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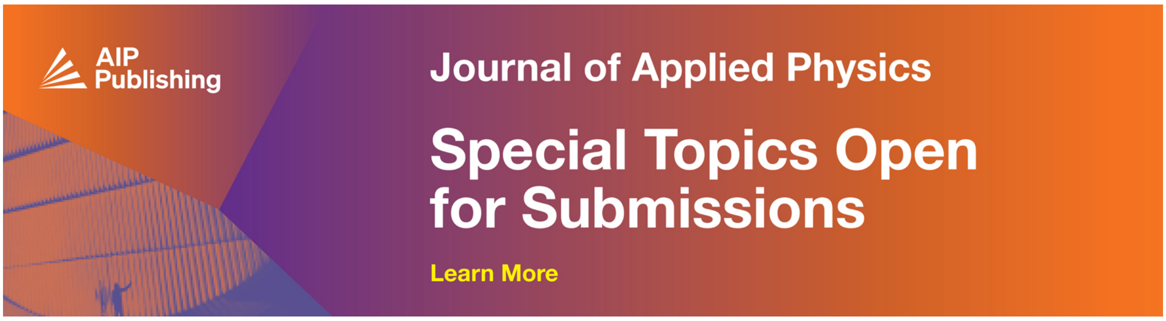

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ABSTRACT

Owing to their ability for fast switching and the large property contrast between the crystalline and amorphous states that permits multi-level data storage, in-memory computing and neuromorphic computing, the investigation of phase change materials (PCMs) remains a highly active field of research. Yet, the continuous increase in electrical resistance (called drift) observed in the amorphous phase has so far hindered the commercial implementation of multi-level data storage. It was recently shown that the resistance drift is caused by aging-induced structural relaxation of the glassy phase, which is accompanied by a simultaneous decrease in enthalpy and fictive temperature. This implies that resistance is related to enthalpy relaxation. While the resistance is known to drift even at room temperature and below, evidence for enthalpy relaxation at room temperature in amorphous PCMs is still missing. Here, we monitor changes in enthalpy induced by long-term room-temperature aging in a series of PCMs. Our results demonstrate the simultaneity of resistance drift and enthalpy relaxation at room temperature, and thus provide further insights into the mechanism of resistance drift and its possible remediation.

I. INTRODUCTION

Due to their large difference in physical properties like reflectivity and resistivity between the amorphous and the crystalline phases, phase change materials (PCMs) find many applications in memory storage technology.[1–6] The property difference between both phases was recently explained by a difference in chemical bonding between the covalent amorphous and the metavalent crystalline phase.[7–12] Advanced PCM-based memory devices involve multi-level data storage where intermediate non-binary resistivity states are achieved by varying the amount of amorphous and crystalline volume fractions.[13] However, the resistance of the amorphous phase of PCMs is found to continuously increase during room temperature storage in a process called resistance drift. Eventually, this drift may lead to overlap of the resistivity states and corruption of the stored data.[13,14] Some device-engineering solutions have been investigated[15] but their increased complexity conflicts with mass production considerations and a material solution is favored. For this reason, the origin of resistance drift needs to be elucidated in more detail in order to adopt new strategies to overcome its limitation on the development of advanced PCM memory devices. Recently, the resistance drift of amorphous PCMs at elevated temperatures was shown to be caused by structural relaxation of the glassy phase, which is always accompanied by a change in the enthalpy state.[16] These results imply that resistance drift should inherently be combined with an enthalpy release. However, while several studies have reported resistance drift at low temperatures like room temperature and below,[17–21] evidence for the release of enthalpy in the same temperature regime is missing. This raises the question of whether or not amorphous PCMs undergo enthalpy relaxation at low temperatures.

