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Intermediate crystallization kinetics in Germanium-Tellurides

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ABSTRACT

Germanium-Telluride has been widely studied as a phase-change material due to its fast crystallization speed. The understanding of the crystallization kinetics is important to evaluate the potential applications of the material, but this is limited by the conventional calorimetry with low heating rate and narrow temperature range. We here employed an ultrafast calorimetry method, named flash differential scanning calorimetry, to investigate the crystallization kinetics of Ge_xTe_{100-x} in a wide compositional range ($15 \leq x \leq 55$). By means of the X-ray diffraction, we found the complicated competition between crystalline GeTe and Te (or Ge) phases in these binary alloys. The crystallization kinetics of first crystalline phase were estimated and it was found that, Ge_xTe_{100-x} generally has intermediate crystal growth speed and fragility, which is ascribed to the border between covalent and metallic properties. Component dependences of maximum crystal growth rate (U_{max}) and fragility were investigated, revealing the component in $x = 20.4$ has the lowest U_{max} of 1.22×10^{-3} m s^{-1} with the smallest fragility of 42.2, and the component in $x \approx 50$ possesses the largest U_{max} of 3.5 m s^{-1}. It confirms that, GeTe is the most suitable phase-change material for information storage and $GeTe_4$ is the best media for information transparency in Ge-Te binary. Moreover, a tri-counter pattern was carried out for obtaining the crystal growth rate directly in studied supercooled Ge_xTe_{100-x} liquids ($15 \leq x \leq 55$). In addition, we first found a peculiar component $Ge_{22}Te_{78}$ with terrible thermal properties, i.e., phase separation, low crystallization temperature, ultrahigh fragility and anomalous crystallization kinetics. More importantly, together with the crystallization kinetics parameters of other glass formers, it was found a specific relation between reduced glass temperature (T_{rg}) and U_{max} for which can be benefit to simplify material screenings and performance optimizations.

1. Introduction

Telluride-based chalcogenides, such as GeTe, Sb_xTe_{100-x} and $(GeTe)_x(Sb_2Te_3)_{100-x}$, are of great interest in phase-change memories (PCMs) [1,2] based on the huge difference in electronic and/or optical constant between amorphous and crystalline phases of the materials [3]. Various applications of PCMs generally require the materials with a fast crystallization speed at a temperature close to melting temperature (T_m) that would accelerate switching speed, and a low crystallization speed at a temperature close to glass transition temperature (T_g) that can improve data retention. Understanding crystallization kinetics of these materials in their supercooled liquids, which is the key for data storage of PCMs, would enable the best material compositions to be screened. On the other hand, Ge-Te based chalcogenides exhibit excellent transparency in the far infrared up to 20 μm [4], and this are widely used in waveguide-based applications such as spatial detection [5], biosensing [6], and environmental metrology [7]. Amorphous thermal and structural stability are two important factors for these applications. The amorphous thermal stability can be estimated from the study of crystallization kinetics, i.e., the lower crystallization speed indicates the better amorphous thermal stability. The amorphous

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structural stability is usually evaluated by fragility which can be derived from the crystallization kinetics. Therefore, the crystallization kinetics of supercooled liquids is significant to design the material composition with the best performance.

Conventional differential scanning calorimetry (DSC) has been demonstrated to be a useful tool in the study of crystallization kinetics. However, one of the drawbacks is the low heating rate (1–100 K $\min^{-1}$) in the conventional DSC that limits the experiments in a narrow range of the heating rate. Another issue is related to the amount of the materials needed for the experiments. Usually more than 1 mg in the weight used in the conventional DSC requires the glasses to be prepared by the melt-quenching method, but this is somehow difficult since the Ge-Te alloys can be vitrified only in a narrow compositional range around eutectic point where Ge content is 15 at.% [8]. Therefore, the amorphous Ge-Te in a wide compositional range can only be fabricated as thin film by thermal co-evaporation or sputtering. Obviously, films with a thickness of 0.1–1 μm cannot meet the requirement of large amount of the materials in conventional DSC. These restrictions mentioned above result in the difficulty in the crystallization kinetics study for Ge-Te glasses. Recently, a commercialized ultrafast scanning calorimetry named Flash DSC has been successfully used to study the glass transition and/or crystallization kinetics of polymers [9–11], metallic glasses [12,13], and PCMs [14–16]. Flash DSC has ultrafast heating or cooling rate up to 1×10^6 K s^{-1} and high precision with small sample down to several nanograms in weight [9], and this provides a convenient way to investigate the crystallization kinetics for Ge-Te glasses in a wide compositional range.

