

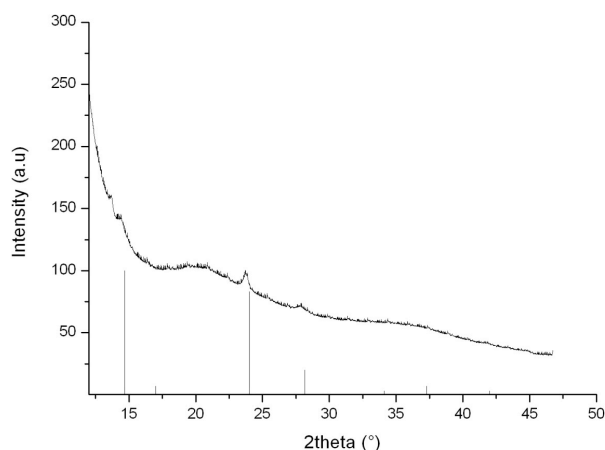
## Experimental report CH-3583: *In situ* study of the growth of chalcopyrite nanocrystals

The aim of our study was to follow *in situ* the growth of ternary and quaternary semiconductor nanocrystals (NCs). The synthesis of this type of NCs is very challenging as at the same time, the size, composition and crystalline phase have to be controlled. We first chose to focus on  $\text{CuFeS}_2$  NCs as a low-cost and environmentally benign alternative to CIGS or PbS based absorber materials for thin film solar cells.

**For all experiments, in order to introduce the reagents (metal salts, stabilizing ligands) in the thin-wall glass capillary required for the synchrotron experiment, we had to dissolve the powders in an appropriate solvent at approximately 100°C. Then the capillary was filled with this mixture in a glove box, flame-sealed and cooled down to room temperature. At the ESRF, the samples were heated with a controlled ramp using the appropriate oven provided by the ESRF experimental environment and SAXS as well as WAXS measurements were carried out at different heating and reaction moments.**

### $\text{CuFeS}_2$ nanocrystals

In the case of  $\text{CuFeS}_2$  NCs, the precursors (copper and iron acetylacetonate in dodecanethiol) were precipitating after dissolution at 100°C during the cooling down to room temperature. Therefore the solution was not homogenous prior to the synchrotron experiment, making it difficult to obtain any exploitable data. The best WAXS data is shown in Fig. 1.