Our strategy for correlating the resistance drift to the release of enthalpy at low temperatures, if present, consists of the following three steps. First, we reproduce the observation of resistance drift at low temperatures similar to that observed in the literature. Second, we characterize the enthalpy structural relaxation of the PCM analog $Ge_{15}Te_{85}$ to identify the main features of relaxation in these systems, and third, we investigate samples of the PCMs GeTe, $Ge_3Sb_2Te_6$, $Ag_4In_3Sb_{67}Te_{26}$ (AIST), and $Ge_3Sb_6Te_5$ for any change in enthalpy subsequent to long-term storage at room temperature.

II. RESULTS

In the first step, we characterize the resistance drift of three PCMs at room temperature along with the PCM analog $Ge_{15}Te_{85}$. The $Ge_{15}Te_{85}$ compound is considered a PCM analog because its composition is close to those of traditional PCMs and it exhibits a similar peculiar physical behavior such as a liquid–liquid phase transition[22] and resistance drift inversion.[16] Samples were prepared by magnetron sputter deposition for measuring the resistivity in a four-contact van der Pauw[23] setup. The resistivity was measured at a temperature of 50 °C to ensure reliable isothermal conditions at a temperature as low as experimentally possible in our setup. The measurement interval was seven days for the materials GeTe, AIST, and $Ge_3Sb_6Te_5$. The measurement on $Ge_{15}Te_{85}$ was taken for reference, as the resistance drift phenomenon was also reported for this material.[16,24] The resulting resistivity was then normalized to the initial value and is presented in Fig. 1. In this double-logarithmic representation, after the onset behavior of the relatively low slope,[25–27] the continuous increase in resistance (resistance drift) is clearly visible for all four materials. These measurements show that

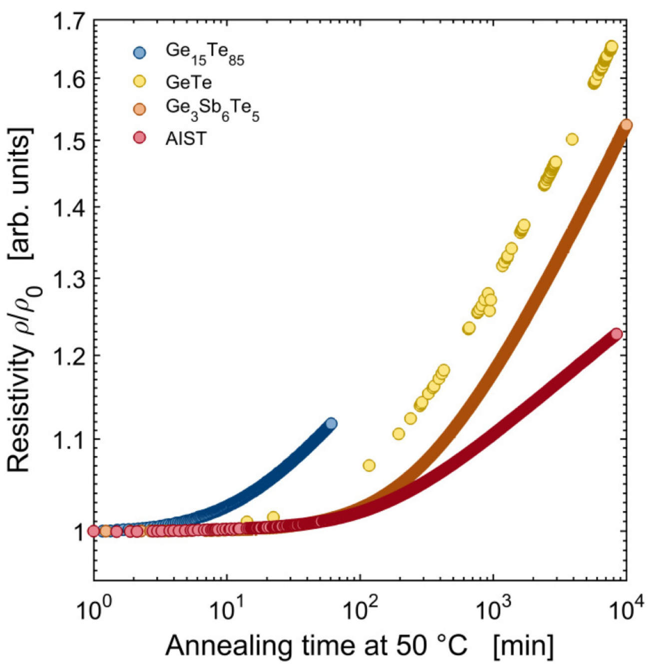

FIG. 1. Drifting resistivity of $Ge_{15}Te_{85}$, GeTe, $Ge_3Sb_6Te_5$, and AIST as a function of annealing time at a constant temperature of 50 °C. The resistivity is normalized to the first value measured after reaching the annealing temperature. After the onset behavior of relatively low slope, all materials show the characteristic constant-slope resistance drift phenomenon.

resistance drift also occurs at low temperatures as was previously reported in the literature for various PCMs.[17–21]

