Acceleration of Crystallization Kinetics in Ge-Sb-Te-Based Phase-Change Materials by Substitution of Ge by Sn

Peter Zalden,* Christine Koch,* Melf Paulsen, Marco Esters, David C. Johnson, Matthias Wuttig, Aaron M. Lindenberg, and Wolfgang Bensch

Thin films of \((\text{Ge}_{1-x}\text{Sn}_x)\text{Sb}_2\text{Te}_{11}\) are prepared to study the impact of Sn-substitution on properties relevant for application in phase-change memory, a next-generation electronic data storage technology. It is expected that substitution decreases the crystallization temperature, but it is not known how the maximum crystallization rate is affected. \(\text{Ge}_8\text{Sb}_2\text{Te}_{11}\) is chosen from the \((\text{GeTe})_y(\text{Sb}_2\text{Te}_3)_{1–y}\) system of phase-change materials as a starting point due to its higher crystallization temperature as compared to the common material \(\text{Ge}_2\text{Sb}_2\text{Te}_5\). In situ X-ray diffraction at 5 K min\(^{-1}\) heating rate is performed to determine the crystallization temperature and the resulting structure. To measure the maximum crystallization rate, femtosecond optical pulses that heat the material repetitively and monitor the resulting increase of optical reflectance are used. Glasses over the entire composition range are prepared using a melt-quenching process. While at \(x = 0, 97\), subsequent pulses are required for crystallization, one single pulse is enough to achieve the same effect at \(x = 0.5\). The samples are further characterized by optical ellipsometry and calorimetry. The combined electrical and optical contrast and the ability to cycle between states with single femtosecond pulses renders \(\text{Ge}_4\text{Sn}_4\text{Sb}_2\text{Te}_{11}\) promising for photonics applications.

1. Introduction

Phase change materials (PCMs) are characterized by a unique combination of properties: they can form two (meta-)stable states with a pronounced property contrast. The two states, one with glassy (amorphous) and the other with crystalline atomic structure, can be produced by the application of electrical or optical pulses of different intensity.\(^{[1,2]}\) Both states possess a large contrast in electrical resistivity and in optical reflectivity, which is caused by a change of the type of bonding upon switching.\(^{[3–6]}\) A melt-quenching process causes the material to be in a glassy state, which can be crystallized by a thermal stimulus of lower intensity over a longer period of time. The electronic memory based on this switching mechanism is non-volatile and can be programmed without a prior reset of the storage cell, making it attractive for commercial data storage technology.\(^{[7,8]}\) Besides their application in memory technology, PCMs are also utilized in the field of photonics where they can be used as switchable optical modulators and bridge the gap between electronic and optical computation devices.\(^{[9–12]}\) Due to the simultaneous optical and electronic contrast, their state can be read and written using both, optical and electrical pulses. This can open up new opportunities in quantum computation, where optical laser modes are used to exchange information.\(^{[13,14]}\) PCMs interacting with these optical modes can therefore interface optical and electronic technology.
While the melt-quenching process of common PCMs can be facilitated with single femtosecond pulses, crystallization requires multiple such ultrashort optical pulses for the common geometry of thin films on a silicon substrate.[15,36]

A prototypical group of PCMs is located on the pseudobinary line (GeTe)₀(Sb₂Te₃)₁₋ₓ. Increasing the content of GeTe raises the crystallization temperature due to an enhanced thermal activation energy.[2] This makes the corresponding amorphous state more stable against crystallization but also increases the optical pulse duration required for crystallization, which indicates a decrease of crystallization-rate.[15,27] Isoelectronic substitution[28–23] and stoichiometric modifications[24–26] are promising approaches to optimize the materials’ properties further. Trends upon substitution could enable the systematic tailoring of a material based on multiple compositional parameters. It was found that replacing Ge in GeTe with Sn increases the reflectivity of the crystalline state and reduces the resistance shift coefficient.[20,27] For example, substituting as well as doping with Sn decreases the crystallization temperature, which might speed up crystallization of these materials.[16,28–31] The enhanced transformation rate would be advantageous for memory devices as long as the corresponding amorphous state can still be kept stable for at least 10 years.[3] This requirement limits Sn-substitution in GeTe because amorphous SnTe crystallizes at temperatures as low as 180 K.[32]

