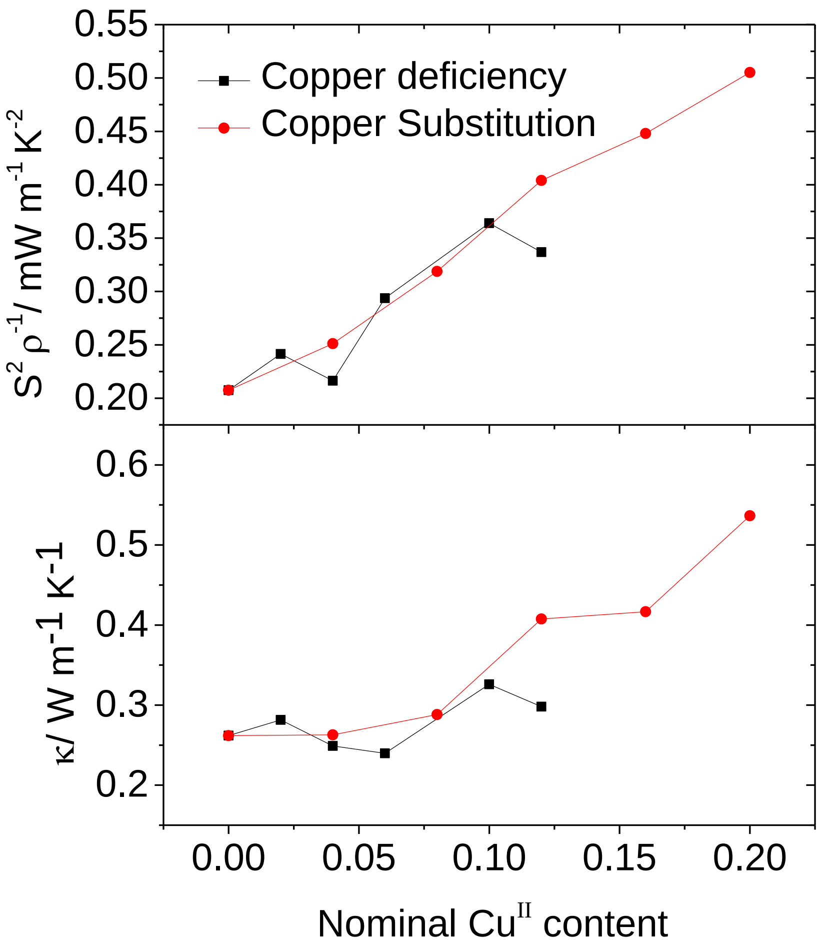
$Cu_{5+x}Fe_{1-x}S_4$

Cu Substitution – Thermal Transport Properties



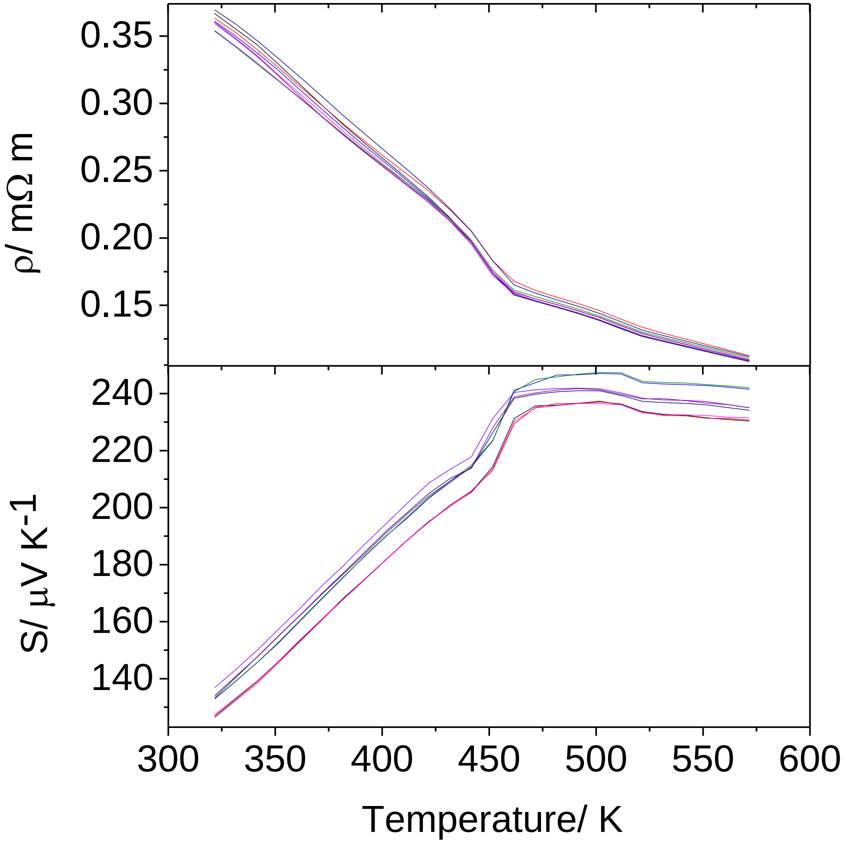
- κ_T increases with copper content
  - principally due to κ_{el}
- κ_{lat} decreases with increased Cu substitution
- κ_T exhibits a minimum near the 2a→a phase transition
  - This moves to lower T with increasing copper content
- Suggests there a composition/phase transition dependence
  - DSC data on mineral bornite supports this
- ZT≈0.6 samples x=0.04, 0.08