In the subsequent step, we characterize the change in enthalpy of as-deposited PCMs after aging at room temperature for up to three years. To do so, we first characterize the relaxation of the PCM analog $Ge_{15}Te_{85}$ to provide a reference point. As opposed to standard PCMs, $Ge_{15}Te_{85}$ is a good glass-former that does not readily crystallize during reheating across the glass transition,[28] hence its enthalpy relaxation behavior can be clearly characterized for comparison with other PCMs. The change in enthalpy of a relaxing glassy state can be visualized by changes in the excess specific heat capacity $C_p^{\mathrm{exc}} = C_p^{\mathrm{liquid/glass}} - C_p^{\mathrm{crystal}}$ as a function of temperature T, as the heat capacity is a derivative of the enthalpy with respect to temperature. When a standard glass, i.e., a glass created by cooling at the standard rate of 20 K/min,[29,30] is annealed at a temperature below the glass transition temperature T_g, it will release enthalpy until the fictive temperature T_f becomes equal to the annealing temperature upon glass stabilization.[31] The fictive temperature T_f constitutes a measure of the structural enthalpy of the glass expressed in units of temperature, which diverges from the actual temperature when the glass drops out of equilibrium at T_g. An example of the changes in $C_p^{\mathrm{exc}}(T)$ induced by sub-T_g annealing for the PCM analog $Ge_{15}Te_{85}$ is presented in Fig. 2(a). In the as-deposited (un-annealed) state, the material shows an exothermic heat release starting at about 70 °C prior to the glass transition at about 130 °C, which is indicative of a high enthalpy state characterized by a high fictive temperature. During pre-annealing at the sub-T_g annealing temperature of 85 °C for longer and longer annealing times, more and more enthalpy is released during the thermal treatment, causing a reduction in exothermic features and eventually leading to a notable endotherm upon glass transition. The exothermic enthalpy release prior to T_g is clearly a kinetically controlled process that is consequently dependent on the subsequent heating rate. In order to further characterize this process, Fig. 2(b) shows the evolution of $C_p^{\mathrm{exc}}(T)$ for the as-deposited PCM analog $Ge_{15}Te_{85}$ as a function of heating rate ϑ. At the lowest heating rate of 10 K/s = 600 K/min, the exothermic heat release indicative of a high enthalpy state is still observed and a notable endothermic overshoot upon glass transition is missing, just like in the as-deposited state shown in Fig. 2(a). However, increasing the heating rate leads to a reduction of the exotherm and the introduction of an endothermic feature prior to the exotherm that can be identified as the shadow-glass transition[32–34] at about 50 K/s. At 100 K/s, the exotherm is gone and upon increasing the heating rate further, the shadow-glass transition and the actual glass transition start merging. This merging is complete at about 500 K/s after which only a single endothermic overshoot upon glass transition can be observed. Figures 2(a) and 2(b) illustrate the key features of enthalpy relaxation in hyperquenched glasses such as PCMs. Specifically, increasing heating rates kinetically prohibit the exotherm and instead reveal a shadow-T_g that eventually merges with the actual T_g at high heating rates. This emphasizes the benefits of using high heating rates to study glass dynamics features. Increasing the heating rate principally decreases the time for rearrangement processes to occur at a given temperature, thus shifting structural rearrangement processes to higher temperatures, where the glass dynamics is faster. High heating rates, therefore, provide

