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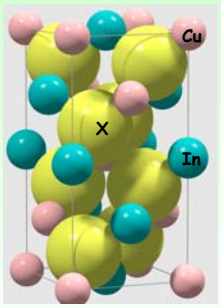
Cation anti-site occupancies as driving force of the structural phase transition in $CuInX_2$ (X=S, Se, Te)

Chalcopyrite type structure $I\bar{4}2m$ — **temperature dependent structural phase transition** → **Sphalerite type structure** $F\bar{4}3m$



Cu site: 0, 0, 0
In site: 0, 0, ½
anion site: u, ¼, 1/8

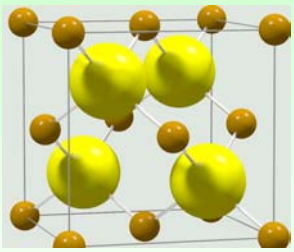
↑ tetragonal distortion

ordered cation distribution

$CuInX_2$	transition temperature
X=S*	968°C
X=Se	807°C
X=Te	662°C

*$CuInS_2$ undergoes another structural phase transition from the Sphalerite type structure to the Wurtzite type structure at 1027°C

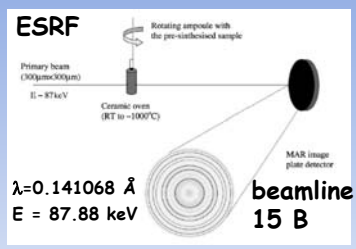
Me site : 0, 0, 0
anion site: ¼, ¼, ¼



statistic cation distribution

in-situ high temperature powder diffraction experiments

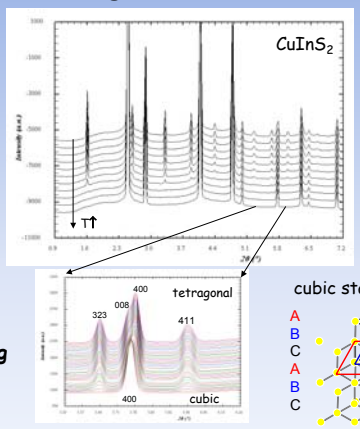
The structural phase transition in the ternary chalcopyrites $CuInX_2$ (X=S,Se,Te) was investigated in-situ for the first time.



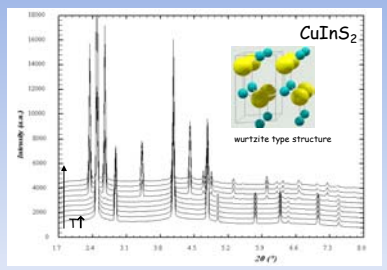
J. M. Merino et al., J. Phys. Chem. Sol. 64 (2003) 1649

Experimental procedure:
Pre-synthesized $CuInX_2$ samples were encapsulated in silica tubes.Sequences of diffractograms were collected during heating the sample with a heating rate of 38 K/h, realising to record an image every centigrade degree.

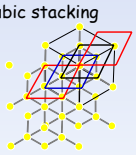
tetragonal - cubic



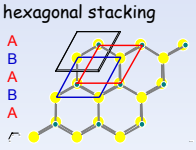
cubic - hexagonal



cubic stacking

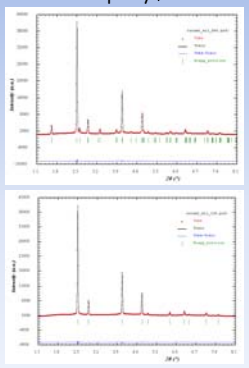


hexagonal stacking



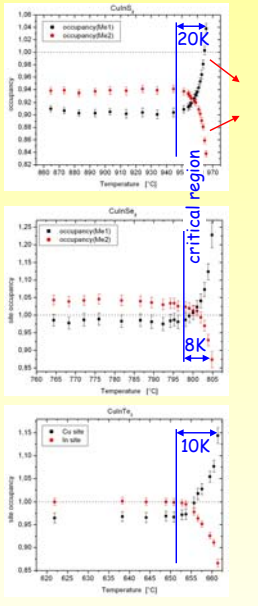
Rietveld analysis

lattice parameter
anion x-parameter
cation site occupancy
} in dependence of temperature



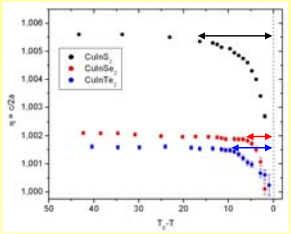
Visualisation of the phase transition

cation site occupancy

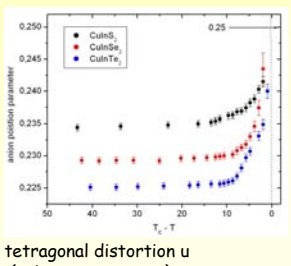


anti-site occupancy

tetragonal deformation and distortion

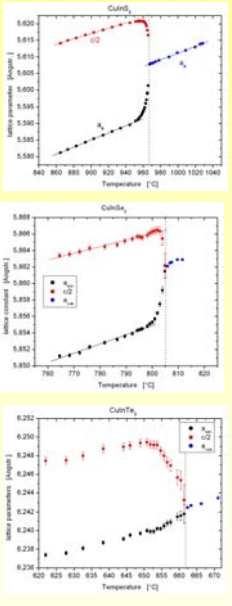


tetragonal deformation η=c/2a



tetragonal distortion u
(anion x-parameter)

lattice parameter



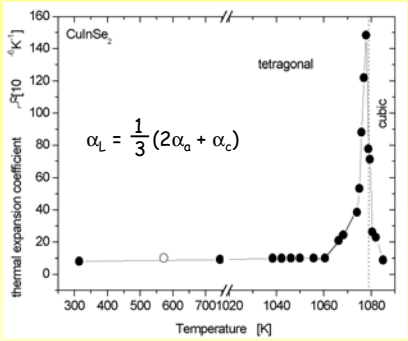
$\frac{da}{dT} = \alpha_a$

$\frac{dc}{dT} = \alpha_c$

lattice parameter vary independently with temperature

anisotropic thermal expansion

linear thermal expansion coefficient



open circle refer to literature (Brühl, Neumann, Pfeiffer, Kühn: Phys. Stat. Sol. (a) 66 (1981) 597)

Summary

The mechanism of Cu-In anti-site occupation was revealed as driving force of the phase transition because it marks the critical region where

- both the chalcopyrite type structure defining parameters η and u change drastic
- the thermal expansion α_L increases strongly

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