	Experiment title: Crystallization mechanisms in the germanium-based systems: simultaneous calorimetric and quick-EXAFS measurements	Experiment number: HC 766
Beamline: BM 23	Date of experiment: from: 03/03/ 2010 to 09/03/ 2010	Date of report: 26/08/2013 <i>Received at ESRF:</i>
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Report:

The aim of this experiment was to implement on a synchrotron beamline a set-up devoted to simultaneous DSC and quick-EXAFS measurements over a temperature range varying from room temperature up to 800 K. Contrary to previous implementations of a DSC on a synchrotron beamline, we have employed a Calvet-type calorimeter which consists of a heat-flux meter enabling precise measurements of the energy associated with the phase transitions. The combination of these two instruments was a non-trivial task since they request different requirements concerning the sample preparation.

During the allocated beam time we successfully managed to

- 1) implement the calorimeter on the BM29 beamline [1]
- 2) Studied the crystallization process in several Ge-based amorphous alloys[1,2]

1) Implementation of the calorimeter

In standard calorimetric measurements, the signal-to-noise ratio is proportional to the amount of sample material. Generally the material is inside a special sample container which ensures the best thermal contact with the outer parts of the calorimeter. By combining calorimetry with EXAFS we had to accept a compromise by which the sample is mechanically fixed and distributed homogeneously over the beam cross section, but is still in an acceptable thermal contact to obtain a precise calorimetric signal. In addition, its thickness has to be chosen in a way to optimize the signal-to-noise ratio in the EXAFS spectra. Our solution to the challenges described above was to disperse the material in a boron nitride (BN) matrix and to press this mixture into a self-sustaining pellet. BN is an inert matrix material which has a better thermal stability than cellulose, since it melts only above 3000 K. It is therefore expected that the temperature range of studies can be extended up to the technical limit of the calorimeter of 900 K. If such a sample preparation in standard for EXAFS experiment it is very unusual in calorimetry. Moreover the positioning of sample is a tricky procedure since the thin pellet has to be introduced, on the edge, inside a 150 mm tube.

In order to study the effect of the X-ray absorption on the calorimetric signal, the melting of a Sn reference was performed under the X-ray beam. The energy of the incident beam was fixed at 11.1 keV which ensures maximum absorption. The heating rate was 5 K/min for the two measurements with and without the beam. As seen in Fig. 1, the DSC curves are very similar except for a slight variation in the baseline, which could be related either to slight differences in the positioning of the sample and the reference or to absorption effects owing to the X-ray beam.

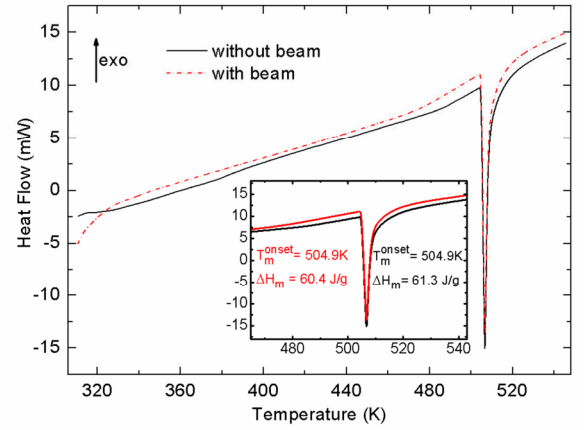


Fig.1 : Melting of a pure Sn reference sample with and without the X-ray beam.

2) Crystallization process in Ge-based amorphous alloys [1,2]

As a case study for our combined set up we studied the crystallization process in two Ge-based amorphous alloys that present a two-step crystallization process: $\text{Ge}_{15}\text{Te}_{85}$ and $\text{Ge}_{15}\text{Sb}_{85}$ but only the results for the $\text{Ge}_{15}\text{Sb}_{85}$ system are given in this report. This system is seen as a potential candidate for phase change memories application because it presents the required characteristic in term of crystallization temperature, crystallization times [3] and it shows pronounced changes of electrical resistivity [4] and optical reflectivity [5] upon crystallization. However, a two-step crystallization process leading to a phase segregation is consistently reported in several DSC measurements [6,7] but the interpretation differs between the authors. Hence, we chose this composition as a model system for our coupled EXAFS and DSC experiments since it allow following simultaneously both the structural transitions and the heat release.