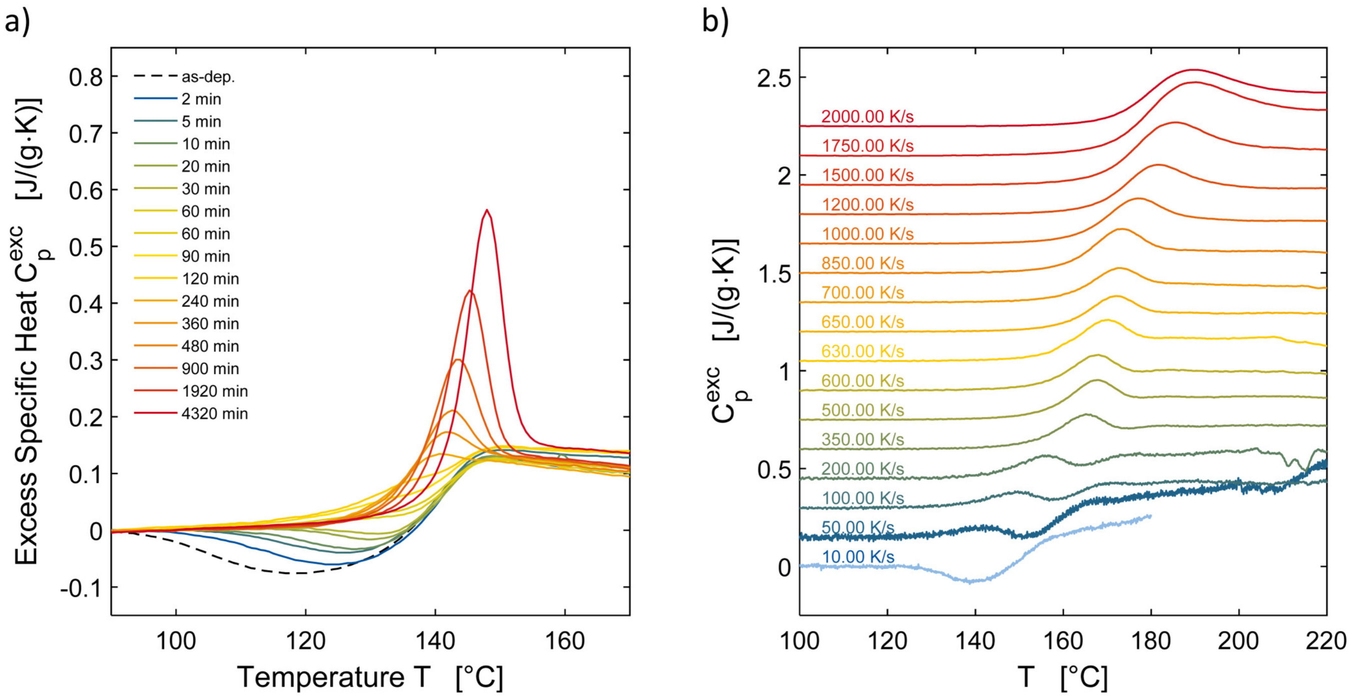

FIG. 2. (a) The effect of pre-annealing at a sub-T_g temperature of 85 °C on amorphous (as-deposited) $Ge_{15}Te_{85}$ (endothermic is up). All curves are measured at a constant heating rate of 40 K/min after aging the sample at the time interval indicated in the legend at the annealing temperature. Pre-annealing for increasing annealing times removes the exotherm prior to the glass transition and leads to an increased endotherm upon glass transition. (b) The effect of heating rate increase on the excess specific heat capacity of as-deposited $Ge_{15}Te_{85}$ (endothermic is up). At lowest heating rates, the exothermic heat release prior to the glass transition is observed. Increasing the heating rate leads to the development of a shadow-glass transition prior to the vanishing exothermic heat release and the actual glass transition. Increasing the heating rate further, the shadow-glass transition and the glass transition merge, resulting in a single endothermic signature.

greater observability of glass dynamics features, enabling us to detect small changes that might otherwise not have been observed. Increasing the heating rate will thus permit us to capture small changes in enthalpy induced by room-temperature aging. Clearly establishing these features and the changes induces by structural enthalpy relaxation will help interpret the $C_p^{exc}(T)$ curves of PCMs aged at room temperature for extended periods of time.

