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Reversible amorphous-crystalline phase changes in a wide range of Se$_{1-x}$Te$_x$ alloys studied using ultrafast differential scanning calorimetry

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The reversible amorphous-crystalline phase change in a chalcogenide material, specifically the Se$_{1-x}$Te$_x$ alloy, has been investigated for the first time using ultrafast differential scanning calorimetry. Heating rates and cooling rates up to 5000 K/s were used. Repeated reversible amorphous-crystalline phase switching was achieved by consecutively melting, melt-quenching, and recrystallizing upon heating. Using a well-conditioned method, the composition of a single sample was allowed to shift slowly from 15 at. %Te to 60 at. %Te, eliminating sample-to-sample variability from the measurements. Using Energy Dispersive X-ray Spectroscopy composition analysis, the onset of melting for different Te-concentrations was confirmed to coincide with the literature solidus line, validating the use of the onset of melting $T_m$ as a composition indicator. The glass transition $T_g$ and crystallization temperature $T_c$ could be determined accurately, allowing the construction of extended phase diagrams. It was found that $T_m$ and $T_g$ increase (but $T_g/T_m$ decrease slightly) with increasing Te-concentration. Contrarily, the $T_c$ decreases substantially, indicating that the amorphous phase becomes progressively unfavorable. This coincides well with the observation that the critical quench rate to prevent crystallization increases about three orders of magnitude with increasing Te concentration. Due to the employment of a large range of heating rates, non-Arrhenius behavior was detected, indicating that the undercooled liquid SeTe is a fragile liquid. The activation energy of crystallization was found to increase 0.5–0.6 eV when the Te concentration increases from 15 to 30 at. % Te, but it ceases to increase when approaching 50 at. % Te. 

I. INTRODUCTION

Phase transformations play a key role in material production, particularly of metals and polymers, but also in a large variety of natural processes. Moreover, many advanced materials increasingly rely on controlled exploitation of phase transformations. Polymers, alloys, polymorphic substances and composites develop a variety of structures, generally with a metastable nature, which depend on the cooling conditions during their production. During heating, reorganization processes such as (re)crystallization, phase separation and melting may occur. Differential Scanning Calorimetry (DSC) has been an important tool to study such processes. With the advent of ultrafast DSC heating and cooling rates of $10^4$ K/s can be achieved. This has dramatically extended the application range of DSC.

In recent years, particularly polymers were studied using ultrafast DSC but also the application of this technique to so-called phase-change materials has demonstrated its power to enter previously unexplorable analysis areas. Also, in the present work we apply this technique to a model-based phase-change material, in particular to study crystallization in SeTe chalcogenide alloys with a wide composition range.

Phase-change materials (PCMs) are currently investigated intensely, mainly to replace the popular Flash-type memory in the near future, which is used in, e.g., mobile phones, tablet computers, USB memory sticks. PCMs already have been applied successfully in optical recording, well-known from the rewritable CD, DVD, and Blu-Ray Disk formats. Phase-change memories can be switched reversibly more than a million times between amorphous and crystalline states and exploit the large differences in optical reflectivity or electrical resistance of the two states. A fast high energy pulse transforms the crystalline cell into an amorphous state by melt-quenching. The crystalline state can be re-obtained via a longer lower energy pulse that heats the cell optimally below the melting temperature, where the mobility of the atoms becomes high, allowing crystallization. This can be done fast (, but not as fast as melt-quenching which is possible in picoseconds. Particularly, the combination of large electrical/optical property contrast with ultrafast crystallization kinetics at elevated temperatures required for fast switching, and ultraslow crystallization kinetics below 100 °C required for data retention is a unique feature of PCMs.

