EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

Experiment Report Form

ESRF	**Experiment title:** An in-depth study of the anomalous aging behavior of the amorphous chalcogenide-based phase-change material $Ge_2Sb_2Te_5$	**Experiment number**: MA-4142
Beamline: ID10	**Date of experiment**: from: 19.04.2018 to: 24.04.2018	**Date of report**: 24.07.2018
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Report:

Phase-change materials (PCMs) can be reversibly switched between the amorphous and crystalline states by electric pulse in nanoseconds and used for computer memory technology. During the beamtime MA-4142 at ID10, we perfomed the multispeckle X-Ray Photon Correlation Spectroscopy (XPCS) measurement for an in-depth study of the anomalous aging behavior of the amorphous chalcogenide-based phase-change material $Ge_2Sb_2Te_5$ and a non-PCM $Ge_{15}Te_{85}$. By studying the decay of the intensity autocorrelation function, the time and temperature dependence of microscopic dynamics during aging were studied. Experiments were carried out with a high coherence X-ray beam with a fixed energy of 8 keV (λ=1.55 Å). The samples were clamped on the holder of the furnace to study the aging as a function of temperature and waiting time.

Experimental challenges:

During the experiments we encountered a few problems related to furnace temperature control. At the beginning the cooling device was not correctly conncected to the furance, which leads to some huge overshoot in temperature, and does not allow us to have a reliable isothermal measurement. Then there is a software problem for controlling the furance temperature. We have to adjust the furnace parameters with a trial-and-error approach to find the suitble parameters for controlling the furnace. This leads to a loss of beamtime (2 or 3 shifts) for our planned experiments and loss of samples (crystallizaton problem).

Preliminary results

In Figure 1, the temperature dependence of τ obtained from XPCS for $Ge_{15}Te_{85}$ shows (1) generally decreasing trends with increasing temperature; (2) zig-zag behavior during thermal cycling; (3) isothermal aging itself seems to be stationary (i.e. little aging occurs), and (4) the shape-parameter β of the KWW function for the correlation function is less than 1.0, indicting a stretched exponential decay.

These observations appear to be in line with previous studies that a decreasing trend of τ with a higher temperature. The isothermal aging is stationary, which resembles the case of the other covalently bonded silica. The fact that β <1 for $Ge_{15}Te_{85}$ is observed well below the glass transition (T_g=130 ºC) indicates that a stretched exponential decay is not related to the supercooled liquid state in this system.

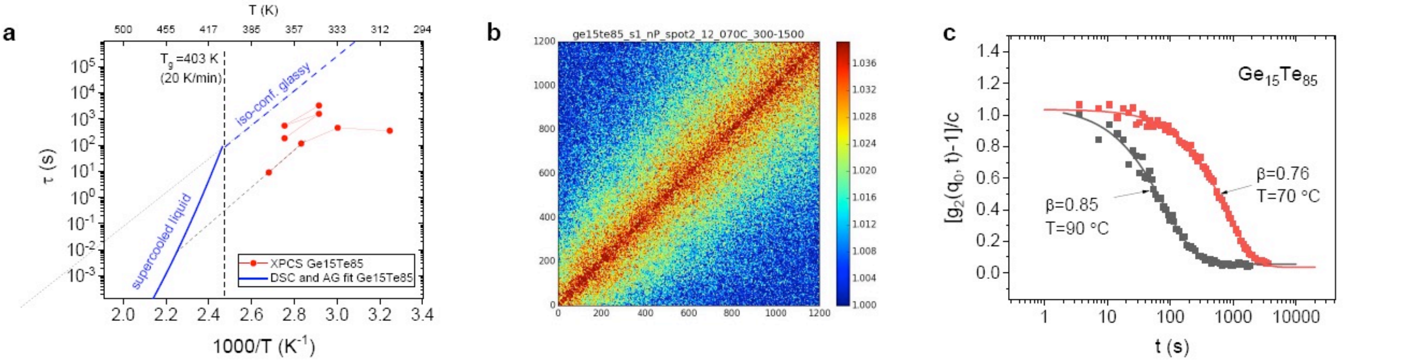

FIG. 1. (**a**) τ as a function of temperature for $Ge_{15}Te_{85}$ **(b)** TTCF of $Ge_{15}Te_{85}$ during isothermal aging at 70 C. Each frame corresponds to 3.6 s. (**c**) The decay of density correlation functions. Solid lines through the data are best fits to the KWW equation. The shape parameters β<1 indicate stretched exponential decays.