GeₓSb₂Te₅ is a suitable starting material to study the effect of substitution with Sn because of its relatively high initial crystallization temperature (417 K), which offers a chance of forming a glass at ambient conditions over the entire substitution range.[2,13] GeₓSb₂Te₅ crystallizes into a disordered, metastable state, which is a mixture of two Peierls-distorted rock-salt structures, a cubic (Fm3m) and a trigonal (R3m) phase, with a continuous distribution of the local atomic displacement amplitudes.[20,33] The two sublattices of both structures are occupied with Te on one and with a partly random distribution of Ge, Sb, and vacancies on the other.[34] The chemical bonding in this crystalline state can be categorized as metavalent due to its quasi-octahedral atomic structure, not fulfilling the 8-N-rule, and due to its large optical dielectric constant ε₂.[35,36] Since it is not present in the corresponding amorphous state, this type of bonding is held responsible for the optical property contrast between both states. Based on the “map of PCMs” (see Figure S1, Supporting Information), Sn-substitution increases the number of electrons transferred between the two sublattices (ionicity) and decreases the number of electrons shared (hybridization) and might therefore change the type of bonding present in the material.[3]

GeₓSb₂Te₅ also offers a fast crystallization mechanism[2,23,24] whose transition rate could be increased upon Sn-substitution or doping due to the reported decrease of its activation energy in the similar PCM GeₓSb₂Te₅.[20,24,25] At even higher temperatures, the activation energy of crystallization likely decreases further because of a strong-to-fragile crossover reported in GeₓSb₂Te₅ and other PCMs.[16,28–31] This crossover coincides with a loss of Peierls distortions present in the low-temperature state of several PCMs.[38] Holding the Peierls distortion responsible for the decrease in activation energy of crystallization leads to the prediction that the distortion will decrease upon Sn-substitution, which was indeed observed for Sn-substitution in GeTe.[37] However, despite this understanding of the activation energy of crystallization in the low-temperature state, trends in the high-temperature regime could be different. This is because changes in the strong-to-fragile crossover, caused by Sn-substitution could affect the crystallization rate more significantly.

Here, we report on the crystallization of amorphous films of (Ge₁ₓSn₀.₅₋ₓ)Sb₂Te₁₁ (GSST) with five compositions chosen equidistantly between x = 0 and x = 1. The as-deposited (AD) films of all compositions except x = 0.75 are amorphous but all samples could be melt-quenched (MQ) to the glassy state by exposing them to single femtosecond optical pulses. We have determined the dielectric function, mass density, and thermodynamic properties of the initial states and resolved the crystallization process at low heating rates of 5 K min⁻¹ by means of in situ X-ray diffraction and calorimetry. The repetitive application of femtosecond optical pulses is used to crystallize AD and MQ samples with optical fluences that temporarily cause temperatures up to the melting point. Using this technique, we determine the maximum crystallization rates as a function of substitution and estimate the underlying temperature-dependent viscosity controlling the crystal growth velocity in the regime where fast crystallization is possible. We find that the crystallization rate reaches a maximum when half the Ge atoms are substituted by Sn (x = 0.5). At highest concentrations of either Ge or Sn on the other hand, the crystallization temperature reaches a maximum and we rationalize this observation based on changes in the chemical bonding mechanism.

2. Sample Preparation and Characterization of the Low-Temperature Regime

Thin film samples with a thickness of 27–41 nm were grown on silicon [100] single crystal substrates and thicker layers of the material (≈700 nm) were used for the in situ X-ray diffraction measurements. Ge₆Sn₂Sb₂Te₁₁ and Sn₆Sb₂Te₁₁ were deposited by sputter deposition from stoichiometric target (unicore, 99.999%, 10 cm diameter) bonded to a water-cooled Cu plate. The Ar flow was fixed at 20 sccm and the base pressure in the sputter chamber was <2 × 10⁻⁶ mbar.

GeₓSb₂SnₓTe₁₁, GeₓSb₅SnₓTe₁₁, and GeₓSb₆SnₓTe₁₁ were prepared via thermal co-evaporation of the elements.[38] Therefore, Ge and Sn were evaporated by electron beam guns and Sb and Te by Knudsen cells, containing the utilized elements (Chem pur 99.999%). The base pressure was 8 × 10⁻⁷ mbar. Evaporation rates were monitored by quartz crystal microbalances and are listed in Table S1, Supporting Information; deposition times are listed in Table S2, Supporting Information. All compositions were verified by electron probe micro analysis (EPMA) using a Cameca SX 100 and acceleration voltages of 10, 16, and 22 kV. Selected characteristics and heat treatments of all AD samples discussed in this article are listed in Table 1.

