| ESRF | **Experiment title:**<br>**In situ growth investigations of $Cu_2ZnSnS_4$** | **Experiment number**:<br>HS – 3434 |
|---|---|---|
| **Beamline**:<br>ID15B | **Date of experiment**:<br>from: 28. 11. 2007 to: 4. 12. 2007 | **Date of report**:<br>26. 2. 2009 |
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## Report:

Photovoltaics is one of the most easily implementable renewable energy source. Highly efficient thin film solar cells based on compound semiconducting materials such as $Cu(In,Ga)Se_2$ show a current record efficiency of 19.5% on the laboratory scale [1]. Since the availability of indium is an object of concern regarding the large scale production of $Cu(In,Ga)Se_2$ solar cells, its replacement with Zn and Sn, as well as replacing Se by S, is beneficial in this sense. An alternative compound for thin film solar cells is kesterite ($Cu_2ZnSnS_4$), which crystallizes in a chalcopyrite type related structure. Here all constituents are abundant in the earth crust and nontoxic. The compound possesses promising characteristic optical properties; band gap energy of about 1.5 eV and large absorption coefficient in the order of $10^4$ $cm^{-1}$ [2]. Kesterite thin film solar cells have been grown by a two stage process with firstly depositing a mixture of binary sulfides and metals and subsequently annealing/sulfurization, reaching efficiencies of up to 6.77% [2].

The thin film technology of chalcopyrite type related compounds semiconductors is based on a sulfurization process (annealing in a sulfur-containing atmosphere) of a precursor stacking, which is simple and fast. To optimize the sulfurization process and hence improve the efficiency of the thin film solar cells a detailed knowledge about intermetallic transformations and chalcogenization pathways is indispensable. Ex situ experiments suffer from possible phase back transformations and give no access to kinetic aspects of the crystal growth.

The formation of kesterite ($Cu_2ZnSnS_4$) from different stoichiometric mixtures of binary and ternary sulphides was investigated by in-situ high temperature synchrotron X-ray diffraction.

The reaction of 3 different mixtures of binary and ternary sulfides was investigated:

(1) $2CuS + SnS + ZnS$

(2) $Cu_2S + SnS_2 + ZnS$

(3) $Cu_2SnS_3 + ZnS$

The resulting compound obtained at 700°C was $Cu_2ZnSnS_4$ (kesterite) in each case.

In-situ high temperature powder diffraction experiments from room temperature up to 700°C on different stoichiometric mixtures of binary and ternary sulfides were performed at the high energy beamline ID15B of the European Synchrotron Radiation Facility E.S.R.F. The samples were encapsulated in evacuated quartz ampoules to avoid sulfur evaporation during heating. The experimental set up consisted of a high energy monochromatic beam (87.61 keV energy), a ceramic furnace with two holes at the beam height (incident and scattered beam apertures) and an on-line 2D detector (MAR345 image plate). The data collection (10 sec/measurement) was done during the heating, the annealing (15 min) and cooling cycle.

Heating rates of 180 K/h (image/5K) and 360 K/h (image/10K) were applied. An iron powder reference was used to calibrate the beam energy and the sample-detector distance. The 1D diffractograms were obtained by radial integration of the 2D images. Figure 1 shows as an example some of the diffraction pattern obtained for the mixture 2CuS+SnS+ZnS. From the mapping of the patterns it is possible to follow possibly occuring temperature dependent structural phase transitions and the formation of new binary and ternary phases resulting in the formation of $Cu_2ZnSnS_4$ in detail.

