EUROPEAN SYNCHROTRON RADIATION FACILITY
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Experiment Report Form

	Experiment title: Investigation of atomic-scale aging dynamics in fragile amorphous phase-change materials	**Experiment number**: MA-3291
Beamline: ID10	**Date of experiment**: from: 24.01.2017 to: 31.01.2017	**Date of report**: 10.09.2017
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Report:

Chalcogenide-based Phase-change materials (PCMs) are at the cutting edge of electronic material research for computer memory technology. The concept of using the strong electrical contrast between the amorphous and crystalline states and the ultrafast switching speed for data storage has been long pursued by researchers. Aging may occur in the amorphous state and leads to changes in properties, e.g. drifts in the electrical resistance [1] which challenges realization of multilevel memories. Understanding the physics behind the relaxation and aging dynamics is an urgency in the context of technological applications.

During the beamtime MA-3291 at ID10, we perfomed the first multispeckle X-Ray Photon Correlation Spectroscopy (XPCS) measurement on amorphous PCMs such as $Ge_2Sb_2Te_5$ (GST225) to probe the relaxation dynamics in this class of materials. By monitoring 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). We successfully prepared amorphous thick film samples of PCMs with a thickness of ~7 μm for XPCS measurements using magnetron sputtering deposition. The samples of such a thickness can be clamped on the holder of the furnace and also ensured an appropriate signal contrast.

Experimental challenges:
During the experiments we encountered several problems related to unexpected beam-induced effects on detected signals. We realized that the beam-induced effects on measured signals differ from that in covalently bonded oxide glasses (e.g. SiO_2) and also from that in metallic glasses. As it was the first XPCS on the amorphous PCM, we have to spend several shifts of beamtime to rule out the possible beam effects on our

measured structural relaxation time. This leads to a loss of beamtime for our planned experiments. Thus, we did not have time to measure the composition $Ge_{15}Te_{85}$.

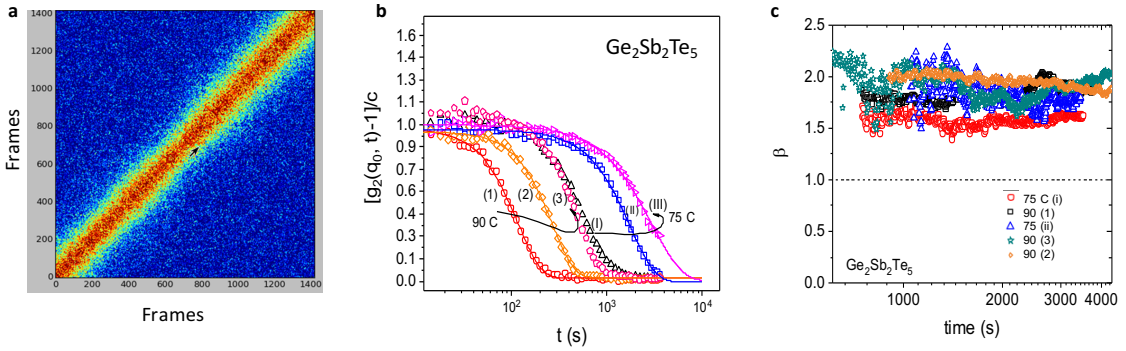

FIG. 1. (a) TTCF of $Ge_2Sb_2Te_5$ during aging at 75 °C. Each frame corresponds to 3.6 s. **(b)** The decay of density correlation functions. Solid lines through the data are best fits to the KWW equation. (**c**) The shape parameters β>1 indicate compressed exponential decays.

Preliminary results

We applied a heat-anneal-cool-anneal (HACA) thermal protocol to the quenched amorphous $Ge_2Sb_2Te_5$. Figure 1 shows the representative two-times intensity autocorrelation function (TTCF) during isothermal aging. The width of the intensity profile along the main diagonal is proportional to the structural relaxation time τ. The steady width with time indicates a weak or almost stationary isothermal aging. This fragile glassformer does not show frequent avalanch-like relaxation events suggested by ref. [2]. From TTCF, we extracted the intensity correlation functions $g_2(q_0,t)$ at q_0 of the maximum of S(Q) during thermal cycling between 75◦C and 90◦C (see Fig.1b). The $g_2(q_0,t)$ functions are fitted with the Kohlrausch-Williams-Watts (KWW) expression, $g_2(t)=1+Aexp[-2(t/\tau)^{\beta}]$, where τ is the structural relaxation time, β is the shape parameter. As shown in Fig.1c, the β values are between 1.5 and 2.0 as a function of waiting time, indicating a compressed exponential decay in the glassy states. The results are consistent with β values (>1) observed in metallic glasses, which was commonly interpreted as ballistic-type motions related to internal stresses stored during quenching.