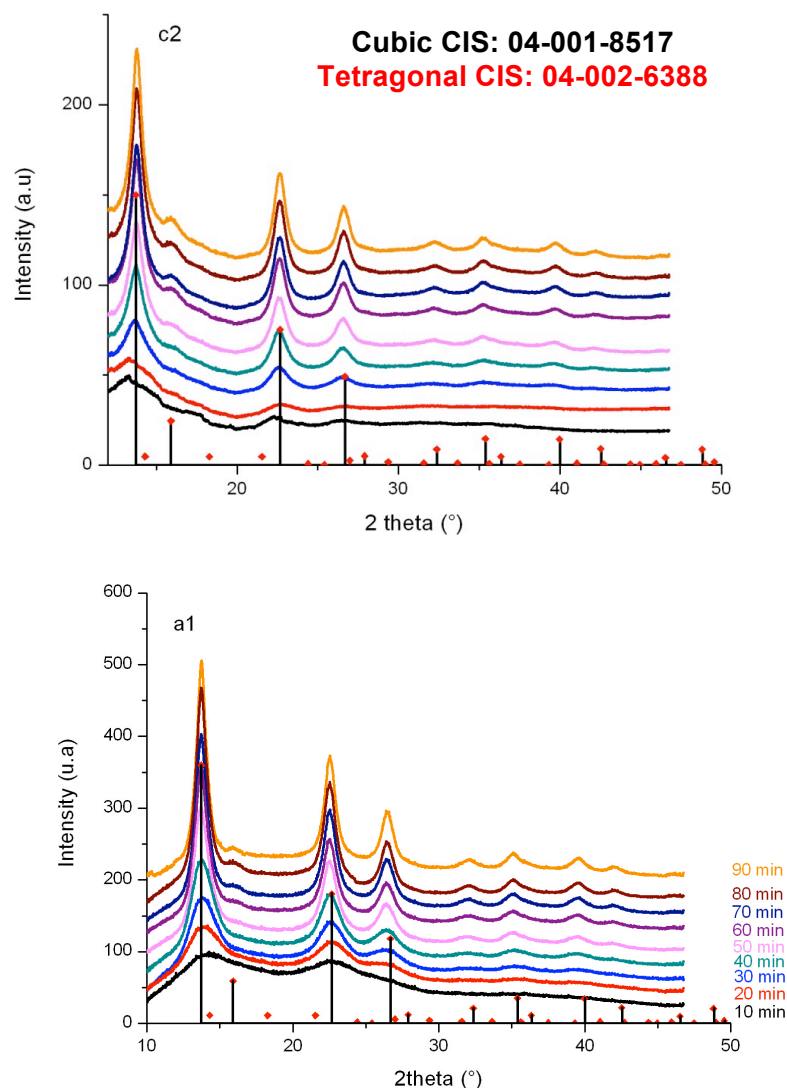


**Fig. 1: WAXS spectrum of  $\text{CuFeS}_2$  NCs (end of reaction)**

### $\text{CuInS}_2$ nanocrystals

$\text{CuInS}_2$  NCs can be easily synthesized by heating a mixture of indium acetate and copper iodide in dodecanethiol to  $T > 200^\circ\text{C}$ .<sup>1</sup> In addition, the reaction is carried out with a high precursor concentration, providing enough scattering matter in the small volume of the glass capillary. During the preheating stage at 100°C, the precursors form a gel after cooling down to room temperature. This gel likely originates from the coordination of indium acetate and dodecanethiol as observed by the group of Tang *et al.*<sup>2</sup> By consequence we did not encounter the problem of inhomogeneity prior to the heating stage at the synchrotron. The growth was followed by SAXS and WAXS for different preheating times at 100°C (preparation of the sample at CEA) and for different temperature ramps ending at 230°C.

We were able to observe the influence of the first heating step (100°C) on the NCs growth (cf Fig. 2 and Table 1). Interestingly, as the preheating time increases, the growth rate decreases. On the other hand increasing the temperature ramp was – as expected – increasing the growth rate of the NCs.



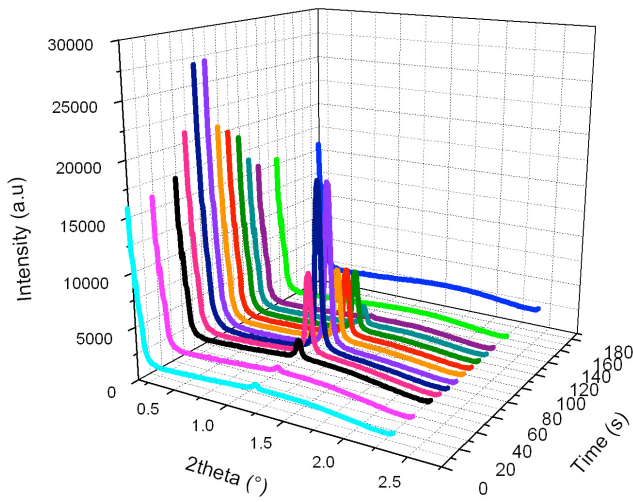
**Fig. 2:** WAXS spectrum for CuInS<sub>2</sub> NCs. Sample a1 was preheated for 60 min at 100°C, sample c2 30 min.

