



	<b>Experiment title:</b> Investigation of the temperature dependent phase transitions in $ABX_2$ ternary chalcopyrites (A=Cu, B=Al, Ga, In, X=S, Se, Te)	<b>Experiment number:</b> HS-2661
<b>Beamline:</b> ID 15B	<b>Date of experiment:</b> from: 9-Mar-05 to: 15-Mar-05	<b>Date of report:</b> 29. 9. 2005
<b>Shifts:</b> 18	<b>Local contact(s):</b> Guillaume Geandier	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> <b>S. Schorr*, Institute of Mineralogy, Crystallography and Materials Science, University Leipzig, Germany</b> <b>A. Franz*, Institute of Mineralogy, Crystallography and Materials Science, University Leipzig, Germany</b> <b>B. V. Korzun, Institute of Physics of Solids and Semiconductors, Minsk, Belarus</b>		

## Report:

$ABX_2$  compounds (A=Cu; B=Al, Ga, In; X=S, Se, Te), which belong to the I-III-VI<sub>2</sub> chalcopyrites (sg.  $I\bar{4}2d$ ), are potential photovoltaic materials. The chalcopyrite structure is closely related to that of the sphalerite analogs ZnX (sg.  $F\bar{4}3m$ ), but with a tetragonal deformation  $\eta = c/2a$  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  $R_{BC}$  ([1]-[3]). The parameters  $\eta$  and  $u$  are the structural degrees of freedom of the chalcopyrite-type structure.

The high temperature behaviour of the  $CuBX_2$  chalcopyrites is different, for  $CuInX_2$  and  $CuGaTe_2$  a structural phase transition from the chalcopyrite ( $\alpha$ -phase, cations are ordered on two structural sites) to the sphalerite type structure ( $\beta$ -phase, cations are disordered) is reported in literature. The other compounds melt with no high temperature phase transitions (references see table 1).

The aim of the experiment was to follow the temperature dependent structural phase transitions in  $ABX_2$  chalcopyrites in situ.

The  $CuGaX_2$  and  $CuInX_2$  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. The  $CuAlX_2$  samples were prepared by a method described in [4]. Then the samples were encapsulated in evacuated silica 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 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 (87keV energy) was used which gives the advantage of high penetration. The data collection was done during heating the sample with an gradient of 300K/h and roughly 100K before the in literature reported phase transition or before the melting point with 38K/h, which realises recording an image every centigrade degree (10sec measurement + readout the 2-D detector).

The lattice constant, anion position (in case of chalcopyrite type structure), isotropic temperature factors and cation site occupancies were determined by Rietveld analysis of the data using the FullProf program [12]. The results about the occurrence of a structural phase transition  $[chp] \rightarrow [sph]$  are summarized in table 1. For the chalcopyrite  $CuAlS_2$ ,  $CuAlTe_2$ ,  $CuGaS_2$  and  $CuGaSe_2$  a high temperature behaviour different to the literature was found, in  $CuAlTe_2$  and  $CuGaSe_2$  even a phase transition.

Table 1. High temperature behaviour of the  $\text{CuBX}_2$  ( $\text{B}=\text{Al, Ga, In; X}=\text{S, Se, Te}$ ) as reported in literature in comparison with the present experimental results. [chp] – chalcopyrite type structure, [sph] – sphalerite type structure, (c)-melts congruently, (i)-melts incongruently

$\text{ABX}_2$	high temperature behaviour reported in literature	references	results of the experiment presented here
$\text{CuAlS}_2$ (c)	no structural phase transition up to the melting point	[4]	no structural phase transition but decomposition (at $1178^\circ\text{C}$ ) before melting
$\text{CuAlSe}_2$ (c)	no structural phase transition up to the melting point	[5]	no structural phase transition up to the melting point
$\text{CuAlTe}_2$ (i)	no structural phase transition up to the melting point	[6]	structural phase transition: [chp] $\rightarrow$ 2 phases ( $836^\circ\text{C}$ - $840^\circ\text{C}$ ) $\rightarrow$ [sph]
$\text{CuGaS}_2$ (c)	no structural phase transition up to the melting point	[7]	no structural phase transition but decomposition (at $968^\circ\text{C}$ ) before melting (like $\text{CuAlS}_2$ )
$\text{CuGaSe}_2$ (i)	no structural phase transition up to the melting point	[8]	structural phase transition: [chp] $\rightarrow$ unknown phase ( $1002^\circ\text{C}$ - $1004^\circ\text{C}$ ) $\rightarrow$ [sph]
$\text{CuGaTe}_2$ (c)	structural phase transition [chp] $\rightarrow$ [sph] at $\sim 800^\circ\text{C}$	[9]	structural phase transition [chp] $\rightarrow$ [sph] at $761^\circ\text{C}$
$\text{CuInS}_2$ (c)	structural phase transition [chp] $\rightarrow$ [sph] at $980^\circ\text{C}$	[10]	structural phase transition [chp] $\rightarrow$ [sph] at $968^\circ\text{C}$
$\text{CuInSe}_2$ (c)	structural phase transition [chp] $\rightarrow$ [sph] at $810^\circ\text{C}$	[11]	structural phase transition [chp] $\rightarrow$ [sph] at $806^\circ\text{C}$
$\text{CuInTe}_2$ (c)	structural phase transition [chp] $\rightarrow$ [sph] at $672^\circ\text{C}$	[9]	structural phase transition [chp] $\rightarrow$ [sph] at $662^\circ\text{C}$

