



	Experiment title: Study of the temperature dependent phase transitions in the solid solution systems $2(\text{ZnX})\text{-CuInX}_2$ (X=S, Se, Te)	Experiment number: HS-2391
Beamline: ID15 B	Date of experiment: from: 3-Mar-04 to: 6-Mar-04	Date of report: 30. 8. 2004
Shifts: 9	Local contact(s): G. Geandier	<i>Received at ESRF:</i>
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Report:

The ternary chalcopyrites $A^I B^{III} C^{VI}_2$ form a large group of semiconductors with a wide range of structural, chemical and electronic properties [1]. Their crystal structure is closely related to that of the isoelectronic II-VI zinc-blende binary analogs and belongs to the space group I-42d. Each anion is coordinated by two A and two B cations, whereas each cation is tetrahedrally coordinated by four anions. The significant structural differences with respect to the zinc-blende structure (s. g. F-43m) are a tetragonal distortion of the unit cell with a deformation parameter $\eta=c/2a \neq 1$ and the anions are displaced from the ideal tetrahedral site by an amount $|u - 1/4|$ (u is the anion x coordinate) reflecting the unequal cation-anion bond lengths R_{AC} and R_{BC} [2, 3]. The parameters η and u are the structural degrees of freedom of the chalcopyrite-type structure. Because the observed optical band gaps of the $A^I B^{III} C^{VI}_2$ semiconductors are more than 50% smaller than their binary analogs [4] it makes some of the ternary chalcopyrites (e. g. CuInSe_2) among the strongest known absorbers in the solar spectrum [5] and is largely responsible for the emergence of ternary chalcopyrites as solar cell materials. Ternary chalcopyrites CuInX_2 with X=S, Se, Te undergo a temperature dependent structural phase transition from the chalcopyrite (α -phase) to the zinc-blende type structure (β -phase) and in case of X=S another phase transition to a hexagonal phase (δ -phase) [6] with wurtzite-type structure [7].

The aim of the experiment was to follow the temperature dependent structural phase transitions in the CuInX_2 chalcopyrites and in some selected samples of the $2(\text{ZnX}) - \text{CuInX}_2$ solid solution series in detail. The latter are potential photovoltaic materials and formed by substituting $2\text{Zn}^{2+} \leftrightarrow \text{Cu}^+ + \text{In}^{3+}$. The samples were prepared by solid state reaction from the pure elements in sealed evacuated silica tubes and analysed at room temperature by X-ray powder diffraction and microprobe. Then the samples were encapsulated in evacuated quartz ampoules (4mm diameter) to avoid e. g. sulfur evaporation during heating in the experiment. Powder diffraction experiments were performed at the high energy beamline ID15 B in a

temperature range from 300°C to 1100°C using a furnace for 2-D diffraction. A high energy monochromatic beam (87keV energy) was used which gives the advantage of high penetration. The data collection was done during heating the sample just below the melting point with an gradient of 300K/h and ~ 100K before the first phase transition with 38K/h, which realises recording an image every centigrade degree (10sec measurement + readout the 2-D detector).

The lattice constant, anion position, isotropic temperature factor and cation site occupancies (see fig. 1-3) were determined by Rietveld analysis of the data using the FULLPROF program [8].