Reaction time	a1/ 60 min at 100 °C	c2/ 30 min at 100 °C
30 min	2.2+-0.2nm	3.5+-0.5nm
40 min	2.4+-0.2nm	4.4+-0.3nm
50 min	4.3+-0.5nm	4.4+-0.5nm
60 min	4.3+-0.3nm	4.8+-0.3nm
70 min	4.2+-0.4nm	5.0+-0.1nm
80 min	4.7+-0.3 nm	5.6+-0.6nm

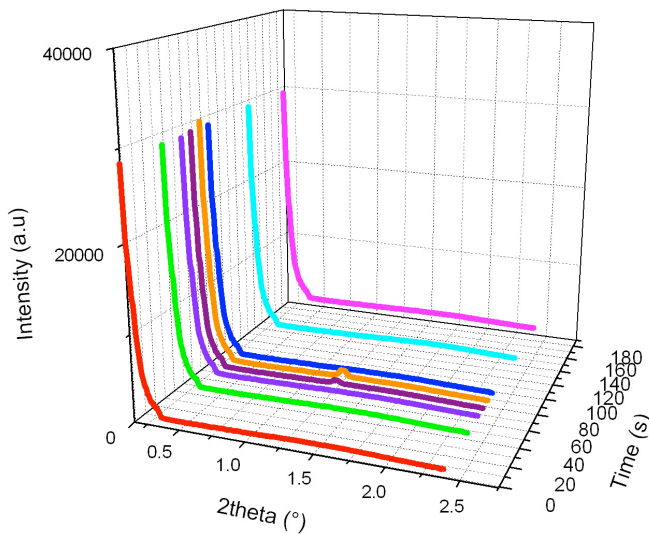
**Table 1:** Crystallite size of CuInS<sub>2</sub> NCs depending on the reaction time at 230°C.

## SAXS measurements

In addition to the discussed differences, the first preheating step appears also to lead to a different precursor organization prior to nucleation. In the SAXS measurements we observe a strikingly different behavior for the two samples. For the a1 sample (previously heated for 60 min to 100°C and then cooled down to RT) presented in Fig. 3, a peak at 1.27° ( $\lambda = 0.772\text{\AA}$ ) is present at the beginning of the heating which disappears after 120 s (during the temperature ramp from RT to 100°C). For the c2 sample (previously heated for 30 min to 100°C and then cooled down to RT) shown in Fig. 4, the same peak appears after 70s (during the temperature ramp from RT to 100°C) and disappears 20 s later. It would be very interesting to investigate in more detail what happens in the precursors solution before the formation of NCs that leads to the observed changes in the nucleation and growth processes.



**Fig. 3:** SAXS spectrum for CuInS<sub>2</sub> NCs preheated for 60 min to 100°C (sample a1).



**Fig. 4:** SAXS spectrum for CuInS<sub>2</sub> NCs preheated for 30 min to 100°C (sample c2).

## CZTS

In the quest for novel materials composed of earth abundant elements and showing appropriate properties for solar cell applications (large absorption coefficient, band gap around 1.5 eV),  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) plays an important role. Therefore we included this material in our *in situ* study of the formation of multinary semiconductor NCs. The synthesis we used is based on Ref. 3. In this case we found out that during the preheating stage at 120°C NCs of CuS were formed (see Fig. 5). Heating to 280°C leads to the dissolution of this binary compound and formation of the pure kesterite phase of CZTS. As shown in the Table 2, during the heating to 280°C, the initial diffraction peak of CuS ( $2\theta=23.6^\circ$ ) shifts to  $23.25^\circ$  in accordance with the formation of CZTS (Fig. 6).