Series Comparison at 550 K



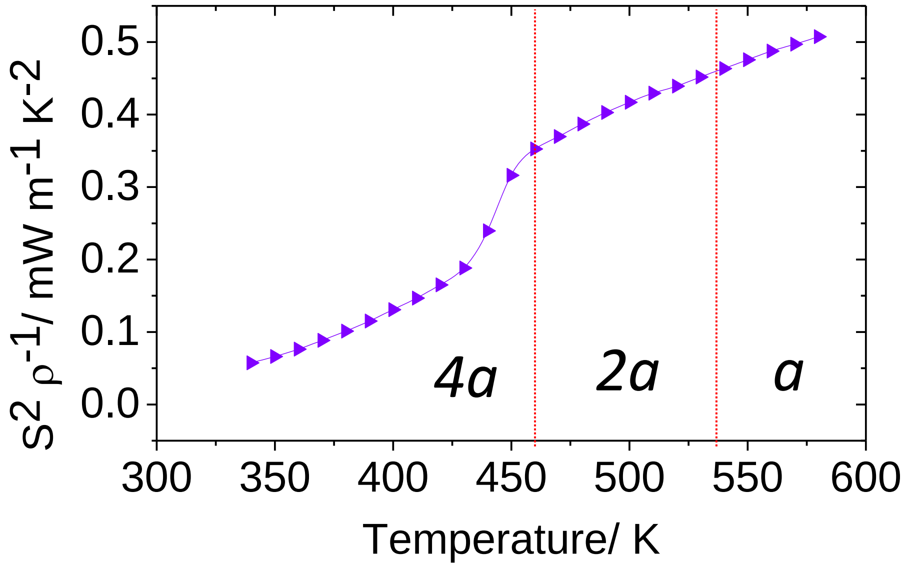
- Cu Deficiency series
  - $Cu^{I}_{5-x}Cu^{II}_{x}FeS_4$
- Cu Substitution Series
  - $Cu^{I}_{5-x}Cu^{II}_{2x}Fe_{1-x}S_4$
- Higher effective doping with Cu substitution
  - a given increment in x gives more Cu^{II}
- Similar properties between series with nominal Cu^{II} content
- Small deviations from ideal bornite stoichiometry significantly enhance ZT