Structural relaxation of the glassy phase is exponentially slower at a lower annealing temperature, but it will not vanish completely at a non-zero absolute temperature. This means that the change in enthalpy state at low temperatures can always be induced by increasing the annealing time. Here, the time of storage at room temperature (RT) since the preparation of the sample material was a minimum of two years and up to three years in order to enhance any possibly occurring enthalpy relaxation as much as possible and practically feasible. While one portion of the prepared material was stored at room temperature, the remaining material was stored in a freezer at about −30 °C for the entire time to reduce enthalpy relaxation to insignificant levels and to keep it in the un-annealed as-deposited state. Then, the excess specific heat capacity $C_p^{exc}(T)$ for both phases was measured at a variety of heating rates by ultrafast (flash) differential scanning calorimetry (FDSC). Any difference between the measurement data of the (un-annealed/freezer-stored) as-deposited phase and those of the RT-stored samples would constitute evidence that enthalpy relaxation had occurred during the long-term storage at room temperature. The results for the materials GeTe, $Ge_3Sb_2Te_6$, AIST, and $Ge_3Sb_6Te_5$ are presented in Fig. 3. In all four cases, the excess specific heat capacity $C_p^{exc}(T)$ curves for the un-annealed as-deposited state and the curves of the samples stored at room temperature show a significant difference. Furthermore, the change in $C_p^{exc}(T)$ curves between the as-deposited and RT-stored samples shows qualitative changes that are fully consistent with annealing and enthalpy relaxation, i.e., emergence of the shadow-T_g and the disappearance of the pre-T_g exotherm. This demonstrates that PCMs undergo significant enthalpy relaxation consistent with glass dynamics. The only difference between the as-deposited and RT-stored samples is the thermal history, which means that the difference in $C_p^{exc}(T)$ can only be interpreted to mean that enthalpy is released in amorphous PCMs even at temperatures as low as room temperature.

While all PCM show qualitative evidence of enthalpy relaxation, they also reveal distinct behaviors in the shape of their heat capacity curves. This is expected due to two features: first, they have slightly different glass-forming ability, i.e., $Ge_3Sb_6Te_5$ is a significantly better glass former that undergoes a calorimetric glass transition before crystallizing,[35] and second, the four PCMs have