The structural relaxation time τ obtained from XPCS measurements are shown in Fig. 2a. We find that the temperature dependence of τ shows a more than expected drastic increase upon cooling (blue arrows) which has an activation energy ~1.5-2 times larger than that upon heating (red arrows). This can be clearly seen from the remarkable difference in the slopes of cooling and heating paths. This anomalous aging behavior stands in contrast to the conventional aging conception, where the glass structure is "frozen-in" and τ follows the Arrhenius law upon both heating and cooling with approximately parallel 'slopes' [3]. A further analysis using the Angell-plot (see Fig.2b) shows that the temperature-dependence of τ upon heating obeys the Arrhenius law with a universal pre-exponent 10^{-15}s, suggesting that the system stays in an iso-configurational glassy state (ICGS), while it falls out of the ICGS towards a new lower mobility state during cooling.

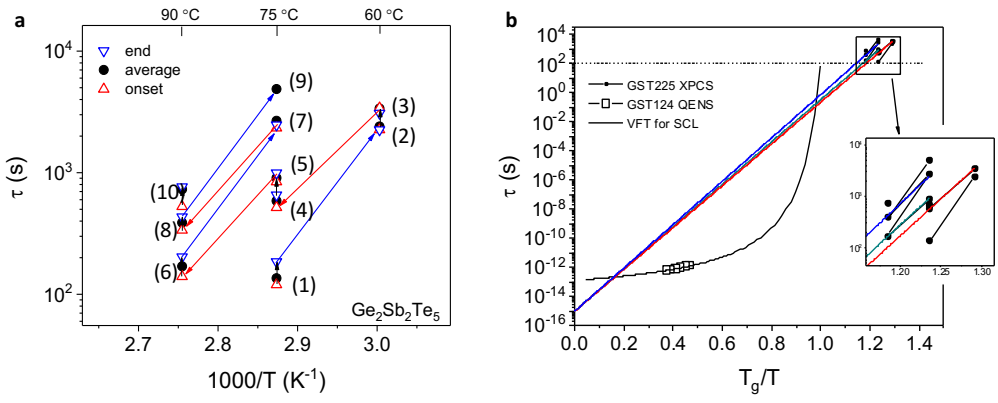

FIG.2. Anomalous aging behavior in the GST225 PCM observed for the cyclic heat-anneal-cool-anneal protocol. (**a**) Arrhenius plot of relaxation time τ obtained from XPCS. In contrast to the conventional conception of aging, the τ exhibits an anomalous, drastic increase during cooling. This rate of change during cooling (blue arrows) exceeds that upon heating (red arrows), as seen from the remarkable difference in slopes. (**b**) Angell-plot shows that the 'heating slope' follows the iso-configurational glassy state (straight lines) with a universal pre-exponent 10^{-15}s, while the 'cooling slope' falls out of the lines.

In concluding, the observed microscopic anoamlous aging during the HACA protocol cannot be explained by conventional glass aging theories [4]. Such a behavior has not been either reported in macroscopic properties or observed in previous XPCS studies. A physical understanding of the microscopic anoamlous aging and its relation to macroscipic aging is an urgent desire for glass theories and technological applications.

[1] J. Y. Raty, W. Zhang, J. Luckas, C. Chen, R. Mazzarello, C. Bichara, and M. Wuttig, Nat. Commun. **6**, 7467 (2015).
[2] Z. Evenson, B. Ruta, S. Hechler, M. Stolpe, E. Pineda, I. Gallino, and R. Busch, Phys. Rev. Lett. **115**, 175701 (2015).
[3] C. a Angell, K. L. Ngai, G. B. McKenna, P. F. McMillan, and S. W. Martin, J. Appl. Phys. **88**, 3113 (2000).
[4] I. M. Hodge, Science **267**, 1945 (1995).