Amorphous thin films of $\text{Ge}_{15}\text{Sb}_{85}$ were deposited on a silica substrate by dc-magnetron sputtering from a stoichiometric target. The film was subsequently scraped from the substrate and the necessary quantity to obtain an edge-jump around 1.5 was diluted with boron nitride and pressed to a pellet. This corresponds to 5 mg of $\text{Ge}_{15}\text{Sb}_{85}$ at the Ge K-edge and 17 mg at the Sb edge.

The DSC scan, represented in Fig. 2, shows two exothermic peaks at onset temperatures equal to 514(1) K and 604(1) K with enthalpies of 37(1) J/g and 6(1) J/g, respectively. These results are in agreement with the two-step crystallization process reported in literature and suggest a phase separation tendency upon crystallization. As seen in Fig. 2, the EXAFS oscillations show significant changes in both, amplitude and frequency simultaneously to the exothermic peaks. At the Ge edge, changes in amplitude and frequency of the oscillations are visible upon first crystallization, which indicates a strong rearrangement of the atoms. When the second crystallization occurs, only an increase in the amplitude is observed and can be attributed to a more pronounced short-range order. At the Sb edge, only changes of the amplitude are visible simultaneous to the first exothermic peak, while no change in the frequency is observed during the second heat release. These results suggest that there is a stronger rearrangement of the Ge bonds during the crystallization process and that the second crystallization mainly involves Ge atoms.

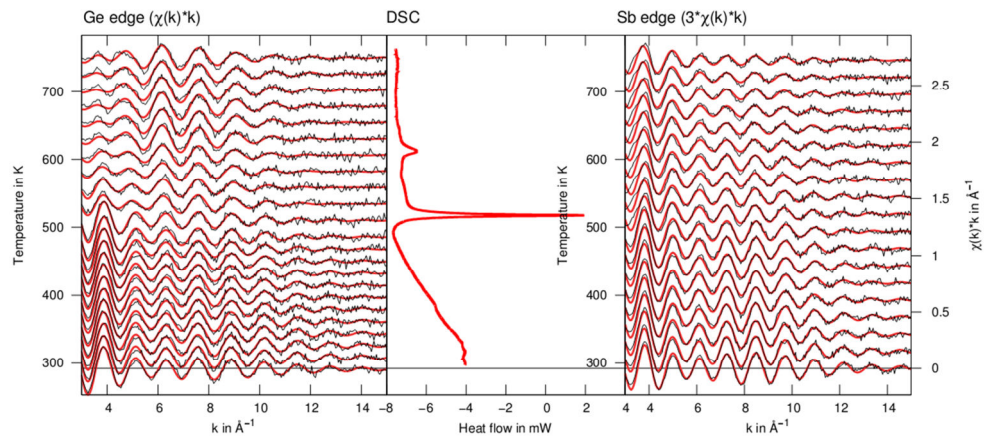


Fig.2 : EXAFS oscillations $k\chi(k)$ at the Ge edge (left) and the Sb edge (right) together with the calorimetric signal obtained simultaneously.

The EXAFS analysis was performed using the *ifeffit* program for each data set. The two edges were fitted independently and only the first peak of the modulus of the Fourier transform was taken into account during the data refinement in R-space. The temperature dependence of the distances, coordination numbers and Debye-Waller factors are given in Fig. 3 for the Sb edge.

