Supplementary Information

Highly tunable β-relaxation enables the tailoring of crystallization in phase-change materials

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1. Supplementary Figures

Supplementary Fig. 1. Full scans of the Ge$_{15}$Sb$_{85}$ powder samples using powder mechanical spectroscopy. (a) Storage modulus $E'$ (black symbols) and loss modulus $E''$ (red symbols) of the as-deposited sample. (b) The annealed samples at 458 K ($\sim 0.92 \cdot T_\alpha$) for 3 hours and (c) for 6 hours. A constant frequency of 1 Hz and heating rate of 3 K/min were used, and a temperature calibration of -18 K is applied to all measurements.

Supplementary Fig. 2. Full scans of the Ge$_{15}$Te$_{85}$ samples using same setting parameters as Supplementary Fig. 1. (a) The as-deposited; (b) Annealed at 382 K ($\sim 0.92 \cdot T_\alpha$) for 6 hours. Storage modulus $E'$ and loss modulus $E''$ are represented by black and red symbols, respectively. A constant frequency of 1 Hz and heating rate of 3 K/min were used, and a temperature calibration of -18 K is applied to all measurements.

Supplementary Fig. 3. The probability of crystallization during a fine-pulse duration scan.
at a constant power of 40 mW for as-deposited, 3 hours and 6 hours annealed Ge\textsubscript{15}Sb\textsubscript{85}, respectively. The fitting for minimum crystallization time is based on the Gompertz function, which is a sigmoid function that depicts the growth mode being slowest at the start and saturated for a relatively long time. The asymptote parameter \( a \) is confined to 100 as the success rate should be no larger than 100%. The standard deviation of Y-axis (probability of crystallization), \( S_y \), can be evaluated by the equation: 
\[
S_y = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (Y_i - \bar{Y})^2}
\]
The calculated standard deviation of as-deposited, annealed at 185\(^\circ\)C for 3h and 185\(^\circ\)C for 6h films are 3.52%, 1.85% and 3.51%, respectively.

Supplementary Fig. 4. The repeated measurements of the PTE diagram. To ensure the replicability, we carried out independent measurements of amorphous Ge\textsubscript{15}Sb\textsubscript{85} samples with a relatively low resolution (30*30 points). The results are in good agreement with the PTE diagram shown in the main text (Fig. 2a).

Supplementary Fig. 5. DSC scans of Ge\textsubscript{15}Sb\textsubscript{85} at different heating rates from 3 to 60 K/min for (a) as-deposited, (b) 3hr-annealed at 458 K and (c) 6 hr-annealed at 458 K.
**Supplementary Fig. 6.** Flash DSC scans of Ge_{15}Sb_{85} at the heating rates from 100 to 30000 K/s for (a) as-deposited, (b) 3hr-annealed at 458 K and (c) 6hr-annealed at 458 K. Note that the curves are vertically shifted for clarity and the lowest curve corresponds to 100 K/s with a lower signal-to-noise ratio.

**Supplementary Fig. 7.** DSC scans at different heating rate for (a) as-deposited and (b) 6hr-annealed Ge_{15}Te_{85}.

**Supplementary Fig. 8.** Flash DSC scans at higher heating rates for (a) as-deposited and (b) 6hr-annealed Ge_{15}Te_{85}. Note that due to the low melting point, a heating rate above 3000 K/s shifts the $T_p$ into the melt, partially bypassing the crystallization.
**Supplementary Fig. 9.** (a) The zoom-in of the first $S(q)$ peaks of Ge$_{15}$Sb$_{85}$ upon isothermal annealing at 458 K for 6 hours. (b) The difference plot $\Delta S(q)=S(q,t)-S(q,t=0\text{hr})$. The trend of the peak sharpening is observed upon annealing.

**Supplementary Fig. 10.** The reduced pair distribution functions $G(r)$ during the isothermal annealing of the amorphous Ge$_{15}$Sb$_{85}$ at 458 K up to 6 hours. The spectra are vertically shifted for an easy view. Inset: the zoom-in of the peak intensity and full-width-half-maximum (FWHM) of the first main peak of $G(r)$. Only the 0hr-annealed and 6hr-annealed curves are shown in the insets.
Supplementary Fig. 11. The calculated partial and total pair distributions of amorphous Ge$_{15}$Sb$_{85}$. The plots are obtained from AIMD simulations employing the PBE exchange correlation function. Plotted for a direct comparison are the total and partial $G(r)$ of the non-annealed sample, of a sample kept at ~458 K for 1 ns and 2 ns before re-quenched to ~285 K.

Supplementary Fig. 12. (a) Simulated $S(q)$ of Ge$_{15}$Sb$_{85}$ for neutron scattering (ND). (b) Simulated $S(q)$ of Ge$_{15}$Sb$_{85}$ for X-ray scattering (XRD) compared with the experimental XRD data (red curve). The agreement is satisfactory for a qualitative interpretation, as all the main features are reproduced in the simulation. (c) Simulated $g(r)$ functions are compared with the
experimental $g(r)$ (red curve) converted from $G(r)$. Note that the number density $\rho_0$ upon annealing at 458 K is needed to convert $G(r)$ to $g(r)$ via $g(r) = G(r)/4\pi\rho_0 + 1$. Unfortunately, we do not have this density information and thus assumed $\rho_0$ is roughly equal to the value of room-temperature density. The level of agreement is in line with previous computational work on PCMs employing standard PBE functionals.