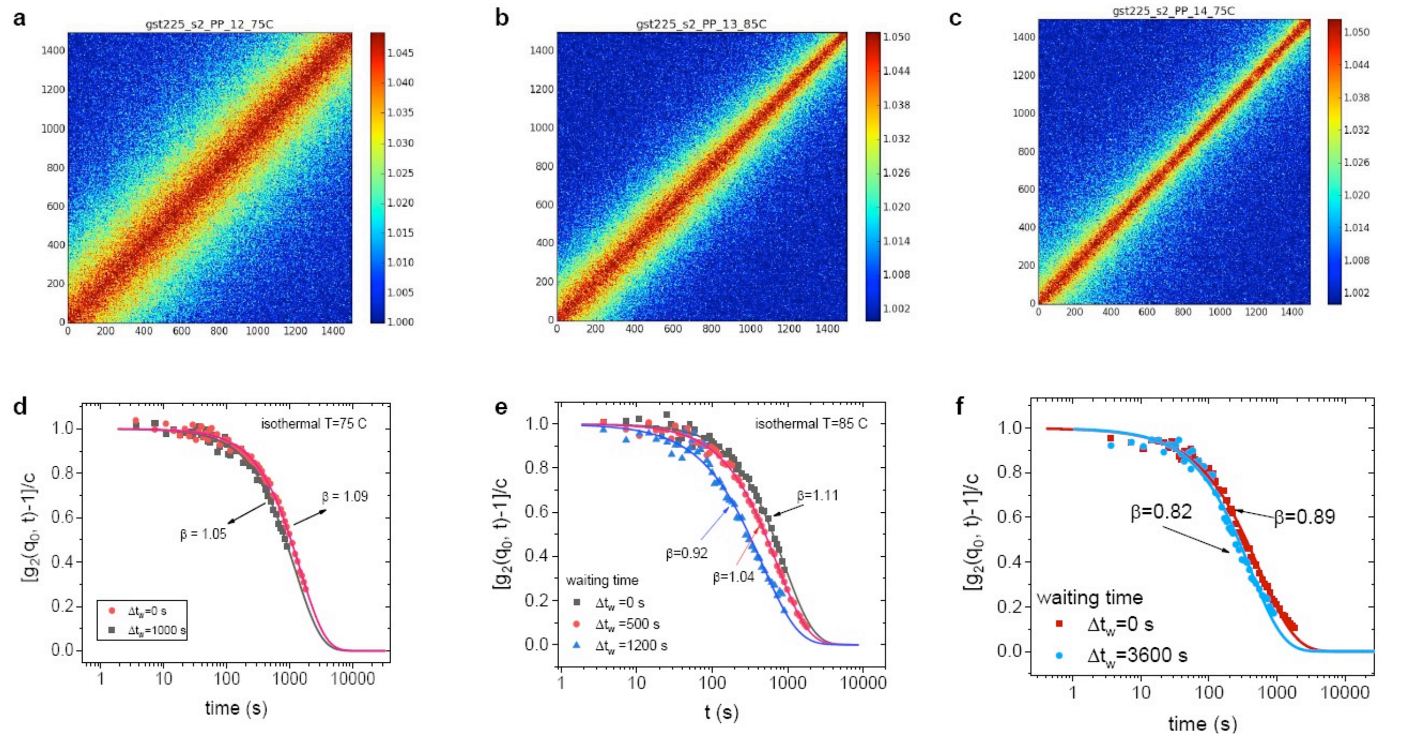

FIG.2. The anti-aging behavior in the GST225 PCM observed during isothermal aging. (**a-c**) TTCF indicate the anti-aging processes during isothemral measurements at temperatures below T_g. (**d-f**) The corresponding decay of the autocorrelation functions with a KWW fit, which yields a β. The β value changes from above than 1.0 to below than 1.0 in (e) in the glassy states.

Figure 2 shows the TTCP for isothermal aging of $Ge_2Sb_2Te_5$ (GST225), where τ becomes smaller during isothermal aging at temperatures well below T_g. This so-called anti-aging is observed continuously for a long time of 4.5 hours, where β changes smoothly from above 1.0 to below 1.0. This seems to show that β <1.0 is not related to supercooled liquid state. The observation is striking that for such a long time, τ keeps decreasing while temperature keeps constant. In general, τ should become larger during aging, but in this case τ goes smaller. This implies that relaxation or aging in GST225 is a statistic process on the energy landscape. This kind of anti-aging is only observed in GST225 but not in $Ge_{15}Te_{85}$, probably because GST225 is very fragile (m=90) while $Ge_{15}Te_{85}$ is strong glassformer (m=50). This only leads to the idea of the rugged energy landscape in GST225, where the relaxation proceeds as a statistic process of hopping around the energy barriers that are high and low in a N-dimensional space.

In concluding, the observed anoamlous aging behavior has not been reported in previous XPCS studies. The microscopic origin of anoamlous aging may be related to the rugged energy landscape and fragility that differ in PCMs and non-PCMs. Understanding the underlying mechanism is an urgent desire for the glass physics and computer memory technologies.