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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Phase relations in the quaternary systems $Cu(In_xGa_{1-x})_3Se_5$ and $Cu(In_xGa_{1-x})_5Se_8$	**Experiment number**: HS-3562
Beamline: ID15 B	**Date of experiment**: from: 7/05/08, 16:00 to: 13/05/08, 8:00	**Date of report**: 31/07/2008
Shifts:	**Local contact(s)**: Marco DI MICHIEL	*Received at ESRF:*

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Report:

Cu-containing compounds, as a part of the I-III-VI_2 chalcopyrite family (e.g. I = Cu, Ag; III = Ga, In; VI = Se, Te), are extremely interesting among promising materials for solar cell applications. Among them, devices based on polycrystalline $Cu(Ga_xIn_{1-x})Se_2$ have shown the highest performance in the field of thin film photovoltaics [1]. Nevertheless, Cu-poor surface compositions with I-III_3VI_5 or I-III_5VI_8 stoichiometries have been reported on chalcopyrite-based thin films like $CuInSe_2$ [2], $CuGaSe_2$ [3] and $Cu(Ga_xIn_{1-x})Se_2$ [2]. Despite the fact that these Cu-poor phases are supposed to form the absorber buffer interface, a very sensitive part of the solar cell, they are not sufficiently studied up to now. The aim of this experiment was to clarify, by means of X-ray diffraction at different temperatures, the phase transitions (from a tetragonal phase at 293K to a cubic high temperature phase) and phase diagrams in several poorly known ternary and quaternary compounds belonging to the solid solution series $Cu(Ga_xIn_{1-x})_3Se_5$ and $Cu(Ga_xIn_{1-x})_5Se_8$ ($0 \leq x \leq 1$).

Different polycrystalline samples were pre-synthesised and annealed for several weeks at both the HMI and the UAM, and then vacuum-sealed in several quartz ampoules. As mentioned above, the compounds prepared in advance belonged to the $Cu(Ga_xIn_{1-x})_3Se_5$ solid solution, with x = 0, 0.1, 0.2, 0.33, 0.5, 0.66, 0.8, 1, and to the $Cu(Ga_xIn_{1-x})_5Se_8$ solution, with x = 0, 0.2, 0.3, 0.5, 0.7, 0.8, 1. The experimental method consisted in the collection of a sequence of diffractograms, during heating of the samples, produced by monochromatic synchrotron radiation close to 90 KeV, 300×300 μm of beam size, and using a Pixium large area 2D flat panel detector. The ampoules were rotated and placed in a ceramic oven, using a S-type thermocouple closely placed to the ampoule to measure the temperatures. In addition, at the end of the experiment, another S-type thermocouple was placed in an empty ampoule and heated to calibrate the real temperatures of the samples.

Two diffractograms of LaB_6 in powder form at two different sample-detector distances were taken to calibrate the energy of the beam, and another two diffractograms at two sample-detector distances for each

sample were taken before heating to precisely determine the sample-detector distance, and hence to carry out a radial integration of each diagram in order to obtain a set of linear profiles.

Two different heating rates were tried with two ampoules of the same sample, namely $CuGa_3Se_5$, in order to choose the most appropriated rate to go over the phase transition slowly enough to determine the temperature range in which the transition takes place. In such way, the following samples ($CuIn_3Se_5$ and $Cu(Ga_xIn_{1-x})_3Se_5$ with x = 0.1, 0.33, 0.5, 0.66 and 0.9) were heated up to 600ºC at 300ºC/hour, taking images every 10º, and then heated at 36ºC/hour till the end of the transition, around 850ºC, taking diffraction images every degree. With the $Cu(Ga_{0.5}In_{0.5})_3Se_5$ sample an additional procedure was also tried, rapidly heating up to two different temperatures, 750ºC and 850ºC, and then keeping them until the phase transition was over, while taking images every 2 minutes, in order to get information about the diffusion mechanisms acting in the phase transition. The last part of the experiment was devoted to heat this compound till the melting point, continuously collecting images.