As observed in the unsubstituted material, amorphous GeₓSb₁₁Te₁₁ crystallizes upon heating into a phase mixture of rock-salt structures with different degrees of local atomic distortion.[23] Upon further heating, the structures of both materials change due to ordering effects of the initially random distribution of vacancies and therefore the initially formed, pseudo-cubic structure is commonly considered metastable. Only this pseudo-cubic structure occurs upon fast crystallization, for example, when using laser pulses to crystallize the amorphous material.[16,30] Even the PCM AgₓInₓSb₁₀Te₂₆ (AIST),
which directly crystallizes into a trigonal crystal structure upon conventional heating at a few K min$^{-1}$, forms a cubic structure upon laser-induced crystallization.$^{[16,33,39]}$

Figure 1 shows the in situ X-ray diffraction patterns of the films recorded in Bragg-Brentano ($\theta$-\(\theta\)) geometry using Cu K$\alpha_{1,2}$ radiation. Thin films were investigated in an Anton Paar chamber under a He atmosphere and heated at a rate of 5 K min$^{-1}$ between the diffraction measurements, which were performed using temperature steps of 5 K near the crystallization temperature and 10 K otherwise. Each measurement took 1 h, leading to an effective heating rate between 0.08 and 1.7 K min$^{-1}$. The heat treatment induces crystallization of the films as evidenced by the occurrence of sharp X-ray reflections in the powder patterns. Crystallization temperatures for the different films are summarized in Table 1. They decrease continuously with increasing content of Sn, reaching a minimum between $x = 0.5$ and $x = 0.75$. It is important to note that the two samples with the highest crystallization temperatures ($x = 0$ and $x = 1$) were prepared by sputter deposition whereas the others were grown by thermal co-evaporation. While different deposition techniques could contribute to the difference in crystallization temperatures, it is unlikely to be the only explanation, because (i) the trend between $x = 0$ and $x = 0.25$ continues toward the evaporated sample $x = 0.5$, and (ii) a difference in crystallization temperatures of more than 30 °C has not yet been reported for PCMs of identical stoichiometry. As a result of the low phase transition temperature, the films with

| Composition | Crystallization temperatures [K] | Annealing temperatures [K] | Thin samples: Thickness [nm] |
|-------------|----------------------------------|---------------------------|----------------------------|
| $x = 0$     | Ge$_2$Sb$_2$Te$_3$              | 417                       | 438                        | 27                         |
| $x = 0.25$  | Ge$_2$Sn$_{0.25}$Sb$_{0.75}$Te$_3$ | 385                       | 408                        | 40                         |
| $x = 0.5$   | Ge$_2$Sn$_{0.5}$Sb$_{0.5}$Te$_3$  | 366                       | 393                        | 40                         |
| $x = 0.75$  | Ge$_2$Sn$_{0.75}$Te$_{0.25}$    | N/A                       | N/A                        | 41                         |
| $x = 1$     | Sn$_8$Sb$_2$Te$_{11}$           | 403                       | 423                        | 33                         |

Table 1. Results of sample composition analysis using EPMA measurements, crystallization and annealing temperatures, and film thicknesses obtained from the refinement of XRR data of the relevant samples. All values were obtained by analyzing the AD thin films.

Figure 1. In situ X-ray diffraction patterns as a function of temperature, recorded upon heating the as-deposited films of (Ge$_{1-x}$Sn$_x$)$_8$Sb$_2$Te$_{11}$ at an effective heating rate of approximately 0.1 K min$^{-1}$ (a–e). Crystallization is observed through the formation of sharp reflections. Ge$_2$Sn$_2$Sb$_2$Te$_3$ (d) is the only composition that was already crystalline after deposition. The color scale is normalized such that the maximum corresponds to the highest intensity in the respective panel. Data in panels (a) and (b) reproduced with permission.$^{[23]}$ Copyright 2018, Elsevier. For consistency, the rhombohedral system (rhom.) is used for the data description and correlated to a hypothetical cubic (cub.) indexing in the bottom right table with diffraction angles given for the sample with $x = 0$.  

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$^{[16,33,39]}$
Table 2. Static properties of AD amorphous \((\text{Ge}_{1-x}\text{Sn}_x)\text{Sb}_2\text{Te}_3\) films. Values are determined by in situ XRD measurements (see Figure 1), ex situ XRD measurements (see Figure S2, Supporting Information), XRR measurements (see Figure S3, Supporting Information), and DSC-measurements (see Figures S4 and S5, Supporting Information). Extrapolated values are in italics.

| Property (technique)                      | \(x = 0\) | \(x = 0.25\) | \(x = 0.5\) | \(x = 0.75\) | \(x = 1\) |
|------------------------------------------|-----------|--------------|--------------|--------------|-----------|
| Liquidus temperature in K (DSC)          | 950       | 938          | 932          | 932          | 938       |
| Crystallization temperature in K (XRD)   | 417       | 385          | 366          | <362         | 403       |
| Lattice constant (RTm) in \(\alpha\) (XRD) | 4.25      | 4.27         | 4.31         | 4.40         | 4.47      |
| Distortion angle 60°-\(\alpha\) in degrees (XRD) | 0.4       | 0.1          | 0.0          | 0.3          | 0.5       |
| Latent heat of melting in J g\(^{-1}\) (DSC) | 105       | 111          | 109          | 108          | 108       |
| Latent heat of crystallization in J g\(^{-1}\) (DSC) | 32\(^{[15]}\) | 20          | 29          | 27          | 27        |
| Activation energy of crystallization in eV (DSC) | 3.7\(^{[1]}\) | 2.1         | 2.47         | –           | –         |
| Mass density in g cm\(^{-3}\) (XRR)     | 5.13      | 5.76         | 6.17         | 6.04         | 5.54      |
| Gap energy in eV (ellipsometry, \(\alpha = 10^{4}\) cm\(^{-1}\)) | 0.84      | 0.79         | 0.73         | 0.68         | 0.63      |
| Dielectric function at 1.55 eV (ellipsometry) | 15.9 + 9.6i | 11.1 + 11.4i | 11.3 + 14.0i | 10.4 + 14.2i | 9.7 + 14.3i |
| Initial film thickness in nm (XRR)       | 27        | 40           | 40           | 41           | 33        |
| Molar mass in g mol\(^{-1}\) (nominal composition) | 106.1    | 110.5        | 114.9        | 119.3        | 123.7     |