Despite the interesting results obtained when ultrafast DSC was applied to the prototype Ge$_2$Sb$_2$Te$_5$ material, the disadvantage of the analyses performed is that (i) only single (non-reversible) crystallization events could be monitored for thin film flakes deposited on the sensor and (ii) the PCM studied has an as-deposited structure, whereas melt-quenched structures are more relevant because they are exploited in all
memory applications. The usefulness of PCMs particularly originates from the reversible amorphous-crystalline phase transformation, where the amorphous phase is obtained by melt-quenching. This process was not studied with ultrafast DSC up to now and is the focus of the present work. We have selected a kind of model PCM, in fact SeTe alloys which allow (i) reversible phase switching by melting, melt-quenching into an amorphous phase and crystallization of this phase, (ii) precise control of the thermal history of the materials, and (iii) the execution of multiple measurements on single samples. Such an analysis of PCMs is aimed to provide deeper insights in the extraordinary phase transformation kinetics of these materials excellently suited for data storage applications.

II. MATERIALS AND METHODS

Several Se$_{1-x}$Te$_x$ alloys with $x = (15; 25; 50)$ were prepared by adding for each of them appropriate amounts of the pure constituents (99.999% purity) to a quartz ampoule. The ampoule was brought under vacuum and sealed. The alloy was then left in an oven at 400°C and (i) reversible phase switching by melting, melt-quenching into an amorphous phase and crystallization of this phase, and (ii) precise control of the thermal history of the materials, and (iii) the execution of multiple measurements on single samples. Such an analysis of PCMs is aimed to provide deeper insights in the extraordinary phase transformation kinetics of these materials excellently suited for data storage applications.

II. RESULTS AND DISCUSSION

A typical DSC measurement sequence on a single sample (starting composition Se$_{85}$Te$_{15}$) is shown in Fig. 1(a). Four DSC curves have been recorded using various heating rates (3, 5, 8, 10 K/s), the quench rate was kept prior and in-between the heating steps constant at −4000 K/s. At 200°C the heating rates of 3, 5, and 8 K/s were switched to 10 K/s, to ensure the melting of the sample was measured for these four cases at the same heating rate. This reduced the influence of variations in thermal lag on the measured melting point. Furthermore, it ensured the alloy was in the molten state for the same short amount of time for each measurement. The glass transition $T_g$, crystallization peak temperature $T_c$, and onset of melting $T_m$, are clearly observable in Fig. 1(a) and this was observed in general for all heating rates.

In Fig. 1(b) results at relatively higher heating rates for a different sample (starting composition Se$_{75}$Te$_{25}$) are shown for the same prior melt-quench rate of −4000 K/s. Since heat capacity is measured the glass transition should appear as a step (although complications can arise due to under- or overshoots and for the Flash DSC also due to one-sided heat losses to the cold nitrogen environment) where its midpoint
in heat flow generally can be taken as representative for the glass transition temperature $T_g$. Effectively the same result is obtained when two temperatures are identified, corresponding to changing slopes in the recorded curves, that signify the beginning and ending of the glass transition, where $T_g$ is defined as their average (in compliance with the ASTM E1356 standard). In Fig. 1(b) it can be observed that, when the heating rate (e.g., 2500 K/s) approaches the prior cooling rate of 4000 K/s, indeed the glass transition occurs by a well-defined step. However, increasing the heating rate (beyond 1000 K/s) to 2500 K/s results in a strong deviation of this trend with a considerable broadening of the crystallization peak and thus lowering of its maximum. This effect can be attributed to considerable thermal lag due to thermal gradients in the amorphous droplet-shaped sample for heating rates well beyond 1000 K/s and relatively insignificant lags for heating rates of 1000 K/s or lower. This observation agrees well with our detailed analysis of thermal lag performed in Sec. I of the supplementary material.

Finally, the melting point $T_m$ is defined as the onset of the melting peak. The onset is defined as the intersection point of the baseline of the DSC curve and steepest tangent to the melting peak. To reduce measurement noise, all raw curves were processed with a Savitzky-Golay filter.

The DSC curves such as displayed in Fig. 1 demonstrate that the SeTe alloy can be switched reversibly between the amorphous and crystalline phases by a melt-quench technique using ultrafast DSC. After the melt-quenching, the $T_g$, $T_c$, and $T_m$ can be clearly distinguished during heating.