During the first heat release, clear changes are visible at the Sb edge: the number of Sb-Ge bonds decreases as well as the number of Sb-Sb bonds which suggests that **Sb-Ge bonds are still present in the first crystalline phase**. The decrease of the partial coordination number of Sb-Sb bonds might seem surprising, since it is well known that Sb crystallizes in the A7 structure, where each Sb atom has three short and three

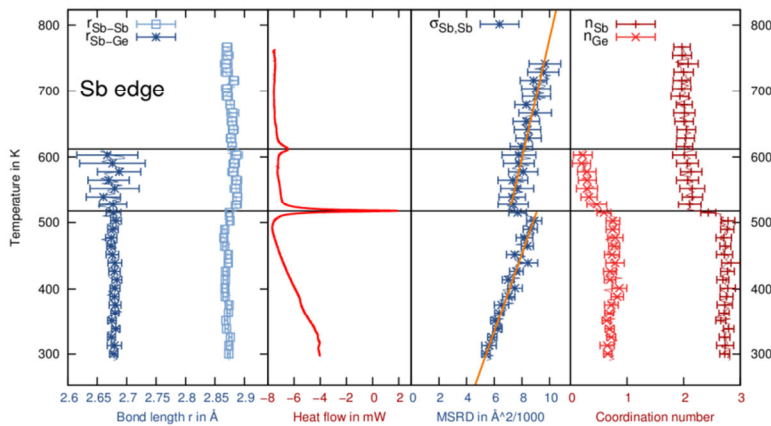


Fig. 3: Temperature dependence of the distances (first panel), Debye Waller factor (third panel) and coordination numbers (fourth panel) at the Sb edge together with the calorimetric signal (second panel).

long bonds with a total number of six Sb-Sb bonds per atom. The significantly lower numbers in this study originate from the fact that only the short distances could be refined in our data. The absence of features from the three longer bonds is most likely due to their large Debye Waller factor at elevated temperatures. When the second crystallization occurs, no change in distances and number of neighbors are observed at the Sb edge, which suggests **that the second transition only involves Ge atoms. The evolution of the Debye Waller factor upon heating is also interesting: due to thermal vibrations, it increases linearly until the first crystallization at 514 K, and then suddenly decreases. This is consistent with the onset of long range order upon crystallization, which reduces the static disorder and usually hardens the solid, thus increasing its Debye temperature. Upon further heating, the Debye Waller factor increases again linearly with a slightly lower slope and is not affected by the second crystallization. The slight decrease in slope is indicative for a hardening of the observed vibrational modes upon crystallization.** The same analysis was performed at the Ge edge the results can be found in [2]. We showed that the Ge atoms are involved in both crystallizations and that the phase segregation of Ge atoms starts immediately after the first crystallization event.

In conclusion, owing to our combined analysis of the data we got new insight in the crystallization process: the first crystallization at 514 K is related to the crystallization of an Sb-rich ($\text{Ge}_{11}\text{Sb}_{89}$) phase and simultaneously the Ge atoms partly segregate and form Ge-rich regions with an amorphous structure. Upon further heating, the as-formed amorphous Ge regions crystallize at 604 K.

References

- [1] P. Zalden, G. Aquilanti, C. Prestipino, O. Mathon, B. André, M. Wuttig, M.V. Coulet J. Synch. Radiation, 19, 806–813 (2012).
- [2] P. Zalden, G. Aquilanti, C. Prestipino, O. Mathon, B. André, M.V. Coulet J. Non Cryst. Solids (2013) <http://dx.doi.org/10.1016/j.jnoncrysol.2013.01.005>.
- [3] J. Siegel, C. N. Afonso, J. Solis, Appl. Phys. Lett., 75 (1999) 3102–3104.
- [4] D. Krebs, S. Raoux, C. T. Rettner, G. W. Burr, R. M. Shelby, M. Salinga, C. M. Jefferson, M. Wuttig, J. Appl. Phys., 106 (2009) 054308
- [5] S. M. Wiggins, J. Bonse, J. Solis, C. N. Afonso, K. Sokolowski-Tinten, V. V. Temnov, P. Zhou, D. von der Linde, J. Appl. Phys., 98 (2005) 113518.
- [6] S. Raoux, C. Cabral, L. Krusin-Elbaum, J. L. Jordan-Sweet, K. Virwani, M. Hitzbleck, M. Salinga, A. Madan, T. L. Pinto, J. Appl. Phys., 105 (2009) 064918
- [7] P. Zalden, C. Bichara, J. van Eijk, C. Braun, W. Bensch, M. Wuttig, J. Appl. Phys., 107 (2010) 104312