\(x = 0.75\) could only be synthesized in the crystalline state as apparent from the diffraction pattern shown in Figure 1d. All diffraction patterns obtained immediately after crystallization can be indexed based on space group \(\text{R}3\text{m}\) with a lattice parameter that continuously increases upon substitution due to the larger radius of the Sn atoms (see Table 2 and Figure S2, Supporting Information for a depiction of the refinement). The position of the reflections also enabled the determination of the lattice angle \(\alpha\), which is 60° in case the \(\text{R}3\text{m}\) lattice also fulfills the higher cubic symmetry. Since the deviation from cubic symmetry is small, and in some samples even absent, we include a comparative summary of Miller indices in Figure 1. The distortion of the lattice is one of the consequences of a Peierls distortion, which reaches a maximum for \(x = 0\) and \(x = 1\) and vanishes within the experimental uncertainty for \(x = 0.5\), thereby confirming the initial trend of a decreasing distortion amplitude upon Sn-substitution. Besides this microstructural difference, the sample with \(x = 0.5\) is the one which crystallizes with the strongest texture. Without texture, the \{110\} reflection at \(\approx 30°\) is expected to be the strongest. For \(x = 0.5\), however, those at 25° and 42° are stronger and indicate that the \{111\}, \{100\}, \{211\}, or \{110\}-orientations are preferred.

3. Laser-Induced Crystallization

We study the crystallization process of GSST by repetitively applying femtosecond optical pulses to the films while monitoring their optical (white light) reflectance. It was shown that for sufficiently low repetition rates and given pulse energy, the crystallized volume fraction is determined by the number of pulses applied, independent of the repetition rate.\(^{[40]}\) Then, the number of pulses can be used to represent the temporal progress of crystallization at specific temperatures, determined by the laser fluence on the sample. The heating effect caused by each optical pulse allows the irreversible crystallization process to proceed for a limited time and is quickly interrupted due to the fast cooling by diffusive thermal transport into the substrate. During the heat-treatment, the crystal growth velocity increases dramatically with temperature from a value of less than \(1 \times 10^{13}\) m s\(^{-1}\) at ambient conditions (because we did not observe crystals with >5 nm diameter after 10 weeks) to peak values on the order of \(1 \times 10^{4}\) m s\(^{-1}\). Because of this pronounced temperature-dependence, the crystal growth distance per pulse is dominated by the highest temperatures reached, even though they occur only for a fraction of the time (see Figure S12, Supporting Information).\(^{[18]}\) We performed these measurements on the AD films as well as on MQ samples, which were obtained after crystallizing AD samples under a He atmosphere (see Table 1) and transform them to the MQ state with a single femtosecond laser pulse of fluence well above the melting threshold.

Results of these measurements are shown in Figure 2 for the MQ state of the material with Sn (\(x = 0.5\), red triangles) and without Sn (\(x = 0\), blue circles). In the resulting data, the impact of the Sn substitution is immediately evident from the two orders of magnitude lower number of pulses required to reach the highly reflecting crystalline state. In case of the Sn-substituted material, one single optical pulse of more than 17 mJ cm\(^{-2}\) is enough to obtain more than 50% of the total increase in reflectance. This gain in crystallization rate is achieved without loss of the final reflectance contrast as can be seen in Figure 2. A reduction of the fluence continuously reduces the crystallization rate for both materials—as expected for a thermally activated process.