Due to the open structure of the UFS-1 sensor, sample material evaporated from the sensor area when heated to the higher temperatures. This material for a large part precipitated on the cold area around the sensor, creating a halo of SeTe around the heated sample area (see Fig. S8 in the supplementary material where the halo can be clearly observed in a SEM image). This mass loss effect could also be seen directly from DSC analysis, since the area of the melting peak reduced slightly in each subsequent measurement (see Fig. S9 in the supplementary material). The sample environment will never be saturated with gaseous selenium or also be observed by the differences in slope, i.e., heat loss for the SeTe glass, undercooled liquid, and crystalline state. The lower the heating rate the steeper the slopes in general become. In the crystalline state the SeTe conduct heats better than in the glassy state and in the undercooled liquid the heat conduction is lowest. Therefore, at the lowest heating rates the negative slope in Fig. 1 is steepest for the crystalline state, somewhat less steep for the glassy state and least (most horizontal) for the undercooled liquid. As a consequence at the lowest heating rates the glass transition, instead of a step, becomes nearly a kink. This can be observed clearly in Fig. 1(a) and the gradual development from a step to this kink can be clearly observed in Fig. 1(b).

Another issue is that it can be debated whether $T_g$ can be measured correctly during heating, since it can be argued that $T_g$ is only determined correctly upon cooling from the equilibrium state. In that sense our reference to $T_g$ in the remainder of this paper should be taken as a reference to a representative (near fictive) temperature directly associated with the glass transition process but not the glass transition temperature in a strict sense.

The crystallization temperature $T_c$ is taken as the temperature where the peak of crystallization occurs (cf. Figs. 1(a) and 1(b)). The peak temperature is taken, because it coincides with the maximum in the reaction rate, which is required for the Kissinger analysis. A clear systematic trend in the evolution of the crystallization peak as a function of heating rate can be observed in Fig. 1(b) for the range 50 to 1000 K/s. However, increasing the heating rate (beyond 1000 K/s) to 2500 K/s results in a strong deviation of this trend with a considerable broadening of the crystallization peak and thus lowering of its maximum. This effect can be attributed to considerable thermal lag due to thermal gradients in the amorphous droplet-shaped sample for heating rates well beyond 1000 K/s and relatively insignificant lags for heating rates of 1000 K/s or lower. This observation agrees well with our detailed analysis of thermal lag performed in Sec. I of the supplementary material.

![DSC Curves](image_url)

**FIG. 1.** (a) A typical set of DSC curves obtained during heating at various rates (from lowest to highest $T_c$ peak temperature: 3, 5, 8, 10 K/s) of a SeTe alloy that was quenched from the liquid state (320 °C) at a rate of −4000 K/s. The heat flow to the sample crucible is plotted versus the sample temperature. A peak indicates an exothermic process. The glass transition $T_g$, crystallization peak $T_c$, and the onset of melting $T_m$ have been obtained using an algorithm to find the tangents to the curve. The inset shows an enlargement of the glass transition region that can be compared with the one in Fig. 1(b). The heating rate between 25 °C and 200 °C is varied. From 200 °C to 320 °C, the heating rate is kept constant at 10 K/s. (b) A typical set of DSC curves obtained at higher heating rates than in (a) with now heat flow divided by temperature $C_p$. Clear evolution in behavior of the glass transition as a function of heating can be observed that is highlighted in the inset. Also a clear evolution in the crystallization peaks can be discerned. Both these evolutions are explained in the main text.
tellurium because the evaporated material is removed almost immediately from the surroundings by precipitation and flushing, causing the sample to continuously lose mass.

Accompanying the sample mass reduction, the melting temperature $T_m$ was also found to increase slightly with each heating run. This indicated a decreased Se/Te ratio, due to disproportionate evaporation of selenium from the alloy. This can be readily explained by noting the different vapor pressures of selenium and tellurium. The higher vapor pressure (lower melting and boiling points) of selenium indicates that a larger driving force for evaporation is present. These evaporation effects were directly proportional to the time spent at high temperatures and therefore we used in general measurement sequences minimizing this time.