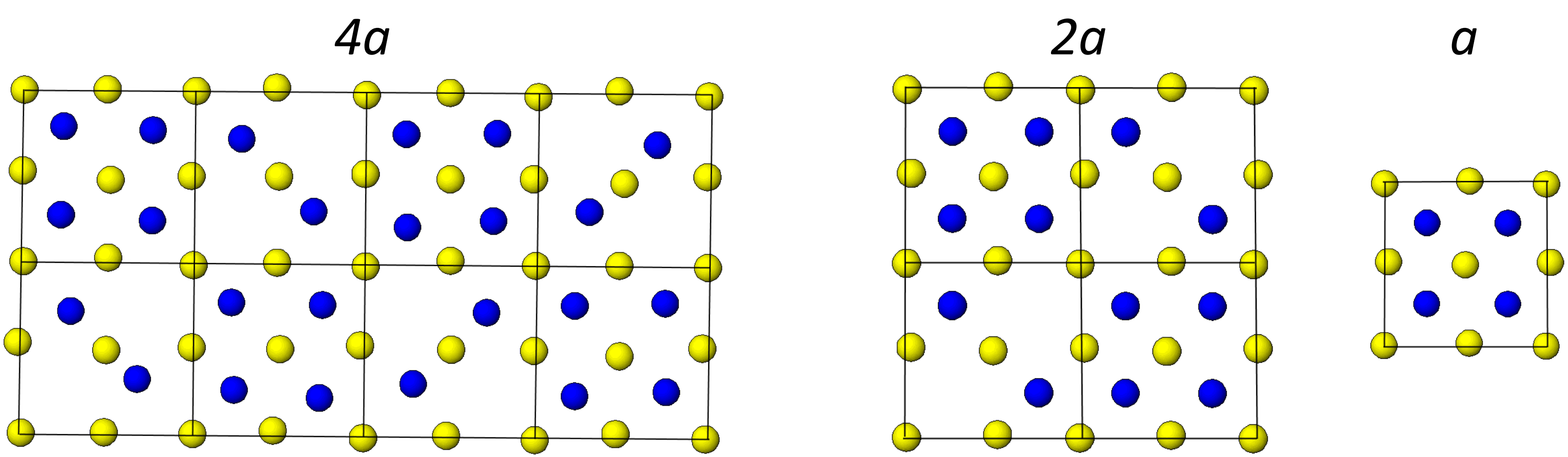
Thermal Cycling of Bornite



- Important to consider the stability of the material
- We wanted to check that these samples were stable
  - 8 cycles
  - 300 – 600 K
  - S & ρ recorded every 10 K
- Data suggests no significant degradation

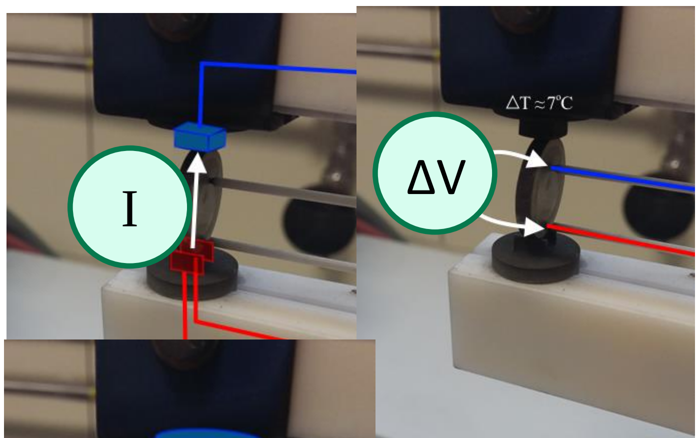
Thermoelectric cell

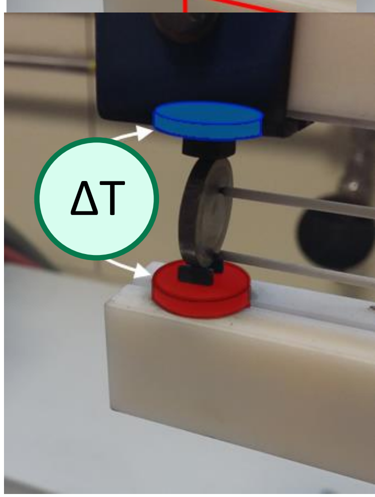




In-Situ Thermoelectric Diffraction Cell

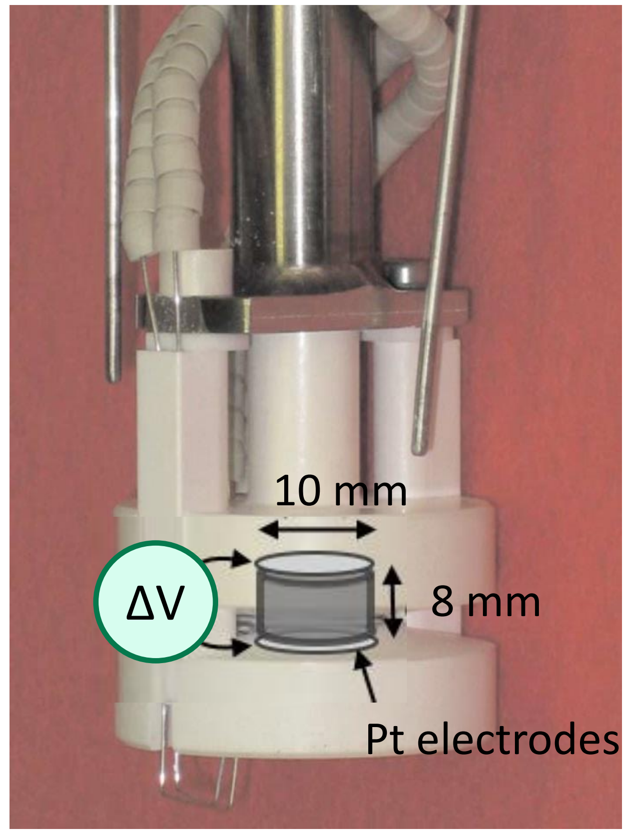
Laboratory Measurement System - Linseis LSR-3





