ESRF	**Experiment title:** Simlutaneous calorimetric and structural measurements of the crystallisation process in phase change materials	**Experiment number**: MI 980
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Shifts:	**Local contact(s)**: Olivier Mathon	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Marie-Vanessa Coulet * IM2NP - UMR 6242 CNRS Aix Marseille Université - Campus de Saint Jérome - 13397 Marseille Cedex 20 - France

Peter Zalden * I. Physikalisches Institut (IA) - RWTH Aachen University of Technology 52056 Aachen - Germany

Giuliana Aquilanti * XAFS beamline - Sincrotrone Trieste S.C.p.A. s.s.14 Km. 163.5 34012 - Basovizza Trieste - Italy

Report :

All materials that can be quenched to a stable amorphous phase at room temperature and crystallize fast, accompanied by a significant electronic contrast can be used for non-volatile phase-change random access memories (PC-RAM). Although the fast crystallisation mechanism in these materials is already exploited in rewriteable optical data storage, it is far from being understood. The full crystallization in small active regions can be completed in some nanoseconds by heating the material above the crystallization temperature. At lower temperatures and heating rates, this process can be slowed down to allow for in-situ experiments.

The aim of this experiment was to perform calorimetric experiments simultaneously with structural determination like EXAFS. This combination of methods allows for obtaining kinetic information about the mechanism of crystallization, by evaluating the structural information from EXAFS at a perfectly defined position of the transformation. Due to the sensitive detection of heat release in the sample (DSC), it is easily possible to interrupt the heating exactly at a specific fraction of the transition.

Several alloys have been chosen, which crystallize on different time scales in order to adapt to the duration of a data acquisition process. Therefore, a good glass former like $Ge_{15}Te_{85}$, has been chosen for most of the experiments. It is based on the same elements as, e.g. the phase-change material GeTe, which has also been investigated.

A commercially available differential scanning calorimeter was modified to be coupled with the X-rays in transmission mode and it has been successfully implemented on the BM29 beamline. The first shifts of the allocated beamtime were used to make the installation and tests of the calorimeter and we checked that:

- the heat signal of the calorimeter is not influenced by the power dissipation of the x-ray beam (with and without sample)
- the use of x-ray transparent windows does not affect the measurement of heat flux
- the absorption in the ionisation chambers is not modified by the working conditions of the calorimeter
- although the pellets were prepared by diluting the sample with BN in a ratio to optimise the EXFAS signal, they gave a good heat signal.

The crystallization of the eutectic alloy $Ge_{15}Te_{85}$ was then studied. This transition is accompanied by two exothermal peaks in calorimetric data, as shown in Fig. 1 (red curve). Up to now, the processes accompanying this transition at the short-range scale have not been investigated. Using X-ray diffraction, Hoyer et al.[1] proposed that the first and second peaks are due to crystallization of Te and GeTe, respectively.

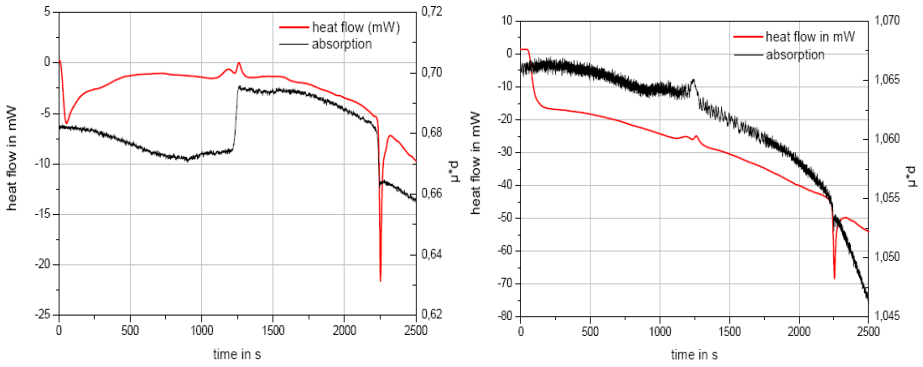

Figure 1 : Simultaneaous heat flux and single energy x-ray absorption meaured as a function of the temperature for the $Ge_{15}Te_{85}$ at the Ge edge (left) and at the Te edge(right)

We measured the short range order in this intermediate structure at 224°C several times. The Fourier transform resulting from the EXAFS spectra taken at 224°C are shown in Fig. 2 (red, blue and green) together with the spectrum of the crystalline phase at 255°C (black). The acquisition of a full EXAFS spectrum takes about 15 min in the used configuration of the beamline. Due to the speed of the transition (200 s), it was not possible to say whether a full EXAFS spectrum could be taken in that region, because the next scan at the same temperature delivers a significantly different result, which converges to that of the crystalline structure. Probably, the nucleation of crystallites was already iniated 224°C and their growth went on even under isothermal conditions.

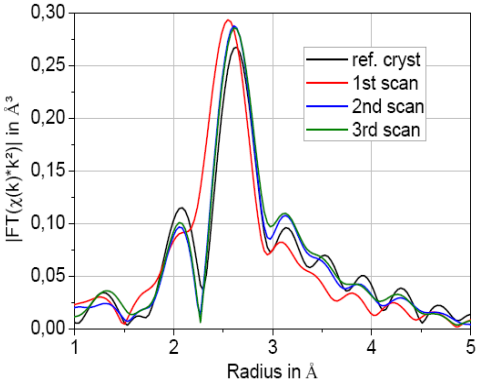

Figure 2: Fourier transform of the EXAFS data for several intermediate structures between the amorphous and the crystal

To overcome this problem, we performed time resolved x-ray absorption at a single photon energy. The results of this experiment are shown in Fig. 1. It can be nicely seen that the second calorimetric peak seems to correspond to a structural rearrangement, while there is no significant rearrangement at the first peak in both edges. This seems to be incompatible with the results by Hoyer et al.[1], who found crystallization of GeTe and pure Te to be the origin of the two transitions. The glass transition, taking place around t =780s (~140°C) seems to correspond to a light change in the absorption data at the Ge edge. Moreover, there is an onset of some process around 180°C (~900 s), which has not yet been reported to our knowledge. It might either be linked to the onset of crystallisation or to a mostly electronic transition, as it occurs at both edges to a similar extent.

Several more experiments have been performed, which aimed at an understanding of crystallization processes in amorphous phase-change materials. We measured the local order of amorphous, crystalline and liquid phases in $Ge_{15}Te_{85}$ and $Ge_{15}Sb_{85}$.

The experimental method of coupling DSC and EXAFS has been succesfully applied to inorganic materials for the first time. We plan to report on this method and some of the results in an experimental paper. During an additional beam-time, which we will apply for, we would like to use the continuous energy scanning mode of BM29 in order to obtain a significantly better time resolution. Using the quick EXAFS acquisition mode, it should be possible to determine intermediate structures and to follow the crystallization mechanism in more detail. This will be especially interesting for materials in which the crystallization process is suspected to have intermediate structures.

[1] Kaban I., Dost E. and Hoyer W. , J. Alloys. Comp. 379 (2004) 166