ESRF	**Experiment title:** **Investigation of the temperature dependent structural phase transition in $(CuGaS_2)_{1-x}(CuGaSe_2)_x$ alloys**	**Experiment number:** **HS-3167**
Beamline:	**Date of experiment:** from: 01-Nov-2006 to: 07-Nov-2006	**Date of report:** 15-09-2007
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Report:

In recent years growing interest has been paid to the I-III-VI_2 complex semiconductor compounds (I-Cu, Ag; III-Al, Ga, In and VI-S, Se, Te). These compounds belong to the chalcopyrite familiy and crystallize in the chalcopyrite type structure (space group $I\bar{4}2d$). They are considered to be possible candidates for application in solar power as absorber material in thin film solar cells, optoelectronics and devices for the transfering and processing of information [1-3].

Obtaining the solid solutions between the compounds of the I-III-VI_2 group, for example $CuGaS_2$ and $CuGaSe_2$, gives the opportunity to vary the physical properties systematically. For example, the optical band gap in $CuGaS_{2-x}Se_x$ mixed crystals varies between 2.43 eV ($CuGaS_2$) and 1.68 eV ($CuGaSe_2$) [4].

Earlier in-situ high temperature diffraction experiments with Synchtron X-rays have shown for the first time the occurrence of a structural phase transition from the chalcopyrite type structure [chp] to the sphalerite type structure [sph] in $CuGaSe_2$ at ~ 1040°C [5]. On the other hand, no phase transition exists in $CuGaS_2$ before the melting of the compound at 1240°C [6,7].

The aim of the current experiment was to verify these results and to obtain the temperature dependent structural phase transition in the $CuGaS_{2-x}Se_x$ mixed crystals. Of special interest was the critical composition at which the phase transition vanishes.

The $CuGaS_{2-x}Se_x$ powder samples were prepared by solid state reaction from the pure elements in sealed evacuated silica tubes. The chemical composition was determined by electron microprobe measurements.

Powder diffraction experiments were performed at the high enery beamline ID15 in a temperature range from 300°C to 1100°C using a furnace for 2-D diffraction and the MAR345 image plate detector. A high energy monochromatic beam (energy of 88.95 keV) was used which gives the advantage of high penetration. The samples were encapsulated in evacuated silica ampoules (4mm diameter) to avoid e. g. sulfur and/or selenium evaporation during heating. The data collection was done during heating the sample, first with a rate of 300K/h and at higher temperatures with a rate of 38K/h. The latter realises recording an image every centigrade degree (10sec measurement + readout the 2-D detector). An Aluminum reference sample was used to calibrate the beam energy (λ= 0.1403676 Å) and the sample-detector distance. The 1D diffractograms were obtained by radial integration of the images.

After visual inspection of the 2D-diffractograms, the temperatures at which the structural phase transition [chp] $\rightarrow$[sph] occurs can be pointed out. Table 1 resumes these temperatures during the heating cycle. The results of the

experiment revealed, that the the structural phase transition [chp] →[sph] in $CuGaS_{2-x}Se_x$ mixed crystals vanishes for $x < 0.7$ (see figure 1).

Table 1: Temperatures of decomposition, phase transition and melting of $CuGaS_{2-x}Se_x$ mixed crystals.
(* - no measurements in this temperature region because of synchrotron beam stability problems)

$CuGaSe_2$ in $CuGaS_2$ [Mol%]	sample composition	decomposition temperature range [°C]	transition temperature [°C]	melting temperature [°C]
100	$CuGaSe_2$	1032 – 1042	1048	1105
80	$Cu_{1.006}Ga_{0.994}Se_{1.588}S_{0.412}$	1057 – 1066	1085	*
70	$Cu_{1.008}Ga_{0.992}Se_{1.323}S_{0.677}$	*	1096	*
60	$Cu_{0.991}Ga_{1.009}Se_{1.246}S_{0.754}$	1126 – 1127	-	1129
50	$Cu_{1.002}Ga_{1.006}Se_{0.962}S_{1.038}$	1143 – 1152	-	1154
20	$Cu_{1.006}Ga_{0.988}Se_{0.463}S_{1..537}$	1193 – 1198	-	1200
0	$CuGaS_2$	1220 – 1239	-	1240