The Johnson Mehl Avrami Kolmogorov (JMAK) model can be used to refine the experimental data because it was found previously to describe the crystallization kinetics of PCMs accurately as shown in Figure 2 (dark yellow lines).\(^{[40]}\) Most commonly, it is assumed that after an incubation time \(t_0\), a constant number density \(\beta\) of nucleation centers transforms the amorphous volume fraction \(1 - x(t)\) by linear, 3D growth with velocity \(u\):

\[
x(t) = 1 - \exp\left(\frac{4\pi}{3} \times (u \times (t - t_0))^3 \times \beta\right) \text{ for } t > t_0 \tag{1}
\]
Figure 2. Reflectance of MQ GSST with $x = 0.5$ (red triangles) and $x = 0$ (blue circles) as a function of the number of femtosecond optical pulses applied to the film for the fluences provided in the legend (unit $\text{mJ cm}^{-2}$). The depicted data sets include those where crystallization proceeds most rapidly. They show that full crystallization requires two orders of magnitude less pulses in the Sn-substituted material. The dark yellow curves are refinements of the JMAK model, Equation (2) for 3D growth. Non-integer numbers of pulses are caused by the asynchronous read-out of the optical reflectance and horizontal error bars indicate the exposure time of the microscope camera used to determine the reflectance. The first laser pulse hits the sample at $1 \pm 0.1$. The temperature dependence of the crystallization kinetics is then described by the temperature-dependent parameters $u$ and $t_0$. It was shown that repetitive optical excitation of amorphous PCMs with $n$ femtosecond pulses causes a crystal growth distance $u \times (t - t_0) = d \times (n - n_0)$ where $d$ is the temperature-dependent crystal growth distance per pulse. Furthermore, the parameters $\beta$ and $d$ are fully correlated in the refinement of this model and are therefore merged to the volumetric growth fraction per pulse $\vartheta = d^3 \beta$ so that the JMAK equation reads

$$x(n) = 1 - \exp\left(-\frac{4\pi}{3}(n - n_0)^3 \times \vartheta\right), \text{ for } n > n_0$$

Equations (2) and (3).

3.1. Impact of Fluence and Substitution

Figure 3 shows the optical reflectance upon crystallization of AD and MQ GSST with $x = 0$, $x = 0.25$, and $x = 0.5$. Further data sets for samples with $x = 0.75$ and $x = 1$ can be found in Figure S10, Supporting Information. Most importantly, the data show that the number of pulses required to crystallize the material decreases continuously with increasing atomic fraction of Sn up to $x = 0.5$. The crystallization rate of the AD and MQ materials is very similar, which is not the case for the common PCM AIST, whose MQ state crystallizes two orders of magnitude faster than the AD material. The initial reflectance $R$ of all amorphous materials is very similar with $R = 0.10 \pm 0.01$. The reflectance of the crystallized state, that is, the optical contrast, is independent of stoichiometry with $R = 0.40 \pm 0.05$ for $x \leq 0.5$. The results for samples with $x = 0.75$ (MQ only) and $x = 1$ (AD only) are shown in Figure S10, Supporting Information. At these higher concentrations of Sn, the optical reflectance of the crystalline states is reduced strongly with the sample $x = 1$ not even having enough contrast to evaluate the reflectance change upon crystallization.

3.2. Laser-Induced Temperature Jumps

The temperature jumps of amorphous GSST upon optical excitation were calculated using a finite element technique based on the parameters summarized in Table 2 and in Section S3, Supporting Information. To accurately describe the absorption of the femtosecond optical pulses, the dielectric functions of the AD films were measured between $x = 0$ and $x = 0.5$ by optical ellipsometry. They reveal that the optical band gap decreases with increasing content of Sn, confirming the decreasing trend in the distortion amplitude of the local Peierls distortion. This trend cannot be explained by the increasing charge transfer (ionicity) because it would cause an increase of the gap energy upon substitution. A linear extrapolation is used to determine the gap energies of materials with $x = 0.75$ and $x = 1$. Using these parameters, the optical absorption profile was calculated using the Fresnel equations of both interfaces of the film with its complex dielectric constants given in Table 2 and the absorption profiles shown in Figure S9, Supporting Information.

In PCMs, the femtosecond optical excitation first causes an electronic excitation, which relaxes by coupling to the lattice with a picosecond time constant, thereby transforming the absorbed energy into heat. Using calorimetry (see Figures S4 and S5, Supporting Information), the crystallization temperature and...
enthalpy as well as the melting temperature and enthalpy were measured to model the specific and latent heat of the materials. Both transition temperatures, listed in Table 2, reach a minimum between $x = 0.5$ and $x = 0.75$, while the enthalpies do not show a dependence on stoichiometry. The models for the specific heat of the amorphous GSST materials are shown in Figure S6, Supporting Information. They are based on the fully reversible latent heat that was found to describe correctly all materials from the pseudo-binary line between GeTe and Sb$_2$Te$_3$.[43] We add to it the difference between the latent heats of melting and of crystallization, which has to be supplied to the amorphous material to reach the liquid state. In the absence of reliable models, we distribute this additional specific heat over the temperature range between the crystallization and melting temperatures. To model the cooling behavior of the films, we assume the thermal conductivity of GSST to equal that determined for amorphous Ge$_8$Sb$_2$Te$_{11}$ using the 3 omega technique as $0.15 \, \text{W K}^{-1} \, \text{m}^{-1}$.[44] Figure S12, Supporting Information depicts the calculated average temperature of the GSST film with $x = 0.5$ for different fluences as a function of the time delay after optical excitation. After optically induced heating, the sample reaches the highest temperature after a few picoseconds and cools down with a nanosecond time constant. Numerical integration of the temperature-dependent crystal growth velocity during this heat-pulse shows that the effect corresponds to a linear growth at the peak temperature for $\Delta t = 19 \, \text{ps}$.[16]