To investigate this composition shift of the alloy, and the connection between composition and the measured melting point, several samples with different melting temperatures were investigated using a SEM combined with EDXS. These measurements were conducted for several different UFS-1 sensors and SeTe alloy droplets, to account for sample variability. By plotting the (EDXS) measured atomic composition against the $T_m$ as measured with ultrafast DSC, a phase diagram was constructed, see Fig. 2, relating the melting point of the alloy to its composition. Fig. 2 shows a very good agreement between EDXS combined with ultrafast DSC measurements and literature, validating the use of the onset of melting as a direct measure of the Te concentration. This onset of melting was therefore used to determine the composition of the alloy for each measurement sequence, making it unnecessary to check composition with EDXS after each heating run.

The fact that the sample size decreases with each run as Se preferentially evaporates is not negatively affecting our results, because the sample is generally completely molten after each run and therefore the thermal contact and composition will be reformed each run. In this respect there is in principle no difference whether for a certain composition the sample is molten for the first time or many times. Of course, only when a sample tends to be largely evaporated, the measurement accuracy deteriorates due to the reduction of the signal to noise ratio. An advantage of the evaporation initially is that the sample size reduces, where particularly the reduction in sample height reduces the potential thermal gradients in the sample and thus increases accuracy.

Using a quench rate of $\sim 4000$ K/s, it was possible to quench SeTe alloys up to at least 40 at. % Te to the amorphous state without an observable crystallization peak during cooling. In the range from $\sim 40$–60 at. % Te an increasing fraction of the material crystallizes upon cooling at $\sim 4000$ K/s and this fraction becomes 100% beyond $\sim 60$ at. % Te. These observations agree with the literature, stating pure Te as a crystalline and pure Se as an amorphous (vitreous) material. The melting temperature is that of a nearly perfectly mixed alloy and therefore is approximately a linear interpolation between the melting points of the pure constituents.

Extended phase diagrams have been constructed for three samples, and are shown in Figs. S10 and S11 of the supplementary material. Combined information of two different samples, showing the consistency of the results and the validity of our methodology (reproducible reversibility with gradual decrease in Se concentration), is shown in Fig. 3. The diagrams show $T_c$ and $T_g$ (obtained during heating after the quenching) for various heating rates, as well as the melting temperatures $T_m$. The results in Fig. 3 below 30 at. % Te are obtained from (Fig. S10(a) for) a sample with starting composition $Se_{85}Te_{15}$ and above 30 at. % Te from (Fig. S11) for a sample with starting composition one with $Se_{35}Te_{25}$. In fact, continuously repeating measurement sequences shown in Fig. 1(a) allowed the construction of the results below 30 at. % Te in Fig. 3 (and all results in Fig. S10(a)). The same holds for Fig. 1(b) and the results above 30 at. % Te in Fig. 3 (or Fig. S11, where in Fig. 1(b) only a limited number of heating rates of the actual sequence were shown to improve visibility).

The extended phase diagrams show clear evolutions of the transition temperatures with Te concentration. A decreasing $T_c$ is observed for increasing at. % Te, while $T_g$ increases and $T_m$ decreases with increasing heating rates; this increase is more pronounced for relatively low Te concentrations. $T_c$ decreases and $T_g$ increases with increasing Te concentration. The data points at the highest Te concentrations, beyond 60 at. % Te, are inaccurate due to too low quench rate for complete amorphization and due to severe mass loss in the sample as caused by evaporation.

![FIG. 2. The atomic composition of the SeTe alloy was measured using EDXS, and plotted against the onset of melting measured by the ultrafast DSC. These points are displayed in red. The blue line is taken from literature (see Ref. 20, and references therein). The experimental results agree well with literature.](image)

![FIG. 3. Extended phase diagram showing as a function of Te concentration the glass transition temperature $T_g$, crystallization temperatures $T_c$, and melting temperatures $T_m$. Particularly $T_c$ increases for increasing heating rates; this increase is more pronounced for relatively low Te concentrations. $T_c$ decreases and $T_g$ increases with increasing Te concentration. The data points at the highest Te concentrations, beyond 60 at. % Te, are inaccurate due to too low quench rate for complete amorphization and due to severe mass loss in the sample as caused by evaporation.](image)
increases slightly for increasing at. % Te. When the heating rate is increased, a significant increase in $T_c$ is observed. This can be explained by recognizing that crystallization is a thermally activated process. When the material is heated at a higher rate, less time has passed at a certain temperature. This means the material has had less time to nucleate and grow. Therefore, the maximum growth rate occurs at higher temperature.