The results about the occurrence of a structural phase transition [chp]  $\rightarrow$  [sph] are summarized in table 1. For the chalcopyrite  $\text{CuAlS}_2$ ,  $\text{CuAlTe}_2$ ,  $\text{CuGaS}_2$  and  $\text{CuGaSe}_2$  a high temperature behaviour different to the literature was found, in  $\text{CuAlTe}_2$  and  $\text{CuGaSe}_2$  even a phase transition.

The structural phase transition in the  $\text{CuInX}_2$  compounds is clearly driven by a Cu-In anti site occupation. Within a critical region the number of electrons at the Cu site increases as well as the number of electrons at the In site decreases with increasing temperature. At the transition point 67% of  $\text{Cu}^+$  are on the Me1 site as well as 67% of  $\text{In}^{3+}$  are on the Me2 site (for  $\text{CuInSe}_2$ ). Although a full disorder is reached with 50%, this level seems to be high enough that the phase transition takes place. The order parameter of the phase transition, expressed by  $\Delta n_e = |n_e(\text{disordered}) - n_e(\text{ordered})|$ , goes with  $|T - T_{\text{trans}}|^\beta$  to zero with the critical exponent  $\beta=0.35(7)$  (for  $\text{CuInSe}_2$ ) which is in considerable agreement to the critical exponent  $\beta=0.332$  calculated for order-disorder transitions according to the Ising model [13]. For more details about the critical behaviour of  $\text{CuInSe}_2$  near the phase transition and the thermal expansion coefficients see [14]. The phase transition in  $\text{CuAlTe}_2$ , for the first time experimentally observed, cannot be described as in the  $\text{CuInX}_2$  compounds. Here no Cu-Al anti site occupancy takes place [15].

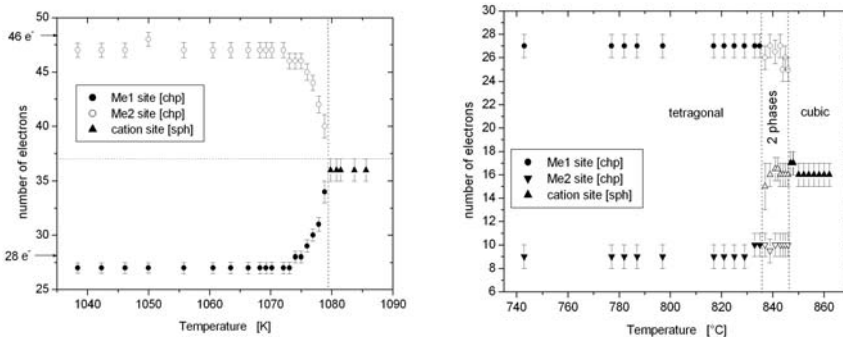


Figure 1: Number of electrons per cation site in dependence on temperature for  $\text{CuInSe}_2$  (left) and  $\text{CuAlTe}_2$  (right). For the first a Cu-In anti site occupancy starting roughly 10K before the transition temperature is clearly visible. This effect cannot be observed in  $\text{CuAlTe}_2$ .

- [1] S. C. Abrahams, J. L. Bernstein, Journal of Chemical Physics 59 (1973) 5415-5422; [2] J. E. Jaffe, A. Zunger, Phys. Rev. B 27 (1983) 5176; [3] J. E. Jaffe, A. Zunger, Phys. Rev. B 28 (1983) 5822; [4] B. V. Korzun et al., J. Mat. Sci.:Mat. In Electr. 16 (2005) 25-28; [5] B. V. Korzun et al., J. Electron. Mat. 24 (1995) 903-906; [6] I. V. Bodnar, Semicond. 37 (2003) 1247-1251, B. V. Korzun, priv. comm.; [7] M. Kotka, J. R. Carruthers, M. Grasso, H. M. Kasper, B. Tell, J. Electron. Mat. 5 (1976) 69-89; [8] J. C. Mikkelsen, J. Electron. Mat. 10 (1981) 541-558; [9] E. I. Rogacheva, Cryst. Res. Technol. 31 (1996) 1-10; [10] J. J. M. Binsma, L. J. Giling, J. Bloem, J. Cryst. Growth 50 (1980) 429-436; [11] M. L. Fearheiley, Solar Cells, 16 (1986) 91-100; [12] Rodriguez-Carjaval, J.: FULLPROF. LLB, Saclay, France.; [13] J. C. Le Guillou, J. Zinn-Justin, Phys. Rev. Lett. 39 (1977) 95; [14] S. Schorr, G. Geandier, Cryst. Res. Technol. (2005) in print; [15] S. Schorr, G. Geandier, B. V. Korzun, in preparation