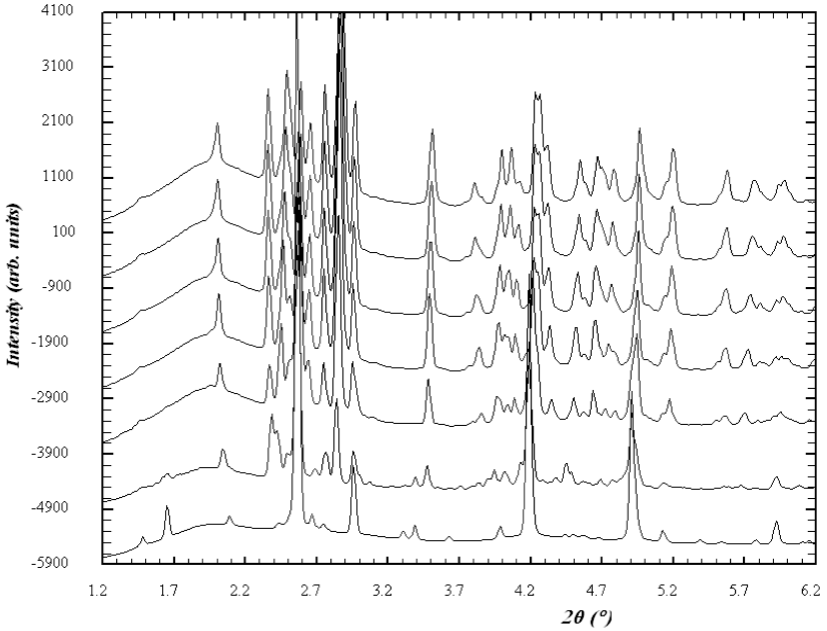


**Figure 1:**
Sequence of diffraction pattern of the mixture 2CuS+SnS+ZnS. The corresponding temperatures are (from top to bottom) 30°C, 129°C, 228°C, 328°C, 431°C, 532°C and 575°C, respectively. The obtained Bragg peaks of the upper pattern correspond to the phases CuS (s. g. $P6_3/mmc$), SnS (s. g. $Pnma$) and ZnS (s. g. $F\bar{4}3m$), for the lower pattern to $Cu_2ZnSnS_4$ (s. g. $I\bar{4}2m$). A heating rate of 180K/h was applied.

A qualitative and quantitative phase analysis as well as the determination of the lattice parameter of the different phases was done by Rietveld analysis of the diffraction data using the FullProf program [3] and led us to determine temperature dependent phase changes qualitatively and quantitatively as well as the lattice constants of the different phases.

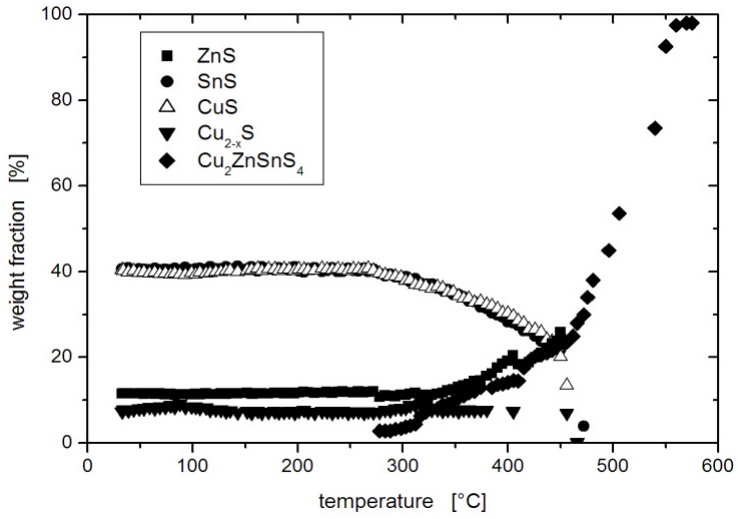


**Figure 3:**
Temperature dependent qualitative and quantitative phase analysis of the mixture 2CuS+SnS+ZnS. A heating rate of 180K/h was applied. The errors are about the size of the plotted symbols.

The lattice parameter of $Cu_2ZnSnS_4$ increase nonlinearly with increasing temperature showing possibly the trend of different formation stages. Comparing the lattice constants *a* and *c* of the several synthesized kesterites at 700°C among each other and with a pre-synthesized kesterite, remarkable variations were obtained, whereas the ratio of the lattice parameter (*c/2a*) are comparable. These features led to the assumption that the cation distribution may vary in dependence on temperature and on the phase mixture used as starting material.

[1] M. Contreras et al., Prog. Photovolt: Res. Appl. 13 (2005) 209
[2] H. Katagiri et al., Appl. Phys. Express 1 (2008) 041201.
[3] J. Rodriguez-Carjaval, Physica B (1993), 192, 55.