Increasing the heating rate also increases $T_g$, but the effect for $T_c$ is clearly more pronounced. In Fig. 3 the difference between the $T_g$’s pertaining to the lowest and highest heating rates decreases with increasing Te concentration. This indicates (based on Kissinger analysis$^{24}$) that the activation energy for crystallization increases with increasing Te concentration. In Fig. 3 it seems that, by extrapolating the observed trends in the data below 40 at. % Te to higher Te concentration, the activation energy for crystallization tends to diverge (become infinite) when the crystallization temperature becomes independent of heating rate, i.e., when straight lines fitted to the data for the various heating rates converge and finally cross when extrapolated to higher Te concentration (see also Fig. S10 in the supplementary material$^{41}$). Moreover, this crossing tends to occur when the crystallization temperature also approaches the glass temperature at Te concentrations of about 70–80 at. % Te. However, Fig. 3 shows that one has to be careful with drawing conclusions from such extrapolations, because it indicates that beyond ~50 at. % Te, the activation energy for crystallization is not increasing further.

Still, the results in Fig. 3 prove that the gap between the glass temperature and the crystallization temperature (observed for a certain heating rate, particularly the lowest heating rate), i.e., a kind of overheating, rapidly decreases for increasing Te concentration (in the range up to 60 at. % Te) by a slight increase of the glass temperature, but particularly by a pronounced decrease in crystallization temperature. Simultaneously the gap between the melting temperature and the crystallization temperature, i.e., a kind of undercooling, rapidly increases by both a pronounced increase of the melting temperature and a pronounced decrease in crystallization temperature. These results thus clearly show that the glass-forming ability of SeTe alloys continuously and strongly decreases in the range from 15 to 60 at. % Te.

The reduced glass temperature ($T_{rg} = T_g/T_m$) shows a slow decrease with increasing Te concentration; approximately 0.66 at 15 at. % Te to 0.60 at 50 at. % Te. This does not really seem significant compared to the change in $T_c$. However, interestingly this observed decrease in $T_{rg}$ agrees with the expectation (see, e.g., Ref. 27) that $T_{rg}$ decreases when the glass-forming ability decreases.

In Fig. 4 the critical quench rate ($Q_{crit}$) necessary to completely vitrify the sample is shown. This rate was determined by the lowest tested rate where a crystallization peak was not detected upon cooling the sample. It is found that this rate increases orders of magnitude from 10 K/s for ~20 at. % Te to 6000 K/s at ~60 at. % Te. Of course the $Q_{crit}$ is a direct measure of the glass-forming ability and thus also demonstrates that this ability strongly decreases in the range from 15 to 60 at. % Te. From the critical quench rates shown in Fig. 4, we can deduce that the temperature gap between $T_c$ and $T_m$ shown in Fig. 3 is an important indicator for the quench rate needed to prevent crystallization, since a lower $T_c$ means an increased driving force for crystallization due to the increased undercooling. This means that as the tellurium concentration increases, the quench rate necessary to vitrify the sample needs to be increased, to counterbalance the increased driving force of crystallization.

By varying the quench rate and measuring $T_c$, it was found that the quench rate does not significantly influence the crystallization temperature $T_c$ (see Fig. S12 in the supplementary material$^{41}$). When crystallization is strongly limited by nucleation, then it is expected that at the lowest quench rates more embryos for nucleation can develop than at the highest quench rates and then a significant decrease in crystallization temperature upon heating is expected after the lowest quench rates. Since, this effect is not observed, it can be concluded that crystallization is not limited by nucleation, but predominantly by growth. This is also corroborated by the observations that the trend in crystallization temperature versus Te concentration does not change when the sample is not fully vitrified anymore after quenching and thus already contains a crystalline fraction either due to incomplete melting of the crystalline material or due to partial crystallization during quenching.