Supplementary Fig. 13. The analysis of angular limited three-body correlation (ALTBC) concerns triples of atoms. Within a given maximum angle $\theta_{\text{lim}}$ between two inter-particle vectors $r_{AB}$ and $r_{BC}$, the statistics of two inter-particle distances $r_{AB}$ and $r_{BC}$ will be determined. Thus, the 2D distribution (contour plot) of $(r_{AB}, r_{BC})$-values indicates the chain-like three-body correlations. If the peaks in the contour plot are off the diagonal $r_{AB} = r_{BC}$, it indicates a chain of alternating short and long bonds and Peierls-like distortions (73).

Supplementary Fig. 14. Total ALTBC functions of amorphous Ge$_{15}$Sb$_{85}$ at ~285 K. (a) Non-annealed. (b) After annealing at ~458 K for 1 ns. (c) After annealing at ~458 K for 2 ns.
Supplementary Fig. 15. The cross-section plots along $r=2.85$-$3.05$ Å of the Sb-centered ALTBC. Three Ge$_{15}$Sb$_{85}$ samples are included, i.e., the melt-quenched sample and samples annealed at $\sim$458 K for 1 ns and 2 ns before re-quenched to $\sim$285 K. The 2D ALTBC contours of two samples are also given. Note that the increase in peak height in cross-section plots is consistent with the trend in total ALTBC; therefore, the Sb-centered contribution dominates the total ALTBC due to its high atomic percentage in the alloy.

Supplementary Fig. 16. The cross-section plots along $r=2.85$-$3.05$ Å of the Ge-centered ALTBC. Three Ge$_{15}$Sb$_{85}$ samples are included, i.e., the melt-quenched sample and samples annealed at $\sim$458 K for 1 ns and 2 ns before re-quenched to $\sim$285 K. The 2D ALTBC contours of two samples are also given. The change in peak height does not show a clear trend as
observed in total ALTBC. Thus, Ge-centered ALTBC does not appear to dominate the total ALTBC.

**Supplementary Fig. 17.** Total nearest-neighbor distribution of amorphous Ge₁₅Sb₈₅. The centers of the histograms shift to higher distances with increasing nearest neighbor order, and the overlaps between histograms of different nearest neighbor orders are also obvious. The peaks of the orders 1, 2, 3, and 4 show a slight but clear enhancement to higher intensity, which is dominated by Sb-centered nearest neighbor distribution, see Supplementary Fig. 18-21. On the contrary, fifth and sixth order peaks reveal weaker values after annealing.
Supplementary Fig. 18. Sb-centered nearest-neighbor distribution of amorphous Ge$_{15}$Sb$_{85}$.

Supplementary Fig. 19. Sb-Sb nearest-neighbor distribution of amorphous Ge$_{15}$Sb$_{85}$. 
Supplementary Fig. 20. Sb-Ge nearest-neighbor distribution of amorphous Ge$_{15}$Sb$_{85}$.

Supplementary Fig. 21. Ge-centered nearest-neighbor distribution of amorphous Ge$_{15}$Sb$_{85}$. 
Supplementary Fig. 22. The drift of the potential and total energy along the isothermal annealing at 300 K and 458 K for 2 ns. At 300 K, the drift is of the order of $4 \times 10^{-3}$ eV/ns per atom. The similar trend in the drift appears at 458 K despite a larger uncertainty. The drifts stem from genuine relaxation of the amorphous state.

Supplementary Fig. 23. Reflectance spectra of amorphous Ge$_{15}$Sb$_{85}$ as measured by FTIR at room temperature. Black solid line is as-deposited Ge$_{15}$Sb$_{85}$, while blue and red solid lines are amorphous Ge$_{15}$Sb$_{85}$ annealed at 458 K for 3 and 6 hours, respectively. The corresponding dashed lines represent the fitting results employing Tauc-Lorentz model.
Supplementary Fig. 24. Illustration for the suppression of $\beta$-relaxation and its influence on crystallization kinetics in Ge$_{15}$Sb$_{85}$. The shadow region represents the upper and lower boundary of $T_\beta$ as a function of $Q$. $T_\beta$ crosses $T_p$ at the heating rate around which the effect of suppressing $\beta$-relaxation starts to show up in crystallization.