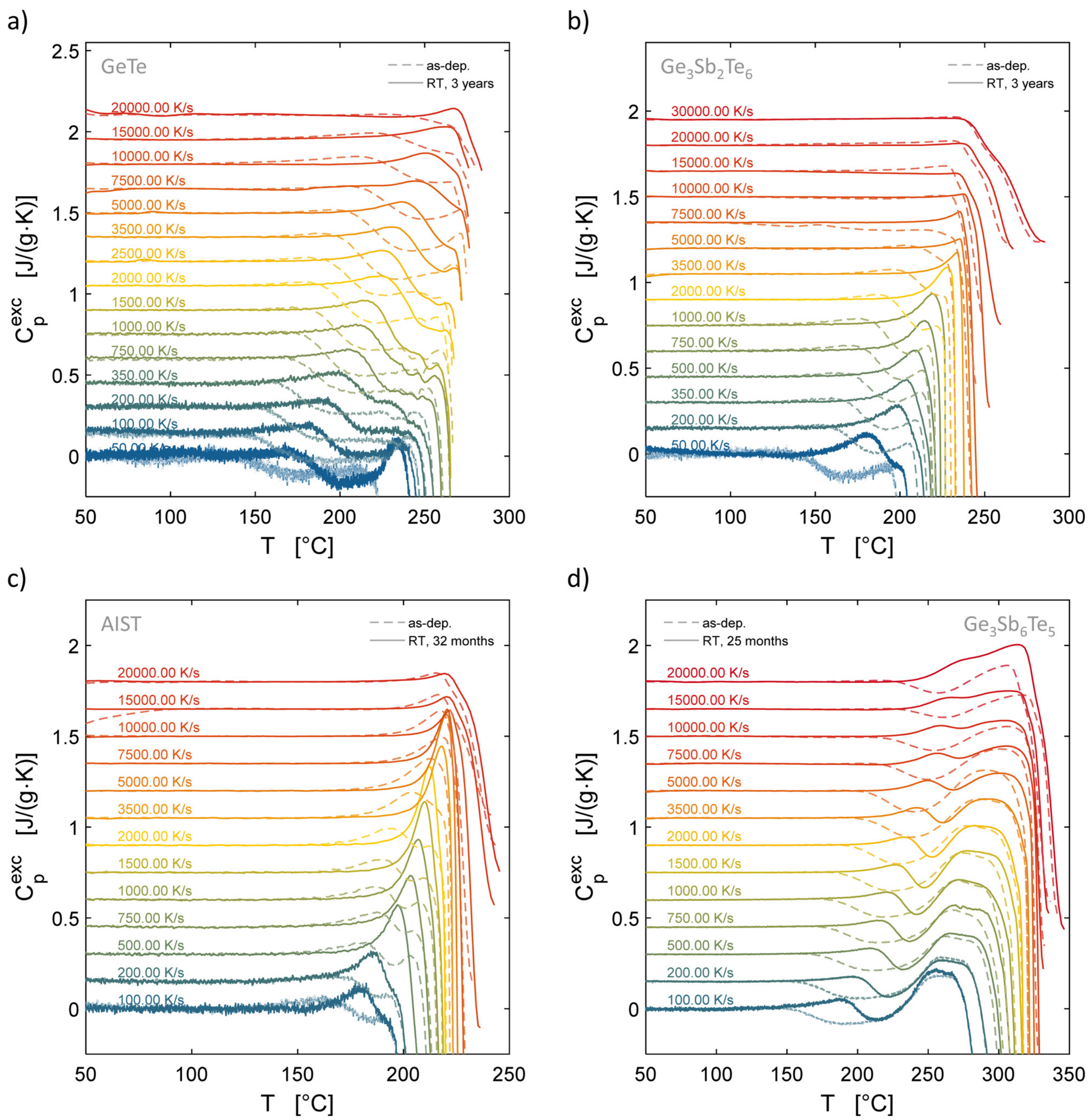

FIG. 3. Comparison of the excess specific heat capacity $C_p^{exc}(T)$ for as-deposited and room-temperature-stored (a) GeTe, (b) $Ge_3Sb_2Te_6$, (c) AIST, and (d) $Ge_3Sb_6Te_5$. The curves of the un-annealed as-deposited state (dashed line) and the RT-stored (solid line) state show a significant difference whereby the release of enthalpy during RT-storage is demonstrated.

slightly different T_g values ($T_g = 182.5$ °C for AIST;[36] $T_g = 190$ °C for GeTe;[37] and $T_g = 193$ °C for $Ge_3Sb_6Te_5$[35]); hence, their relative relaxation kinetics at room temperature are expected to vary in accord with the Tool–Narayanaswamy–Moynihan model.[30] For example, AIST exhibits the most prominent relaxation endotherm after aging due to its lower T_g and its correspondingly shorter relaxation time. On the other hand, $Ge_3Sb_6Te_5$ exhibits both the shadow-T_g and the actual T_g before crystallizing for all heating rates.

III. DISCUSSION

Despite the annealing temperature being about 100 to 150 K lower than the glass transition temperature T_g,[35–38] a significant resistance drift is observed in all (phase change) materials investigated. If the resistance drift is caused by atomic rearrangement processes to a more energetically favorable configuration like the structural relaxation of a glassy phase, an altered atomic configuration would be concomitant with a change in enthalpy, density, and other physical properties, too. In particular, if structural relaxation of a glassy phase is the source of the resistance drift, there must always be a simultaneous enthalpy release. Recently, a demonstration of this viewpoint was reported at elevated temperatures.[16] This study complements these findings by revealing the enthalpy relaxation of amorphous PCMs induced by long-term storage at room temperature. It can then be concluded that the simultaneity of enthalpy relaxation and resistance drift holds even at low temperatures. Indeed, the amorphous phase of PCMs is a glassy phase susceptible to structural relaxation, which may be slow but never ceases at a non-zero absolute temperature. The structural relaxations of PCMs have been also characterized by dynamic mechanical spectroscopy.[39,40] The latter revealed the evidence of β-relaxations below T_g, suggesting the local atomic rearrangement as the main source of glass dynamics.[39] Since some earlier studies argued that β-relaxations are associated with enthalpy relaxations,[41] it raises an open question whether (or how) the resistance drift is related to the β-relaxations in PCMs.