To describe the fluence (temperature) dependence of the crystallization rate, we use a common model based on the kinetic and thermodynamic properties of the material,

$$\frac{dx}{dn} = c \times D(T) \times \left[1 - \exp \left( -\frac{\Delta G(T)}{k_B T} \right) \right]$$

Here, $\Delta G(T)$ is the difference of free enthalpy between the liquid and crystalline states, $c$ is a constant discussed later and $D(T)$ is the diffusivity, which can be approximated by the Stokes-Einstein relation,[45]

$$D(T) = \frac{k_B T}{6 \pi \eta(T)}$$

Figure 3. Reflectance (color-coded) as a function of the number of optical pulses applied (horizontal axes) and their fluence (vertical axes) for a–c) AD and d–f) MQ films of GSST with $x = 0$, $x = 0.25$, and $x = 0.5$. The number of pulses required to crystallize the films decreases with Sn-substitution, whereas for each concentration $x$, the AD and MQ states crystallize similarly.
with the Mauro-Yue-Ellison-Gupta-Allan (MYEGA) model for the viscosity of supercooled liquids: \[^{[46]}\]

\[
\log_{10} \eta(T) = \log_{10} \eta_\infty + \left(12 - \log_{10} \eta_\infty \right) \times \frac{T_m}{T} \times \exp\left(\frac{m}{12 - \log_{10} \eta_\infty} - 1\right) \times \left(\frac{T_m}{T} - 1\right)
\]

(7)

Here, \( \eta_\infty \) is the viscosity at infinite temperature, \( m \) the kinetic fragility, and \( T_m \) the glass transition temperature. The difference in free enthalpy, \( \Delta G(T) \), between the (supercooled) liquid and the crystalline state can be approximated linearly by

\[
\Delta G(T) = G_\infty \times \frac{T_m - T}{T_m - T_c}.
\]

(8)

Equations (5)–(8) show that the temperature dependence of the crystallization rate is determined dominantly by the parameters \( m \), \( T_m \), \( \eta_\infty \), and \( G_\infty \). While \( G_\infty \) is known from the calorimetric measurements, we will in the following determine the parameters \( m \), \( T_m \), and \( \eta_\infty \) from a refinement of Equation (5) to our experimental data. The constant \( c \) is given by a combination of several materials’ properties,

\[
c = 2 \times \exp\left(-\frac{2}{3} \times \left(\frac{2}{3}\right)^{1/3} \times \Delta T \times \frac{8(\pi \lambda)^{1/3}}{\lambda R_h}\right)
\]

(9)

where \( r_0 \) is the atomic radius (1.5 Å), \( R_h \) the hydrodynamic radius of the particles involved (3 Å), \( \lambda \) the diffusional jump distance (3 Å), \( r_0 \) the average radius of grains in the final crystalline state (5 nm) and \( \Delta T \) the effective crystallization time per pulse (19 ps). Several of these parameters are only approximately known and we therefore need to discuss the impact of these uncertainties on the parameters of our refinement. The constant \( c \) is highly correlated with \( \eta_\infty \), but not with the other parameters of the refinement (as can be seen by a careful inspection of Equations (5)–(7)). Therefore, we do not discuss the results for \( \eta_\infty \) but instead provide a direct experimental observation, that is, the maximum of \( dx/dn \) in its place.

The maximum transformation rates \( dx/dn \) obtained from the raw reflectance data are shown in Figure 4a,b, for all compositions investigated here. Using the results of thermal simulations and assuming that each data point corresponds to crystallization at the peak temperature reached at the given fluence, one can obtain a calibration of all data sets on a normalized temperature axis—see Figure 4c,d. These data are refined by adjusting the three free parameters of the model in Equations (5)–(9), which are \( m \), \( T_0 \), and \( \eta_\infty \). Results of the best fit are included as lines in Figure 4c,d. All raw values obtained from the fit are provided in Table S5, Supporting Information. Data points above \( T/T_m = 0.97 \) were not considered in the refinement because at the respective fluence, each pulse would induce partial melting of the material and crystallization cannot proceed.

