ESRF	**Experiment title:** Structural phase transitions in non-stoichiometric $CuGaSe_2$ and $Cu(In, Ga)Se_2$	**Experiment number:** HS-4093
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Report:

We studied the structural phase transitions in copper-poor $CuGaSe_2$ and $Cu(In,Ga)Se_2$ in-situ with high energy X-ray diffraction. These compounds belong to the I-III-VI_2 chalcopyrites (s.g. $I\bar{4}2d$) and are due to their excellent optoelectronic properties suitable for photovoltaic applications. The tetragonal chalcopyrite structure can derived from the cubic sphalerite type structure (s.g. $F\bar{4}3m$) by doubling the unit cell into ***c-direction***. Chalcopyrites like $CuInSe_2$ show structural phase transitions from the ordered tetragonal chalcopyrite type to the disordered cubic sphalerite type crystal structure at high temperature. The driving force of this transition was found to be a Cu-In anti-site occupancy [1]. The phase transition in stoichiometric $CuGaSe_2$ was studied by *Schorr et. al* [2] and showed a different character compared to the transition in $CuInSe_2$. Between the tetragonal and the cubic phase an unknown intermediate phase or phase separation was observed. Therefore we wanted to study the phase transition in $CuGaSe_2$ in more detail.

The samples have been prepared by a solid state reaction of the pure elements at T=850°C in evacuated silica tubes. Details of the preparation method can be found elsewhere [3]. Before the in-situ experiments, the chemical composition and phase homogeneity was checked by means of WDX analysis using calibrated elemental standards.

For the in-situ diffraction experiments performed at the ESRF the samples were encapsulated in quartz tubes (3 mm in diameters) to avoid selenium evaporation during heating.

The results of the investigation of non-stoichiometric $CuGaSe_2$ show a different behaviour during the phase transition than the one observed in the stoichiometric compound. In contrast to the latter studied in [2], we observed no unknown phase or phase separation between the chalcopyrite and the spalerite type phase in non-stoichiometric $CuGaSe_2$. As shown in FIG. 1 the phase transition starts at T=1031°C and is finished at T=1042°C. Between these temperatures both phases are existent. At 1042°C only reflections related to the cubic phase are detected. All patterns were analyzed by means of Rietveld refinement with lattice constants, anion x-coordinate and anisotropic atomic displacement factors as free structural parameters of the fit. The cation site fractions have not be refined yet because of the same atomic form factors for Cu^+ and Ga^{3+} for X-rays. The behavior of the lattice constants with

increasing temperature is shown in FIG. 2. One can see a linear increase of the lattice parameters *a* and *c* until the phase transition takes place. At this point *a* decreases and *c* increases strongly until the transition to the cubic phase is completed.

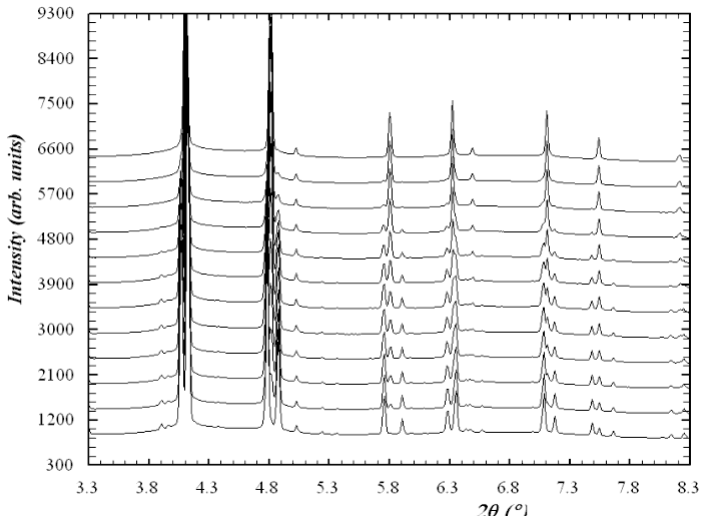

FIG. 1 Diffraction pattern of copper-poor $CuGaSe_2$ between 1031°C and 1042°C (from bottom to top). The phase transition can visually be observed by the decrease of reflections e.g. at 2θ= 3,9°; 4,9°; 5,7° whereas other (2θ=5.8°) increase with increasing temperature.

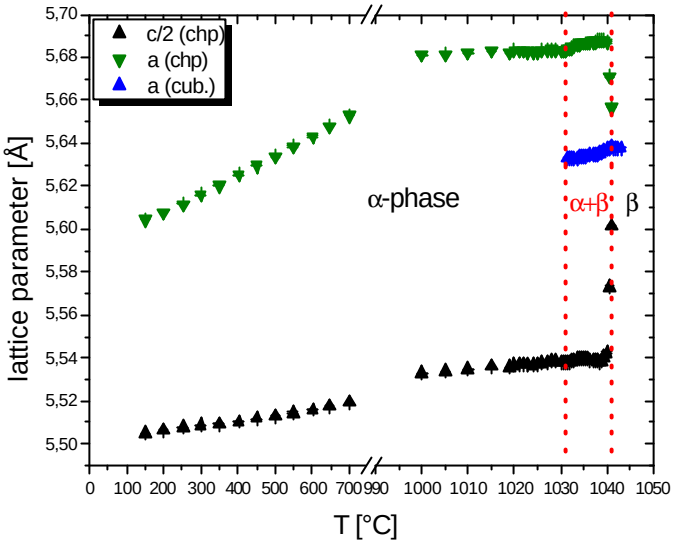

FIG. 2 Copper –poor $CuGaSe_2$: behavior of the lattice constants of the tetragonal and the cubic phase with increasing temperature.

Moreover we studied the structural phase transition in non-stoichiometric $Cu(In_{0.75}Ga_{0.25})Se_2$. The transition temperature was found to be 848 °C and therefore higher than in pure $CuInSe_2$ [1] which is due to the gallium substitution of about 25% in the lattice. The driving force for the structural phase transition in $Cu(In_{0.75}Ga_{0.25})Se_2$ seems to have a similar character like in $CuInSe_2$. The Rietveld method has been applied to these pattern as well, with chalchopyrite structure as basic model. The refined site occupancy factor of the 4a position, where normally copper is situated, increases close to to the phase transition temperature strongly. In return the site oocupancy factor of the 4b position (occupied by In^{3+} and Ga^{3+}) decreases. This behavior can be explanied by an anti-site occupation $Cu_{In/Ga}$-In/Ga_{Cu} which induces the phase transition. In $CuInSe_2$ it was found that at the transition temperature 67% of Cu^+ were found to occupy the Me1 site with a corresponding 67% of In^{3+} at the Me2 site. Although full disorder is reached with 50%, this level seems to be high enough that the phase transition takes place [1].

The present study showed for the first time structural phase transitions in $Cu(In,Ga)Se_2$. This was never proofed before. Moreover it was possible to characterize the phase transition in $CuGaSe_2$ in more detail. These results are important steps for the understanding of the phase diagrams of chalcopyrites, used as absorbers in thin film solar cells, for the tailoring of high efficient photovoltaic devices.

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[3] C. Stephan, S. Schorr, H.-W. Schock, Proceedings of the 2009 MRS Spring Meeting, 2009(1165-M09-08.R1) (2009)