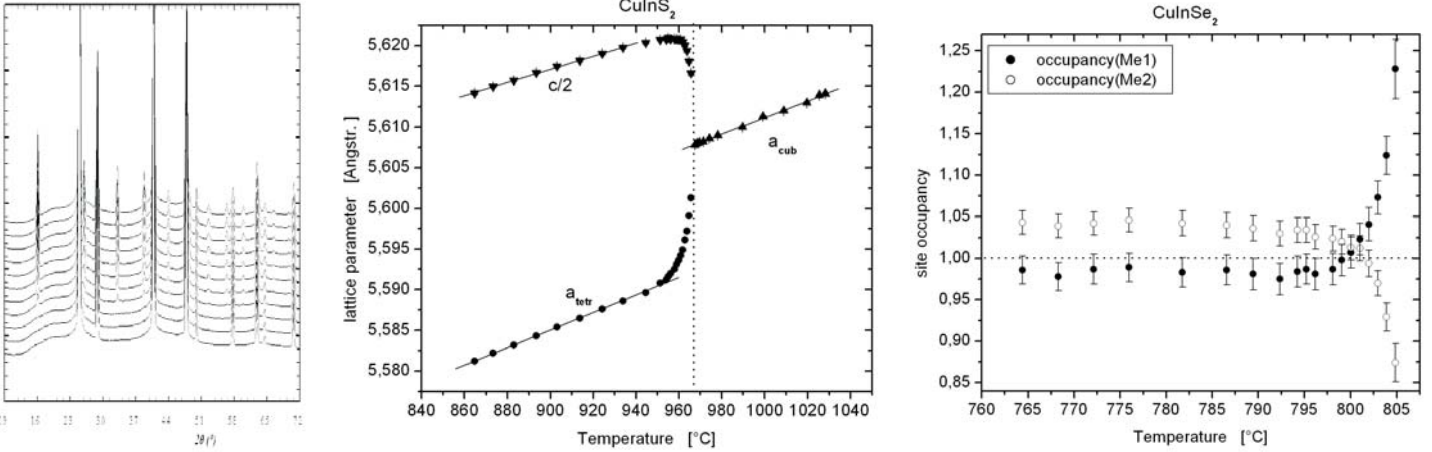


Figure 1: Left: temperature dependent diffractograms of CuInS₂ showing the chalcopyrite-zinc-blende phase transition at 967.6°C. The difference between 2 measurements is 1K. Middle: temperature dependence of the lattice constant at the phase transition in CuInS₂ determined by Rietveld analysis. Right: temperature dependence of the cation site occupancies in CuInSe₂ determined by Rietveld analysis.

	chalcopyrite – zinc-blende	zinc-blende - wurtzite
CuInS ₂	967.6 °C	1027.3°C
CuInSe ₂	806.8°C	-
CuInTe ₂	662.4°C	-

Table1 : Transition temperatures in CuInX₂ (X=S, Se, Te) chalcopyrites.

Just ~ 10-15K (~8-10K for CuInSe₂ and CuInTe₂) before the transition point is reached structural parameters change their behaviour significant indicating the critical region of the phase transition. This fundamental changes in structure go along with a change in the cation site occupancies: the occupancy value of the Cu site (Me1) is increasing, the value of the In site (Me2) is decreasing. This behaviour reveals a Cu-In anti-site occupation, i. e. Cu and In change their sites until a statistic cation distribution is reached which characterizes the zinc-blende type structure. Same behaviour is observed in Zn_{2x}CuIn_{1-x}X₂ samples with x=0.05 but with a much broader (> 100K) critical region. For the first time the temperature dependent behaviour of the degrees of freedom of the chalcopyrite type structure was revealed from in-situ diffraction experiment. The tetragonal deformation η is decreasing dramatically just before the phase transition point even reaching the ideal zinc-blende value (1) in the case of CuInSe₂ and CuInTe₂. Similar behaviour is observed for the anion parameter u, which remains nearly constant and increases strongly before the phase transition point, but here the ideal zinc-blende value (0.25) is not reached.

It can be concluded, that the structural phase transition from the chalcopyrite structure to the zinc-blende structure in ternary chalcopyrites is bound to the anti-site occupation of the both cations, the phase transition occurs as a nearly statistic distribution of the cations is reached.

In contradiction the structural phase transition from the zinc-blende to the wurtzite structure, occurring only in CuInS₂, is realized by stacking faults, where ABCABC stacking in the zinc-blende structure goes over to an ABAB stacking in the wurtzite structure. The observations show that in a temperature range of a few K both phases, cubic and hexagonal coexist.

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