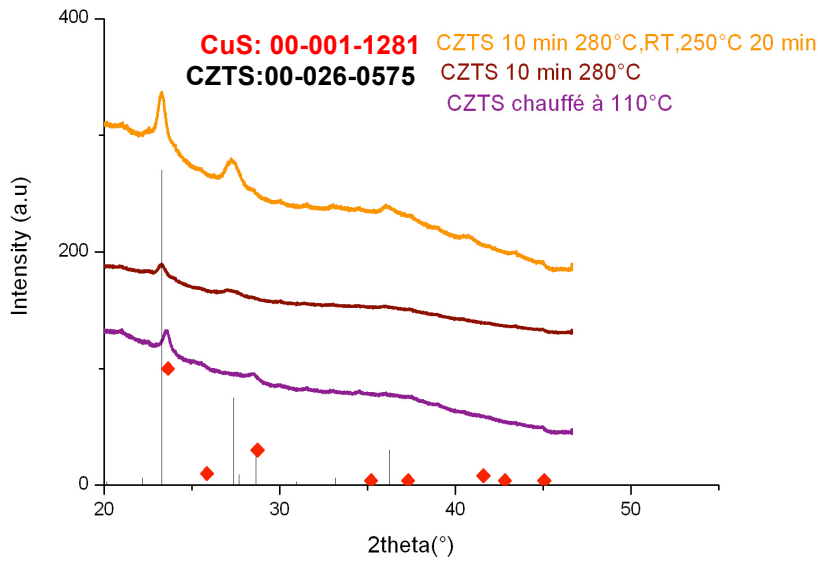


Fig. 5: WAXS spectrum of CZTS NCs for different heating steps

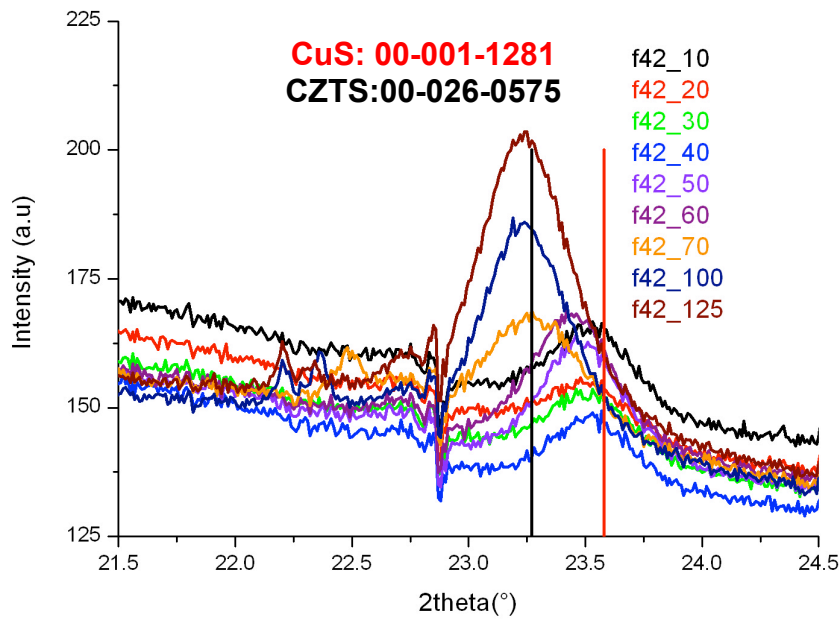


Fig. 6: Evolution of the WAXS spectrum zooming on the most prominent peak during the formation of CZTS NCs when heating from 110°C to 280°C.

	Peak position	FWHM
130°C	23.58	0.444
170°C	23.54	0.477
200°C	23.50	0.533
230°C	23.51	0.529
270°C	23.49	0.527
280°C 0s	23.46	0.443
280°C 100s	23.33	0.431
280°C 400s	23.27	0.376
280°C 650s	23.25	0.463

**Table 2: Peak position and FWHM of the peak shown in Fig. 6 during the heating from 110°C to 280°C.**

## Conclusions

Despite the fact that the data have been disappointing concerning the initially planned compound to be studied  $\text{CuFeS}_2$ , we could react rapidly and accumulate a series of important results elucidating the formation mechanisms of  $\text{CuInS}_2$  and CZTS nanocrystals. In total 25 capillaries have been measured and two publications are under preparation. We showed that both SAXS and WAXS information could be obtained giving *in situ* information about the nucleation process and the growth rate of the nanocrystals. This experiment can be considered as a first successful approach and proof of principle, and on the basis of these results, several aspects will be studied in much more details in the near future.

## References

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