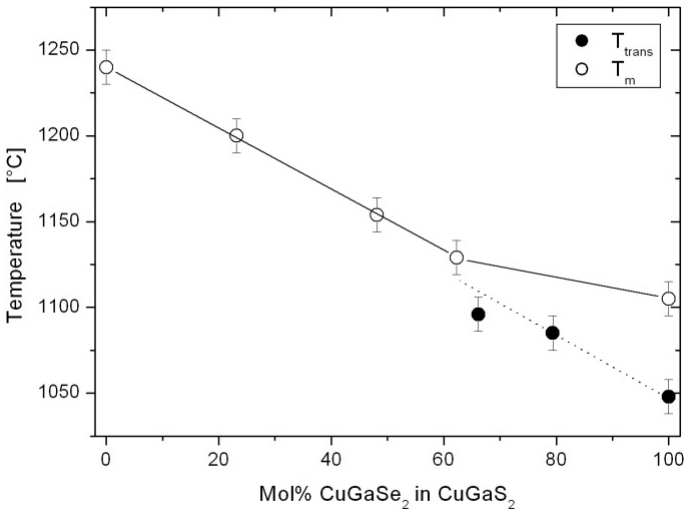

Figure1: Melting temperature (T_m) and temperature of the phase transition (T_{trans}) of $CuGaS_{2-x}Se_x$ mixed crystals

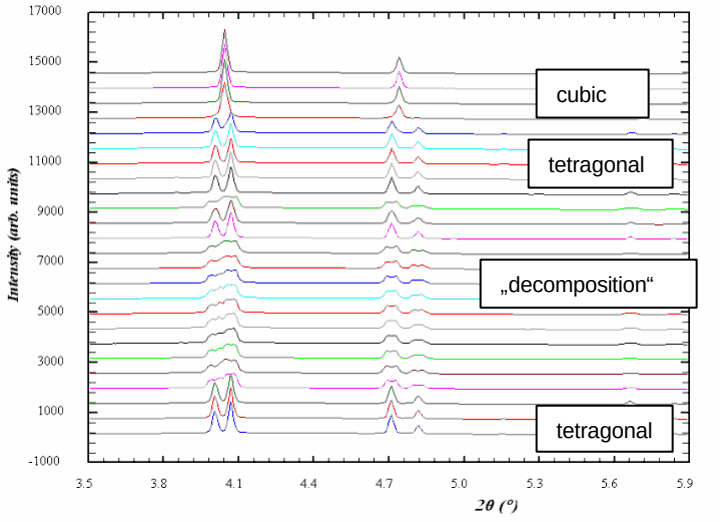

Figure 2: Part of the diffractograms of the $Cu_{1.006}Ga_{0.994}Se_{1.588}S_{0.412}$ mixed crystal in the temperature range 1054°C (down) to 1088°C (top).

Beside the structural phase transition another interesting feature was obtained from the measurements. Before the transition temperature is reached, the diffraction pattern changes drastically indicating a decomposition-like behaviour of the compound (see figure2). The same specific characteristic was also observed in the former experiments [5]. Thus it is obvious, that this is not an artefact of the experiment. The current study has revealed, that this feature not only occurs in $CuGaSe_2$, but also in the $CuGaS_{2-x}Se_x$ mixed crystals (see table 1). Moreover it was shown, that with increasing sulfur content the decomposition temperature range is decreasing (with the exception of $CuGaS_2$).
The least-square structure refinements, Rietveld type, were started to carry out in the most interesting 1D diffractograms at different temperatures.

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