Kissinger analysis$^{24}$ was applied to the crystallization transition to determine the activation energy ($E_c$), i.e., data plotted in a graph of $\ln(\phi/T_c^2)$ versus $(1/T_c)$ should be on a straight line with a slope equal to $(-E_c/k_B)$, with $\phi$ the heating rate, $T_c$ the crystallization peak temperature, $k_B$ Boltzmann’s constant, and $E_c$ the activation energy for crystallization.

Since Kissinger analysis enables the determination of the activation energy of a certain alloy, the composition must not change significantly between heating runs. Fig. 1(a) demonstrates that the composition shift within one measurement sequence can be minimized to less than 2 at. % (since the onset of melting of the four sequential heating curves does not show an observable shift). Furthermore, from Fig. 3 the maximum composition difference observed within a measurement sequence is 2.5 at. % Te. These composition shifts are
analyses to be performed with sufficient accuracy. The composition is denoted by color, with low Te-concentrations in blue, progressing to red for higher Te-concentrations. A linear fit is made through four measurements of one sequence, with different heating rate (in this case 3, 5, 8, 10 K/s) for approximately the same composition. From these fits, the activation energy for crystallization at one alloy composition was obtained. A few fitted lines are shown as a guide to the eye. The slope of the lines clearly increases as the Te concentration increases.

The Kissinger plot shown in Fig. 5, which connects the $T_c$ measurements of one sequence like the one shown in Fig. 1(a), allows determination of the slope from a least-squares fit. All data points are colored coded based on their composition. The plot shows the slopes of a few fits, as a guide to the eye. The slopes of the fitted lines slowly become steeper for an increasing tellurium concentration and therefore the activation energy $E_c$ increases with increasing Te concentrations. The data points show a good compliance with the linear fitted trends, although increased errors are observed for higher Te concentrations. Due to sample mass reduction through evaporation the DSC curve signal/noise ratio decreases as the sample has been through more heating runs and therefore the increase in error can be anticipated. However, an important other source of error is that beyond 30 at. % Te the melting was not performed at sufficiently high temperature (sufficiently long time) to fully melt the crystallized material (see Fig. S13 in the supplementary material). Therefore, beyond 30 at. % Te only part of the sample is vitrified during quenching and this leads to more variations in the results. The same was actually true for the data beyond 30 at. % Te in Fig. S10(a) and therefore we used only the data below 30 at. % of this sample for the construction of Fig. 3. Still, the continuous trend in results below and above 30 at. % Te in Fig. 5 (and Fig. S10(a) of the supplementary material) indicates that results are not sensitively depending on complete absence of prior crystallization.

Compared to Fig. 5, Fig. 6 depicts a Kissinger plot that connects the $T_c$ measurements for a much wider range of heating rates, particularly also employing higher heating rates of which examples are shown in Fig. 1(b). The data in this plot show a clear curvature. This curvature is illustrated by the inset, which shows the local slope of all points in the Kissinger plot. The slope clearly lowers for higher heating rates, regardless of the composition. From lag characterization measurements and from a detailed thermal analysis (see supplementary material, Secs. 1 and 2) it is determined that the lag at heating rates of 1000 K/s is less than 4 K (in agreement with earlier work). It is therefore insufficient to explain the measured curvature, which is also observable for heating rates up to 1000 K/s. Therefore, the curvature is related to the crystallization process in the SeTe alloy itself. This non-Arrhenius behavior can readily be attributed to fragile liquid behavior of the SeTe undercooled liquid. A seminal paper of Martinez and Angell already shows that Se exhibits significant fragility. In that respect our observation of fragility in SeTe alloys might be expected and is thus corroborated by the experimental results here. A similar non-Arrhenius behavior effect was found in the study of Ge$_2$Sb$_2$Te$_5$, where ultrafast DSC was also used to produce data in a Kissinger plot with heating rates up to $4 \times 10^8$ K/s. There the non-Arrhenius behavior was also attributed to fragile liquid behavior (m ≈ 90 whereas m ≈ 15 for strong liquid behavior). In a recent paper on GeTe it was also concluded that the undercooled liquid has a high fragility with at least a value m ≈ 130. Fig. 6 seems to indicate that fragility reduces with increasing Te concentration, because curvature is most pronounced for alloys containing least Te.

