ESRF	**Experiment title:** High-temperature PXRD investigations of the transformation of $Cs_2Ga_2Se_5$	**Experiment number**: HC2939
Beamline: ID22	**Date of experiment**: from: 19/04/2017 to: 21/04/2017	**Date of report**: 13/07/2017
Shifts: 6	**Local contact(s)**: Carlotta Giacobbe	*Received at ESRF:*

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Report:

In this experiment we studied the thermal decomposition of $Cs_2Ga_2Se_5$. Prior experiments on our in house diffractometer already revealed $CsGaSe_2$-*mC*16 as the final product of this degradation. In the course of this process, additional crystalline phases could be detected. The structural characterization, however, failed due to the low quality of the diffraction patterns of these intermediate phases. Using synchrotron radiation with a custom wavelength (λ = 0.399949 Å) at ID22, allowed us to obtain high quality diffraction data for the *in situ* study of all involved phases in this decomposition process (Figure 1).

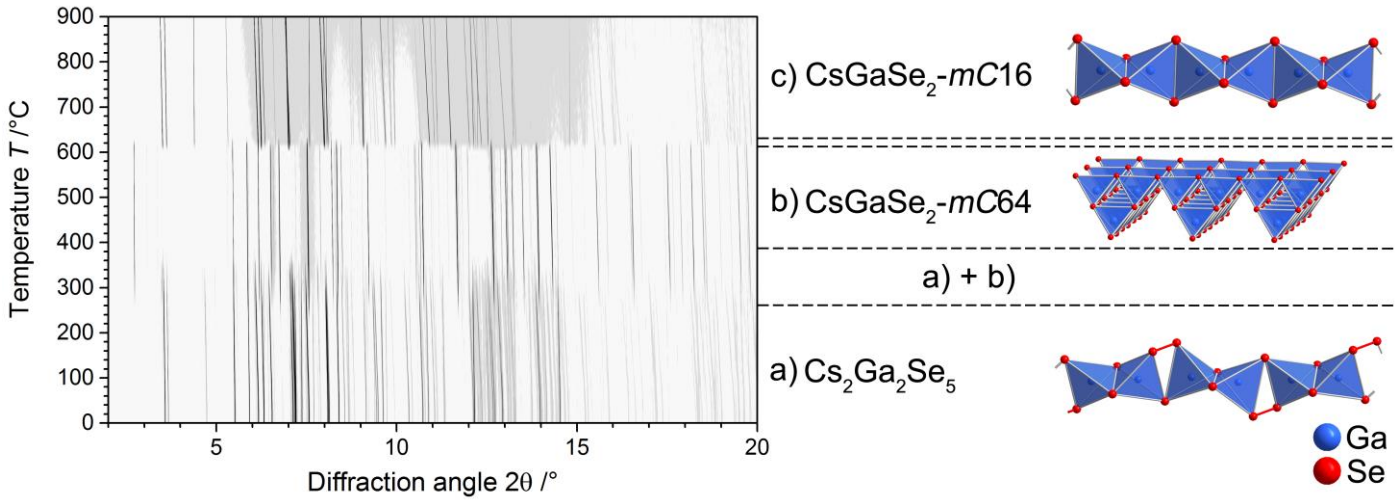

Figure 1: Evolution of the X-ray powder diffraction pattern during the thermal decomposition of $Cs_2Ga_2Se_5$ in the temperature region from 20 – 900 °C (λ = 0.399949 Å). The crystalline phases present in each distinguishable region, including the respective anionic structural motives, are also depicted.

The diffraction patterns during the initial stages of this transformation slightly differ from our results prior to the experiments performed at the ESRF. This fact, however, can easily be explained with the different experimental setup at ID22. Due to the measurement in the very fast rotating capillary in the hot air flow, the sample temperature is obviously quite homogeneous, whereas our capillary furnace seems to provide a slower and inhomogeneous structural transition. Therefore, the previous *in situ* diffraction patterns in the course of the transition always resulted from at least two crystalline compounds.

With the high quality diffraction data collected at the ESRF, we could now clearly identify a two-step degradation of $Cs_2Ga_2Se_5$ (Figure 1). At temperatures above 240 °C, reflections of a new phase (identified as $CsGaSe_2$-*mC*64) were observed. This process is completed at 380 °C. Upon further heating of the sample the compound undergoes a phase-transition to $CsGaSe_2$-*mC*16 at temperatures above 620 °C.[1] These results match our observations of the analogous sulfide system[2] (Figure 2). As the decompostion temperature from $Cs_2Ga_2S_5$ to $CsGaS_2$ is significantly higher compared to the selenides, both polymorphs of $CsGaQ_2$ (*Q* = S, Se) can only be observed in the selenide system.

