ESRF	**Experiment title:** Study of Phase Changes during Solidification in Alloys leading to Ordered Vacancy Compounds around the $CuIn_3Se_5$ Composition	**Experiment number**: HS-1291
Beamline: ID15 B	**Date of experiment**: from: 20/09/2000 to: 26/09/2000	**Date of report**: 11/09/2001
Shifts: 18	**Local contact(s)**: Jose Manuel MERINO ALVAREZ and Marco DI MICHIEL	*Received at ESRF:*

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Report:

The knowledge of the Cu-In-Se system is of high importance in the production of heterojunction thin film solar cells presenting efficiencies up to 18%. The industrial production cannot reach these efficiencies mainly because of the poor knowledge of the Cu-In-Se ternary system. Recent work about these cells shows that the active layer has to be In-rich, suggesting the formation of $CuIn_2Se_{3.5}$ or $CuIn_3Se_5$-like compounds. Because of the lack of knowledge of the In-rich phases, we have further studied this part of the phase diagram. Synchrotron radiation is particularly adequate because of the fast spectra acquisition, which could lead to a detailed study of phase changes with temperature. On the other hand, Rietveld method allows the refinement of several structures as well as the quantification of multiphase systems. The aim of the study has been the obtention of the temperature ranges where several In-rich compounds are stable for certain compositions.

Five different ampoules were prepared in this way with the following compositions: $CuIn_2Se_{3.5}$, $CuIn_{4.1}Se_{6.6}$, $CuIn_5Se_8$ and two ampoules, with slightly different stoichiometries of $CuIn_3Se_5$. The pre-reaction of the elements was carried out by gently heating the ampoules up to 1100ºC and slowly cooling them down to room temperature.

Monochromatic synchrotron radiation, close to 90 keV and 300×300 μm of beam size, was used to produce the diffraction diagrams while a 2D online detector (MAR 345 image plate) was used to record them. The ampoules were placed under a halogen quartz lamp and rotated both to homogeneously heat the samples and to obtain a complete diagram. A K-type thermocouple was used to measure the temperatures. The sample-detector distance was around 1200 mm. The polycrystalline synthesised samples were heated up to the melting point and then cooled down slowly while taking diagrams both during heating and cooling processes. During heating, diffraction images were taken in steps of about 50ºC up to 1000ºC, while images were taken every 5-10ºC during cooling.

Air scattering and quartz ampoule contributions were subtracted from all the diagrams before carrying out a radial integration for all of them in order to obtain a diagram set of linear profiles. A simple program was also developed to fix the angle step size, 0.007º(2θ), and the diagrams are then taken in the 1.4-8.0º(2θ) range with 970 points.

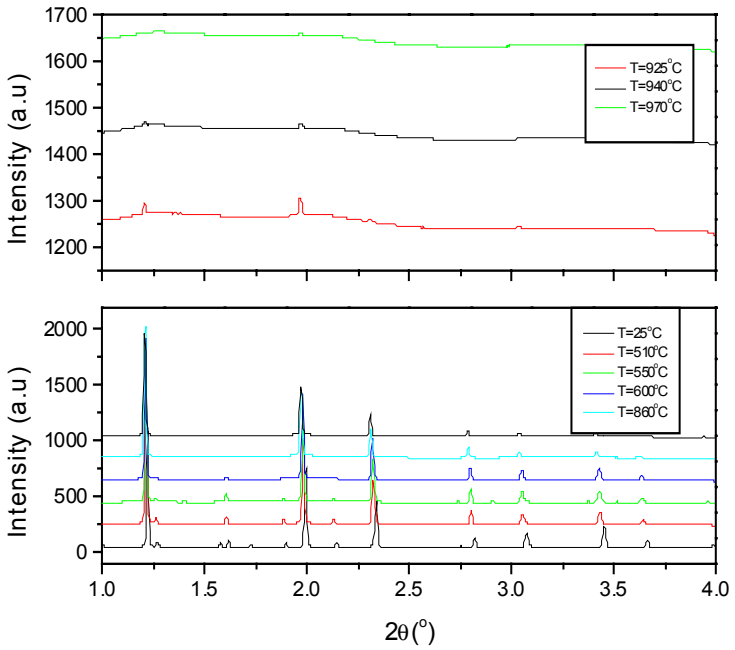

Figure 1 Diffraction diagrams for the $CuIn_2Se_{3.5}$ sample during heating

Firstly, synchrotron data (λ=0.1418 Å) were compared with X-ray conventional data (Cu(K□), λ=1.5418 Å) through the Rietveld refinement of two diagrams taken on the same sample ($CuIn_3Se_5$) at room temperature. Both results show an exceptional similarity being the standard deviations notably lower in the case of synchrotron radiation data. Table I shows the final agreement index and lattice parameters obtained in both cases.

After a detailed visual inspection, we have verified that only during heating the corresponding reflexions to the tetragonal structure are maintained, while new reflexions appear during cooling not corresponding to the initial phase. These are probably due to the segregation of other ternary or binary compounds.

At present, only the $CuIn_2Se_{3.5}$ sample has undergone a detailed study of his behaviour with temperature. The analysis of the other samples is still in progress. A P-chalcopyrite structure (S.G. $P\bar{4}2c$) was verified by Rietveld refinement for the mentioned sample at room temperature. When increasing temperature, a small percentage of a disordered phase, zinc-blende type (S.G. $F\bar{4}3m$) appears at 546ºC, becoming more important as the temperature increases. At 861ºC, only the latter is observed and finally, at 926ºC liquid phase coexists with the disordered phase. Figure 1 shows the different diagrams obtained during heating for the $CuIn_2Se_{3.5}$ sample. The ratio between the scale factors of the coexisting phases was used to quantify the percentage of these phases at each temperature. At 926ºC the zinc-blende type Rietveld refinement was not possible.

The lattice parameters **a** and **c** for the tetragonal phase increase linearly with temperature in the 5.7660-5.8088 Å and 11.5457-11.6218 Å ranges respectively, as a consequence of the thermal expansion effect. The same happens for the **a** parameter in the case of the disordered phase, varying in the 5.7994-5.8326 Å range.

During the cooling process, once the crystallisation has been initiated, the appearance of some new reflexions was observed, which up to now cannot be identified.

For the rest of the samples, the heating process study is still in progress.

Table I. Results from the Rietveld refinement by X-ray and Sincrotron radiation for the same sample.

	R_B	R_F	R_{wp}	R_P	R_{exp}	S	a(□)	c(□)	x(Se)	y(Se)	z(Se)	In_{2b}	Cu_{2e}
*	12.43	14.13	12.34	15.59	14.07	1.11	5.7555(3)	11.524(1)	.2566(34)	.2223(35	.1151(18)	.440(11)	.790(35)
**	6.51	8.87	5.76	4.21	7.69	.75	5.7519(5)	11.519(2)	.2576(12)	.2245(12)	.1214(6)	.457(4)	.80(1)

*X-ray diffraction

** Sincrotron radiation