As already shown above, the crystallization rate in SeTe is predominantly governed by crystal growth (and not limited by crystal nucleation). Crystal growth is, for the temperature regime considered here for the Kissinger plot at relatively large undercoolings, governed by the microscopic atomic mobilities of the undercooled liquid. These mobilities are, according to the Stokes-Einstein relation, inversely proportional to the macroscopic viscosity $\eta$. We are certain that we have an
undercooled liquid, because our measurements demonstrate that we are above the glass transition temperature. The activation energy of the (overall) crystallization process in SeTe, as can be derived from the Kissinger plot, is thus directly related to the temperature dependence of the viscosity. For a strong liquid this temperature dependence is of Arrhenius type. For a fragile liquid this temperature dependence would indicate that the local slope in the Kissinger plot decreases for increasing peak temperatures and thus for increasing heating rates, exactly what is observed in Fig. 6. Therefore, it is clear that the Kissinger plot in Fig. 6 is consistent with fragile liquid behavior.

Moreover, the inset in Fig. 6 demonstrates that the local slope in the Kissinger plot becomes steeper for increasing Te concentration, meaning that the activation energy $E_c$ increases with increasing Te concentration. This holds in general for all heating rates.

Based on the results such as obtained from Figs. 5 and 6 (where from Fig. 5 only the results below 30 at. % Te were incorporated, because of incomplete melting of the sample beyond 30 at. % Te), Fig. 7 is constructed showing the obtained activation energy $E_c$ as a function of Te concentration for three independent samples. The activation energies were also determined using the Ozawa method,31, 32 yielding similar activation energies, to within 2% of the values obtained using Kissinger analysis. In Fig. 7, each point represents the activation energy obtained from the linear fit of all points of the same composition, such as displayed in Figs. 5 and 6, neglecting curvature effects which, as shown above, become more pronounced when higher heating rates are included.

Fig. 7 shows that the range of heating rates, particularly the highest heating rates, affects the values obtained for the activation energy $E_c$. An important factor explaining this trend is the curvature in the Kissinger plot shown in Fig. 6. If the curvature is neglected to fit the data linearly, the calculated slope will be too flat and $E_c$ thus too low. This error will increase when the range in heating rate, particularly the maximum heating rate is increased. It explains why the heating rate ranges with maximum values of 100 and 1000 K/s in Fig. 7 tend to give systematically lower values for $E_c$ than the ones for the lower maximum heating rates, because fragility of the supercooled liquid leads to curvature in the Kissinger plot. However, on top of the curvature effect due to fragility, the heating rate ranges with maximum values of 2500 and 5000 K/s become even more curved due to thermal lag effects and therefore give relatively even lower values for the activation energy $E_c$. Despite this (obscuring) influence of heating rate range, also the influence of Te concentration on the activation energy $E_c$ can still be observed well in Fig. 7. It shows that the increase in activation energy as a function of Te concentration is most pronounced for 15–30 at. % Te and gradually reduces with increasing Te concentration. Finally, the increase in $E_c$ tends to disappear beyond about 50 at. % Te.

However, curvature effects in the Kissinger plot cannot explain the large difference in the activation energy observed between the heating rate ranges 0.25–5 K/s and 3–10 K/s. Several literature values20, 33, 34 are plotted as well in Fig. 7, where particularly the results of Gosh et al.,20 show fair agreement with our data measured in the range 3–10 K/s, whereas the results of Svoboda et al.33 agree better with our data measured in the range 0.25–5 K/s. Moreover, in Fig. S14 of the supplementary material41 we show results for a total of seven different samples (instead of 3 different ones in Fig. 7), where the various trends are less clear than in Fig. 7, but demonstrating better that there is quite some sample-to-sample variation. However, still a similar trend is observed for various samples in Fig. S14, even though they show relatively large differences in the ordinate values. This trend indicates that there is an increase of 0.5–0.6 eV in the activation energy of crystallization when the Te concentration increases from 15–30 at. %. So, the relative large differences observed for the activation energy of crystallization in literature is reproduced here as sample-to-sample variations particularly giving various offset values in the activation energy. Therefore, it is relevant to try to find possible origins of these sample-to-sample variations in the absolute values of the activation energies.

