Proposal title: In situ x-ray diffraction and diffraction anomalous fine structure study of phase segregation mechanism in GST thin films

Proposal number: A02-2-882
Beamline: BM02
Shifts: 15
Date(s) of experiment: from: November 02 2022 to: November 07 2022
Date of report: March 12 2023

- Objective & expected results (less than 10 lines):

The objective of this proposal was to shed light on the phase segregation and intermediate phases in N-doped Ge-rich materials and with different Sb/Te ratio. For that purpose, we aimed to determine the Ge atomic local environment and local order by *ex situ* Multi-wavelength Anomalous Diffraction and Diffraction Anomalous Fine Structure spectroscopy at the Ge K-edge carried out on samples having different levels of crystallization (annealed at different temperatures).
Also, on the same type of samples, we aimed to perform *in situ* x-ray diffraction during annealing with different heating ramp up to extract activation energy of Ge diffusion stoichiometry to conclude about the effect of N-doping and Sb/Te ratio on Ge diffusion inside the chalcogenides.

- Results and the conclusions of the study (main part):

During this campaign of experiments at BM02-D2AM beamline at ESRF, we performed two types of experiments:

- *ex situ* Multi-wavelength Anomalous Diffraction (MAD) measurements: The experiment was done at Ge K-edge for Ge-rich GeSbTe at different levels of crystallization as shown in Figure 1. Although we faced the problem of low signal to noise ratio, inherent to powder diffraction, a strong sample fluorescence, and some set up issues, which prevented us to acquire extended-DAFS oscillations,

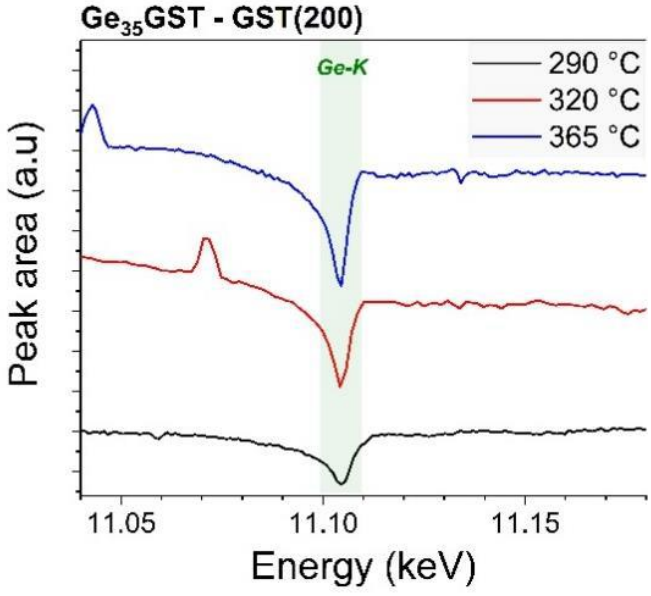

Figure 1: GST (200) integrated Bragg peak as function of energy near the Ge K-edge for Ge-rich GeSbTe sample annealed at different temperatures at CEA-Leti

it was possible to extract reliable spectra close the Ge K-edge. The data reduction and analyses are in progress. By fitting these results, one will conclude on the Ge crystallographic site(s) occupation in the 225 phase and about the Ge content and its evolution with the annealing.

- *in situ* XRD analyses performed with a custom-built equipment: We performed the experiment on un-doped and N-doped Ge-rich GeSbTe, in order to extract the activation energy of Ge diffusion during the crystallization process with different heating ramps. The data processing is still ongoing but an overview of the results of one of the samples is shown in Figure . By a deconvolution of the XRD diagram and fitting Bragg peaks, we can plot different peaks parameters as a function of the temperature with different heating ramp, as illustrated in Figure 3. Then with a Kissinger plot, we can extract the activation energy of a specific phenomenon like Ge diffusion to understand the segregation phenomenon to Ge and GST 225 cubic phases.

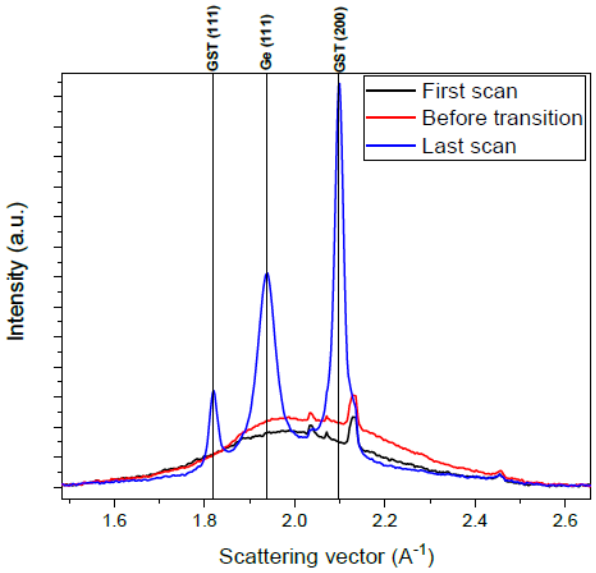

Figure 2: Crystallization evolution upon annealing of Ge-rich GST using a heating ramp of 10°C/min

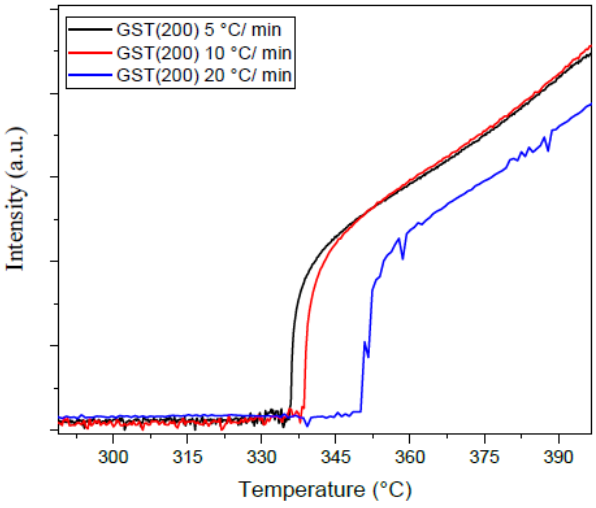

Figure 3: Extraction of GST (200) integrated intensity upon annealing at different heating ramp

- Justification and comments about the use of beam time (5 lines max.): **-**

The use of beamtime went smoothly. For such a complex experiment combining two different x-ray techniques analyses on different materials, 15 shifts of beamtime is a the very minimum.

- Publication(s): **-**

A publication about the results of this experiment will be prepared after the end of the current data processing.