The peak transformation rates \( dx/dn \) and the fragilities are shown in Figure 5 together with the statistical error bars from the nonlinear regression. They show that the crystallization rate of amorphous GSST reaches a maximum when half of the Ge atoms are replaced by Sn. At the same time, the fragility appears to reach a minimum but the corresponding error bars are similar in magnitude to the observed trend and must be interpreted with caution. However, the statistical certainty of our data allows us to rule out that the fragility increases with Sn-substitution. The size of the error bars is caused mostly by the relatively short fluence range over which reliable data could be obtained. The highest crystallization rate obtained is 0.78 per pulse and implies that a significant increase of the optical reflectance can be achieved by just a single femtosecond optical pulse.

4. Discussion and Conclusion

Upon Sn substitution, the crystallization temperature of amorphous GeSbTe decreases until a minimum is reached between \( x = 0.5 \) and 0.75. For higher contents of Sn, however, the crystallization temperature increases again. This is a remarkably different behavior than what is found in the Ge–Sn–Te system, where the crystallization temperature \( T_c \) continuously decreases with increasing Sn fraction \( z \) with \( T_c = 452 \text{ K} \) at \( z = 0 \), \( T_c = 393 \text{ K} \) at \( z = 0.5 \), and \( T_c = 180 \text{ K} \) at \( z = 1 \).\[^{[27,32]}\] The difference in the two trends upon substitution becomes most prominent when comparing the crystallization temperatures of SnSbTe (403 K) and SnTe (180 K) and must originate from the substitution of Sn by Sb, leaving some lattice sites vacant to maintain the average number of valence electrons on the Sn/Sb-sublattice. We can conclude that the crystallization temperature is lowest when only Sn–Te bonds are present in the amorphous material and that it increases when Sn is substituted either by Ge or by Sb and vacancies.

We rationalize both of these trends based on the electron transfer (ET) and electron sharing (ES) formalism proposed recently to explain the unique combination of properties in the crystalline state of these materials.\[^{[36]}\] In this formalism, the substitution of Sn by Ge or by Sb and vacancies increases the number of electrons shared and decreases the number of electrons transferred. Comparing the relative changes associated with these two trends, the decrease of electrons transferred dominates (see also the calculation in Section S1, Supporting Information). While this formalism was so far applied only to the crystalline state, the trend was confirmed by ab-initio molecular dynamics simulation on the amorphous GeSbTe system as well.\[^{[37]}\] To relate this trend to the crystallization temperature, we consider that the formation of a Peierls distortion was recently made responsible for the mechanism by which the activation energy of atomic diffusion increases upon quenching, thereby stabilizing the glass.\[^{[30]}\] The higher electron transfer in SnTe causes a localization of charge and therefore competes with the Peierls distortion.\[^{[9]}\] Therefore, SnTe forms undistorted cubic crystals at ambient conditions and a weak Peierls distortion can only occur at very low temperatures and only in crystals with few defects.\[^{[35]}\] GeSbTe and SnSbTe on the other hand are Peierls distorted at ambient conditions (see the distortion angles given in Table 2) and indeed their crystallization temperature is higher than that of SnTe. Upon Sn substitution in GeSbTe, the electron transfer increases and the Peierls distortion goes down until a fully cubic structure is reached at \( x = 0.5 \) (GeSbSnTe), which is very close to
lowest crystallization temperature in the GSST system between $x = 0.5$ and $x = 0.75$. Substituting Ge by Sn beyond $x = 0.75$ increases both, the distortion angle and the crystallization temperature, which indicates that the total electron transfer likely goes down. While this formalism does not enable a quantitative prediction of crystallization temperatures, it can describe the trends on a qualitative level based on parameters of the chemical bonds.

The highest crystallization rate is observed for the material with $x = 0.5$, which crystallizes two orders of magnitudes faster than the materials with $x = 0$ and $x = 1$. Following the model employed to refine the experimental data, this enhancement of the crystallization rate can be caused by a change of any of the parameters that directly correlate with it, namely, (a) the effective crystallization time per pulse $t_0$, (b) the final grain radius $r_0$, (c) the diffusional jump distance squared $\lambda^2$, (d) the hydrodynamic radius $R_h$, (e) the atomic radius $r_{at}$, and (f) the viscosity at infinite temperature $\eta_\infty$ or combinations of several parameters. The effect mentioned in (a) can be ruled out as dominant origin of the differences upon substitution, as it would require a two orders of magnitude decrease of the thermal conductivity of the material. This is impossible because the thermal conductivity of amorphous PCMs is within $\approx 20\%$ of the minimum thermal conductivity that was proposed as a lower limit of the thermal conductivity of highly disordered crystals.\cite{48,49} Given the very similar viscosities of liquid Ge and Sn, (f) is also unlikely to be the main cause of the differences and the atomic radius (e) is similar.\cite{50,51} Most likely a combination of parameters (b–d) enables the faster crystallization at $x = 0.5$. It is noteworthy that this composition is found to have the lowest (but still high) fragility, which implies that it has the lowest activation energy of diffusion (and crystallization) at low temperature, which our results indeed indicate. Commonly, a high fragility is considered favorable for phase-change applications,\cite{52} but the decreasing trend together with the increasing crystallization rate underlines that fragility is not the only parameter to tune in order to optimize the kinetic properties of a PCM.