We first need to recognize that the activation energy determined is an overall activation energy. It does not directly give us the energy barrier atoms need to overcome to allow the transition from the amorphous to crystalline phase, but it is the result of the contributions of both nucleating and growing crystals in various configurations. Due to the differences in sample mass and geometry, samples might show slightly different crystallization characteristics, where different crystallization mechanisms and also different crystal structures can be involved. A variable which was not well-controlled was the sample size. A bigger sample has a relatively low surface area compared to the bulk. This might lead to another crystallization regime.34–37 Moreover, SeTe and even pure Se are characterized by a relatively large variety of allotropes that can develop.38–40 Nucleation and growth processes for these different structures will vary and will thus also show variations in their activation energies. These results clearly indicate the importance to be able to perform repetitive measurements on single samples in order to observe trends that cannot be
detected otherwise due to sample-to-sample variation. This clearly shows the importance of the present methodology to be able to reversible switch the samples in an ultrafast DSC.

An increase in activation energy for increased Te concentration has been observed, while the crystallization temperature decreases. This might at first glance seem counter intuitive, but it shows that the difference in Gibbs free energy ($\Delta G$) between the amorphous and the crystalline phases increases relatively faster than the activation energy for crystallization $E_c$ increases in order to compensate for the observed increase of $E_c$.

### IV. CONCLUSIONS

A reversible amorphous-crystalline phase change in a chalcogenide material has been investigated for the first time using ultrafast DSC. SeTe alloys with a concentration in the range between 15 and about 60 at. % were switched reversibly between the amorphous and crystalline phases. Using a quench rate of $-4000$ K/s, it was possible to quench SeTe alloys up to at least 40 at. % Te to the amorphous state without an observable crystallization peak during cooling. The ultrafast DSC measurements showed good signal/noise ratio and allowed for accurate determination of the glass transition temperature $T_g$, crystallization temperature $T_c$, and melting point $T_m$ upon heating of the quenched materials.

The SeTe alloys slowly evaporated from the sensor. EDXS showed that the composition slowly shifted to higher Te-concentrations. It was proven using EDXS-DSC that the onset of melting measured by the ultrafast DSC is a good indicator of composition for this system. The slow shift in composition allowed for the scanning of crystallization behavior throughout a range of compositions (15–60 at. % Te). Using the observed transition temperatures $T_g$, $T_c$, and $T_m$ as a function of Te concentration our measurement methodology allowed us to construct an extended phase diagram. $T_g$ and $T_c$ increase for increased heating rates. $T_m$ increases slowly with increasing Te-concentration. However, the reduced glass temperature slowly decreases. The crystallization temperature on heating is found to decrease substantially with increasing Te concentration. Together with the significant increase in melting temperature, this is a strong signature that the amorphous phase becomes progressively unfavorable (with respect to the crystalline phase), which is of course excellently corroborated by our measurement that the critical quench rate, necessary to completely vitrify the sample, increases about three orders of magnitude (from $\sim$10 to $\sim$10000 K/s) when the Te concentration increases from 20 to 60 at. %.

Kissinger and Ozawa analyses were performed to determine the activation energies of crystallization of the SeTe alloys. The capability of ultrafast DSC to exploit a large heating rate range enabled detection of non-Arrhenius behavior that can be attributed to fragile liquid behavior of the SeTe undercooled liquid. The activation energy of crystallization was found to increase for increased Te-concentrations; 0.5–0.6 eV when Te concentration increases from 15 to 30 at. %. However, the absolute values of the activation energy for crystallization differed considerably from sample-to-sample. Some potential origins for these differences have been highlighted.

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41 See supplementary material at http://dx.doi.org/10.1063/1.4886185 for ultrafast DSC calibration, thermal lag analysis and additional SEM and ultrafast DSC results on SeTe flakes deposited on the ultrafast DSC sensor chips.