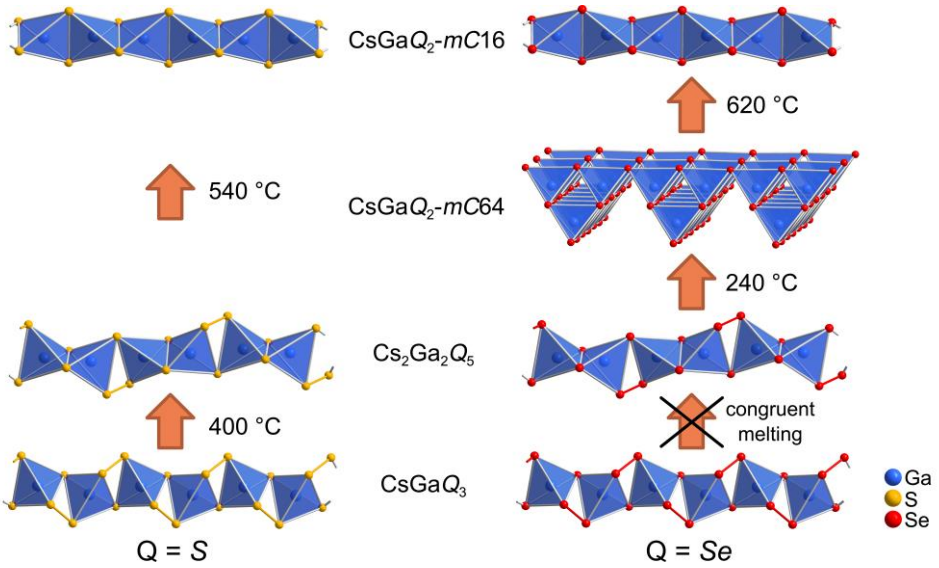

Figure 2: Comparison of the different thermal decomposition pathways of $CsGaQ_3$ and $Cs_2Ga_2Q_5$ (*Q* = S, Se). The respective decomposition temperatures are also shown.

As we could obtain precise cell parameters in a large temperature region from the diffraction experiments (Figure 3), we further decided to study additional thermal properties like the thermal expansion of these three solids. A full analysis of the linear and volumetric expansion coefficients as well as the respective Grüneisen parameters, heat capacities, and Debye temperatures, however, is still in progress.

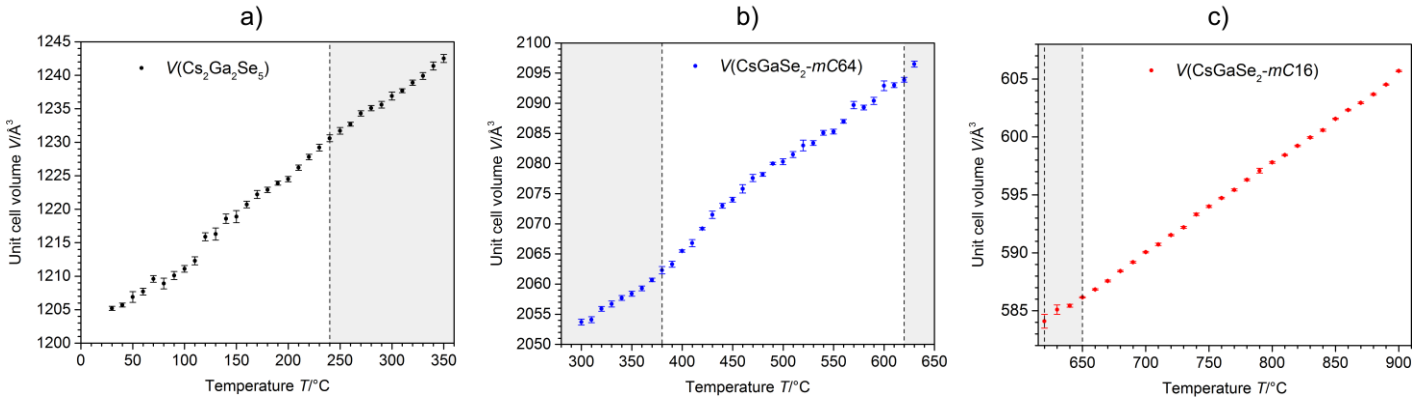

Figure 3: Plots of the unit cell volumina of $Cs_2Ga_2Se_5$ (a), $CsGaSe_2$-*mC*64 (b) and $CsGaSe_2$-*mC*16 (c) against the temperature. The light gray shaded areas indicate multi-phase regions.

References:

[1] D. Friedrich, M. Schlosser, A. Pfitzner, *Crystal Growth & Design* **2016**, *16*, 3983-3992.

[2] D. Friedrich, M. Schlosser, A. Pfitzner, *Crystal Growth & Design* **2017**, in revision.