Nevertheless, this raises the question why enthalpy relaxation was not yet reported for amorphous PCMs at low temperatures, while there exist numerous publications on the resistance drift in this temperature range. This may be due to the relative dependence of enthalpy and resistivity on the fictive temperature T_f during the relaxation process.[42–46] While the enthalpy is proportional to the fictive temperature T_f,[29,31] the resistance changes exponentially with T_f [see, e.g., Eq. (13) in the supplementary material of Ref. 16]. Since the relaxation time increases exponentially with decreasing temperature, only small enthalpy releases occur at low T, which are hard to measure compared to resistance change. The latter can be more easily detected due to its exponential dependence on T_f during long time annealing on the logarithm scale. Additionally, resistance measurements on PCMs are traditionally performed on nanometer thick samples that do not have enough thermal mass for accurate calorimetric measurements. Instead, the present measurements were performed on micrometer thick samples that permit us to clearly resolve $C_p^{exc}(T)$ measurements.

IV. CONCLUSION

This study demonstrates that resistance is drifting simultaneously to the release of enthalpy, which is direct evidence that the PCM's glassy phase is relaxing structurally even at room temperature. The difference in magnitude of changes in resistance and enthalpy at low temperatures is explained by their difference in dependence on the fictive temperature T_f that describes the glassy state and its relaxation. This shows that glass dynamics plays an important role in the behavior and description of the amorphous phase of PCMs. It calls for future studies to seek a more quantitative description of the relationship between enthalpy relaxation and resistance drift. A better understanding of this relationship will help in tackling issues related to resistance drift in PCM-based memory devices. Identifying PCMs with higher T_g or low fragility near T_g could help suppress or limit structural relaxation to mitigate resistance drift.

V. EXPERIMENTAL SECTION/METHODS

The resistance and resistivity is measured in van-der-Pauw (vdP) geometry[23] as a function of temperature and time in a home-made setup under Argon atmosphere. The samples consisted of a glass substrate on which the electrical chromium contacts, the chalcogenide layer, and the $(ZnS)_{80}$:$(SiO_2)_{20}$ capping layer were deposited via magnetron sputter deposition. The deposited chalcogenide film is of a square shape with an edge length of about 1 cm. For magnetron sputter deposition, stoichiometric targets were employed and the base pressure was 3×10^{-3} mbar. The accompanying differential scanning calorimetry (DSC) measurements for investigating the enthalpy relaxation were conducted on a PerkinElmer Diamond DSC and the ultrafast measurements in a Flash DSC 1 (FDSC) by Mettler Toledo. The temperature reading in (F)DSC measurements was corrected by the melting onset of pure Indium measured at a constant heating rate ϑ. Contrary to the vdP samples, for (F)DSC samples, several micrometer thick layers of the chalcogenides are deposited onto metal sheets and subsequently peeled off. These samples do not feature a capping layer.

VI. STATISTICAL ANALYSIS

Power data taken by (F)DSC are converted to a specific heat capacity in Pyris Series Software by PerkinElmer and STARe by Mettler Toledo and is further analyzed in a self-developed program in Matlab by Mathworks. In this Matlab program, the heat capacity data were plotted to visualize the changes in enthalpy.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Julian Pries: Data curation (equal); Formal analysis (equal); Writing – original draft (equal). **Christian Stenz:** Data curation (equal); Formal analysis (equal). **Shuai Wei:** Writing – review & editing (equal). **Matthias Wuttig:** Funding acquisition (equal);

Writing – review & editing (equal). **Pierre Lucas:** Writing – original draft (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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