In conclusion, our measurements show that Sn substitution increases the crystallization rate of Ge$_4$Sb$_2$Te$_{11}$ by up to two orders of magnitude when half the Ge atoms are replaced by Sn. Crystallization reaches a rate at which the impact of a single femtosecond optical pulse is enough to double its initial reflectance and to reach 78% of the contrast of the fully crystallized state. We furthermore show that Sn-substitution decreases the crystallization temperature and its activation energy. Nevertheless, all substitutional compositions of the material can be melt-quenched into a stable glassy state at ambient conditions. Crystallization of Ge$_4$Sn$_4$Sb$_2$Te$_{11}$ goes along with a large increase in reflectance by a factor three and a large increase in electrical conductance. Furthermore, the transition can be reversibly induced by femtosecond optical as well as electrical pulses. Combined with the properties of Ge$_4$Sn$_4$Sb$_2$Te$_{11}$ reported here, the material constitutes a promising candidate as a fast transducer between optical and electrical technology as required in photonics applications.
The reflectance technique was probed using an optical microscope with a beam of 800 nm and a repetition rate of 40 Hz (AD samples) and 8 Hz (MQ samples). The position of the laser beam at the sample positions was determined as 128 μm (1/e–radius) by the imprint technique. The reflectance was probed using an optical microscope with white light illumination from a halogen light bulb. The reflectance was determined as 0.5 for all samples, which crystallizes approximately two orders of magnitude more slowly.

5. Experimental Section

An X’Pert Pro MPD diffractometer (PANalytical, Cu Kα2 radiation, θ–θ geometry), equipped with a Göbel mirror, a parallel plate collimator, and a PIXcel detector was used for X-ray diffraction (XRD) measurements. Transition temperatures were determined with temperature-dependent in situ XRD measurements in an Anton Paar high temperature chamber (HTK 1200 N) under a helium (99.999%) atmosphere to prevent oxidation of the samples. The temperature was increased stepwise with a heating rate of 5 K min⁻¹ from 28 °C up to 360 °C in steps of 5 or 10 K. All patterns were collected within 1 h at constant temperature over a 2θ range of 15–65°.

X-ray reflectivity (XRR) measurements were performed on a flat stage using the same setup as mentioned above using a receiving slit to determine the density of the amorphous films as well as the film thicknesses. The program X’Pert reflectivity was used for evaluation of the data. Film thicknesses were also investigated via a Bruker DektakXT profilometer.

Melting points were determined with a Netzsch STA 409 PC-TG/DSC and a heating rate of 5 K min⁻¹. For that purpose, all compositions were synthesized as bulk materials via a solid-state reaction. Stoichiometric amounts of Ge, Sn, Sb, and Te were mixed, ground in a mortar, and sealed in quartz tubes under vacuum (<10⁻⁴ mbar). All samples were annealed at 950 °C with a heating rate of 3 K min⁻¹. The top temperature was held constant for 73 h. Afterwards, the quartz tubes were quenched in water. The powder was ground in a mortar before the DSC measurements were performed on ~30 mg of each sample. Crystallization temperatures of Ge₂Sn₂Sb₂Te₁₁ and Ge₄Sn₄Sb₂Te₁₁ were determined at different heating rates for the Kissinger analysis.

Thin film samples were exposed to optical pulses for 350 fs, with a wavelength of 800 nm and a repetition rate of 40 Hz (AD samples) and 8 Hz (MQ samples). The spot size of the laser beam at the sample positions was determined as 128 μm (1/e–radius) by the imprint technique. The reflectance was probed using an optical microscope with white light illumination from a halogen light bulb. The reflectance scale was calibrated using an Ag mirror at the sample position. The camera on the optical microscope was recording at 15 fps, limiting the temporal resolution in case of 40 Hz exposure.

For the calibration of this setup, the optical properties of the amorphous films were investigated with a Bruker IFS 66 v/s Fourier transform infrared spectrometer (resolution of 0.12 meV, investigated energy range of 0.05–1 eV) and a J.A. Woollam M-2000U ellipsometer. The ellipsometer was equipped with a deuterium and a halogen lamp that covered an energy range of 0.7–5.2 eV. Incident angles were set at 65°, 70°, and 75°. The SCOUT software was used for data evaluation of the dielectric constants ε₁ and ε₂, the index of refraction n, the extinction coefficient k, and the band gap applying the 10000-method.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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crystallization kinetics, data storage, electro-optical materials, glass formation, ultrafast laser processing

Supporting Information

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