It is worthwhile to mention that the number of allocated shifts was not sufficient for the complete study of the two planned solid solutions, so all efforts were concentrated in one of them: $Cu(Ga_xIn_{1-x})_3Se_5$.

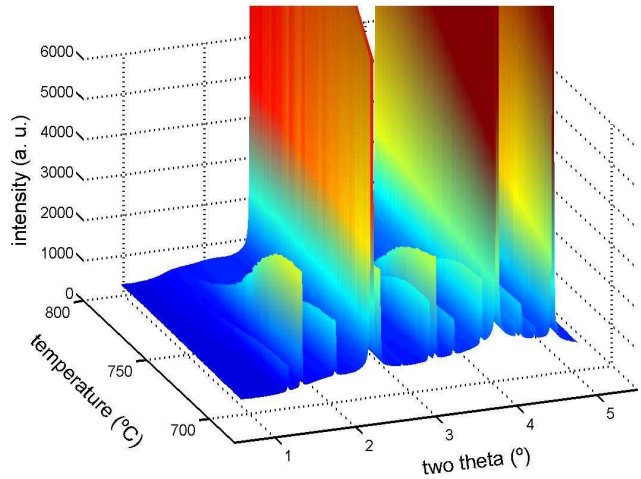

Figure 1 Intensity evolution with temperature of some reflection peaks for the $Cu(Ga_{0.33}In_{0.66})_3Se_5$

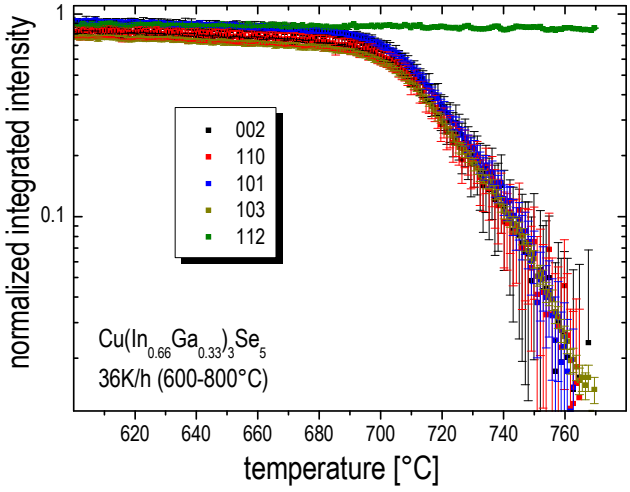

Figure 2 Integrated intensities vs. temperature for the $Cu(Ga_{0.33}In_{0.66})_3Se_5$ sample

The complete analysis of the results for all the measured samples is still in progress. Figure 1 shows the evolution of the intensities of several reflection peaks with temperature for one of the samples, and Figure 2 shows the same after the calculation of the peak integrated intensities using the Le Bail refinement procedure using the Fullprof Program software package [4].

The Rietveld method will be used to refine the structure of the measured samples considering two different structural models: $I\bar{4}2m$ and $P\bar{4}2c$, combined and performed simultaneously with previous neutron diffraction data from this samples, acquired at the Berlin Neutron Scattering Center.

[1] S. Siebentritt, M. Ch. Lux-Steiner, *Mat. Res. Soc. Symp. Proc.* **763**, B5.18.1 (2003).
[2] D. Schmid, M. Ruckh, F. Grunwald, H.W. Schock, *Appl. Surf. Science* **103** (1996) 409-429.
[3] A. Meeder, L. Weinhardt, R. Stresing, D. Fuertes-Marrón, R. Würz, S.M. Babu, T. Schedel-Niedrig, M.C. Lux-Steiner, C. Heske, E. Umbach, *Journal of Physics and Chemistry of Solids*, **64** (2003) 1553-1557.
[4] Thierry Roisnel & Juan Rodriguez-Carvajal http:\\www.ill.fr\pages\Science\Diff\Soft\Fp\.