Measure: Seebeck coefficient
and resistivity as a function of temperature
(Inside a furnace)

Diffraction-Resistance Cell



Measure:
Resistivity and neutron diffraction as a function of temperature
(Inside a furnace)

We plan to expand the capabilities of this device to also measure the Seebeck coefficient

T. Engin, Rev. Sci. Instrum. **79**, 095104, 2008

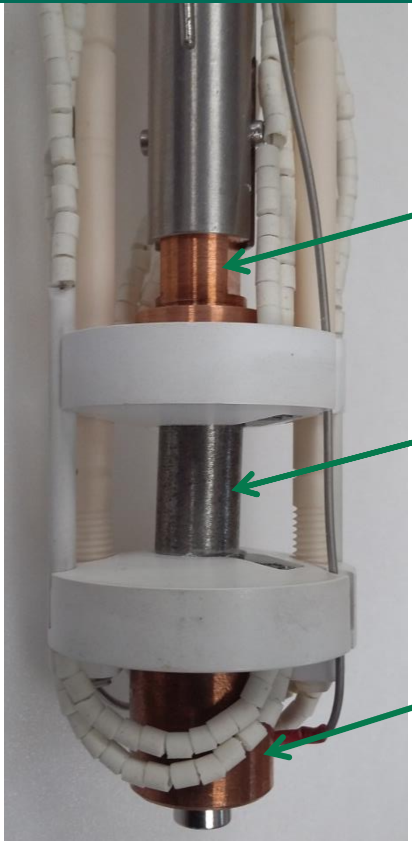
In-Situ Thermoelectric Diffraction Cell

- Image of the prototype
- Aim to measure simultaneously:
  - Seebeck coefficient
  - Electrical resistivity
  - Neutron diffraction

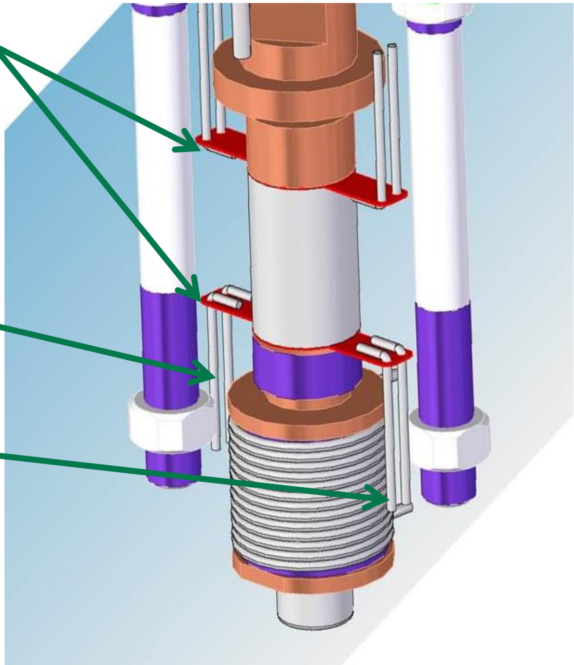
- Glass Sheath Allows for an inert atmosphere or a vacuum
- Inserted into a Furnace

- Sample size (pellet)
  - Diameter: 10mm (Max)
  - Height: 10 – 15mm

In-Situ Thermoelectric Diffraction Cell



- Platinum electrodes
- Spring loaded sample holder
- Pt Wires
- Sample
- Thermocouple Wires
- Resistive heater



- Currently running off-line tests
- If you're interested in using this please get in touch:

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Conclusions

- There is an upper limit of copper deficiency
- Thermal conductivity and electrical property data suggests that the phase transition temperature is composition dependent
- Relatively small changes in the stoichiometry of bornite give marked improvement in ZT
- In the near future simultaneous electronic transport and neutron diffraction measurements will allow us to develop new insights into structure property relationships of thermoelectrics

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