2. Supplementary Table

Supplementary Table S1 Standard deviations of $T_p$ in the FDSC measurements for as-deposited (SD$_{asd}$), 3 hours annealed (SD$_{3hr}$) and 6 (SD$_{6hr}$) hours annealed Ge$_{15}$Sb$_{85}$ samples. The standard deviation values are calculated from the average of 10 measurements for each heating rate.

| Heating rate $Q$ (K/s) | 1E2 | 3E2 | 5E2 | 7E2 | 1E3 | 1.5E3 | 2E3 | 2.5E3 | 3.5E3 | 5E3 | 7.5E3 | 1E4 | 1.5E4 | 2E4 | 3E4 |
|------------------------|-----|-----|-----|-----|-----|-------|-----|-------|-------|-----|-------|-----|-------|-----|-----|
| SD$_{asd}$ (K)          | 0.7 | 0.9 | 1.7 | 1.1 | 0.9 | 1.8   | 2.0 | 1.6   | 1.6   | 1.7 | 1.8   | 2.1 | 1.9   | 5.0 | 3.3 |
| SD$_{3hr}$ (K)          | 1.2 | 1.9 | 1.2 | 0.6 | 1.0 | 2.4   | 2.3 | 1.0   | 1.1   | 1.7 | 2.6   | 6.4 | 3.1   | 3.5 | 7.7 |
| SD$_{6hr}$ (K)          | 0.4 | 1.3 | 1.0 | 1.2 | 1.1 | 1.4   | 1.4 | 1.6   | 1.3   | 2.6 | 3.0   | 2.7 | 5.8   | 6.7 | 4.2 |

3. Supplementary Notes

The timescales of $\beta$-relaxation and crystallization
At the low heat rates $Q$=1-50 K/s, which is within the typical range of conventional DSC, the suppression of the $\beta$-relaxation has little impact on the $T_p$ values. In this regime, the temperature of the $\beta$-relaxation $T_\beta$ occurs well below that of the crystallization. Both occur at the relatively low temperatures, where the overall dynamics are slow. Although the atomic mobility in some local regions, corresponding to the $\beta$-relaxation, is higher than that of the
slow $\alpha$-processes in the surrounding matrix, it is apparently not sufficient to affect the crystallization behavior, probably because the overall mobility is still not enough for nucleation and growth of crystals at this temperature. Therefore, the vanishing of $\beta$-relaxation with low heating rates barely causes any changes in $T_p$.

With the increasing heating rate, both $T_\beta$ and $T_p$ are shifted to higher temperatures. However, their heating-rate dependences differ due to their different activation energies. Using the data in Fig. 1a, we can estimate the peak temperature of $\beta$-relaxations $T_\beta$ as a function of the heating rate $Q$. According to Ref. (25), $T_\beta$ is related to the testing frequency $f$ of DMA (PMS in our case) measurement via the equation $f = f_0 \exp(-E_\beta/RT_\beta)$, where $E_\beta$ is the activation energy of $\beta$-relaxations, $R$ is the gas constant, and $f_0$ is a pre-factor. It has been shown that $E_\beta$ can be expressed by an universal relation with the standard $T_g$ ($T_g$ at 20 K/min in a DSC measurement) of the materials, $E_\beta = (26\pm2)RT_g$ where the pre-factor 26 is a fitted parameter for a range of glassy materials (e.g., metallic, polymeric, molecular and oxide glasses) (74, 75). As demonstrated in Ref. (76), the testing frequency $f$ and the heating rate $Q$ are linked by a linear relation $n_s f = Q$, where $n_s$ is the shift factor. As shown in our previous work, after temperature calibration, $T_\alpha$ measured at 1 Hz in PMS is approximately equal to the standard $T_g$ measured in DSC with a heating rate of $Q = 20$ K/min. This results in a $n_s$ of 1/3 K. If we assume $T_g = T_\alpha = 500$ K and $T_\beta$ is located in the range from 440 K to 490 K at the frequency of 1 Hz, with a known shift factor $n_s$ between the PMS frequency and the heating rate, we can identify the pre-factor $f_0$ (6.78×10^{12} Hz when $T_\beta = 440$ K; 3.33×10^{11} Hz when $T_\beta = 490$ K), $E_\beta$ (108 kJ/mol) and finally the relationship between $T_\beta$ and the heating rate $Q$, i.e. $Q = n_s f_0 \exp(-E_\beta/(R \times T_\beta)) = \frac{1}{3} \times 6.78 \times 10^{12} \times \exp(-\frac{108 \times 10^5}{8.314 \times T_\beta})$ if we assume $T_\beta = 440$ K. Note the value of $f_0$ will be different if a different $T_\beta$ is used. The estimated range of $T_\beta$ at different heating rates is sketched by the shadow region in Supplementary Fig. 24, together with the crystallization peak temperature $T_p$. Note the determination of $T_\beta$ at 1 Hz is not trivial, as the peak of $\beta$-relaxation has partially merged into the $\alpha$-relaxation peak due to the coupling of the two relaxation processes. Therefore, the range of $T_\beta$ at 1 Hz is estimated using an upper and a lower boundary temperature, 440 K < $T_\beta$ < 490 K. As shown in Supplementary Fig. 24, the $T_\beta$ is shifted to higher temperatures with larger heating rates and crosses $T_p$ in the range of ~530 K-550 K at the heating rate of about 50 to 10^2 K/s. At this crossover temperature, the timescales of the crystallization and the $\beta$-relaxation become comparable. As shown in Fig. 3c, at almost the same rate, the effect of thermal annealing on crystallization becomes pronounced. This is hardly a coincidence and implies that $\beta$-relaxation starts to dominate the crystallization when the timescales of both processes are comparable.