Fokin et al. [17] reported experimental maximum crystal growth rate (U_{max}) as a function of the reduced temperature (T_{rg}) for 20 silicate glasses, and claimed a good agreement between theory and experiment. However, such results are limited in silicate glasses, and thus a simplified expression between U_{max} and T_{rg} in diverse glasses is desirable. Recently, Orava et al. [18] investigated the fast and slow crystal growth kinetics in various glasses including metals, oxides, organics, as well as chalcogenides. Correlation between T_g and the temperature T_{max} at which the crystal growth rate is maximum of U_{max} can be formulated. However, such a correlation cannot be built up between U_{max} and T_{rg}, which might be due to the fact that the crystal growth rate used in Ref. 18 is too high or too low and the information on intermediate crystal growth kinetics is absent. Hence, we estimated the crystal growth speeds that are generally slower than those for metals but quicker than those for covalent compounds, and thus we called as intermediate crystallization kinetics for Ge-Te glass. We further discussed the specific relations between U_{max} and T_{rg} (and other parameters).

In this work, we employed the Flash DSC to reveal the crystallization kinetics in Ge_xTe_{100-x} ($15 \leq x \leq 55$) supercooled liquids, and used a viscosity model named Mauro-Yue-Ellison-Gupta-Allan (MYEGA) [19], which has been confirmed to be appropriate to investigate crystallization kinetics in chalcogenide materials [16,20,21]. Vogel-Fulcher equation was employed to describe the relation between T_g and heating rate for estimating the fragility of the Te-rich films that possesses distinct glass transition behavior [22]. It was found that, $Ge_{49}Te_{51}$ (GeTe) possesses the largest U_{max} of 3 m s^{-1}, $Ge_{20.4}Te_{79.6}$ ($GeTe_4$) has the lowest U_{max} of 1.22×10^{-3} m s^{-1} with the smallest fragility of 42.2, and $Ge_{22}Te_{78}$ exhibits peculiar crystallization behaviors and kinetics with an abrupt increase of U_{max} and fragility. Moreover, a specific correlation between U_{max} and T_{rg} is built up for the first time, and this strongly supports the glass former experiences derived from Turnbull.

2. Experimental methods

A series of amorphous Ge_xTe_{100-x} films with a thickness of 1.4 ± 0.2 μm ($15 \leq x \leq 55$) were deposited on SiO_2/Si(100) by the magnetron co-sputtering method using separated Ge and Te target. For each deposition, the base and working pressures were set to ~4×10^{-4} Pa and 0.35 Pa, respectively. The thickness was *in-situ* controlled by a thickness monitor equipped in vacuum chamber and *ex-situ* checked by Veeco Dektak 150 surface profiler. The chemical composition of the film was tuned by the power applied in the sputtering target, and was *ex-situ* examined by energy dispersive spectroscopy (EDS). The flakes were scratched off from the glass substrates for the calorimetry measurements. A pile of scraped off film flakes (the total weight is 1 ± 0.2 mg) was sealed into aluminum pan and tested by NETZSCH instrument DSC204F1 calorimeter at a standard heating rate of 20 K $\min^{-1}$ in a nitrogen-protected ambient. A single flake was loaded on the chip sensor (USF-1) and measured by Mettler-Toledo Flash DSC 1 at a heating rate from 10 to 40000 K s^{-1} under argon gas flow. The methodology of the scraped off flake was examined by optical microscopy and scanning electronic microscopy (SEM). The approximate area that was subjected to ultrafast heating is 60×50 μm^2 as shown in Figs. S1 and S2 in Supplementary Material. The flat morphology of the flake can effectively increase the thermal contact between samples and chip sensor and decrease the experimental uncertainty of the crystallization temperature in the Kissinger plots (see Fig. 1 and Fig. S5). All the measurements were repeated more than 4 times at each heating rate for each film in order to have reproducible results. The details are similar to our previous report [16]. Johnson-Mehl-Avrami (JMA) numerical simulations with the MYEGA model, thermal lag estimation and temperature calibration in the measurement of Flash DSC were emphasized and discussed in details in Supplementary Material.

3. Results and discussion

3.1. Flash DSC traces and Kissinger plots

We examined eleven films with different chemical composition, and the typical Flash DSC traces of the as-deposited films with a heating rate from 10 to 40000 K s^{-1} were shown in Fig. 1. The DSC traces under lower heating rates of 10 and 20 K s^{-1} may be absent in some cases, because the calorimetric signals are extremely weak. On the other hand, the DSC traces under heating rates larger than 5000 K s^{-1} may also be unavailable in some compositions, since the low eutectic melting temperature is ~655 K in Te-rich Ge-Te glasses, resulting in the crystallization signal is overlapped by melting. This is why only the DSC traces up to a temperature of 653 K are shown in Fig. 1. For $Ge_{15}Te_{85}$, there are one glass transition endotherm with onset temperature (T_g) and two crystallization exotherms with peak temperatures (T_p) in each heating rate from 10 to 40000 K s^{-1} as shown in Fig. 1(a). When Ge content increases to ~20 at.%, there is only one T_p as shown in Fig. 1(b) can be observed. This is well agreement with the previous report that was performed by the conventional DSC [23]. However, when Ge content increases to 22 at.%, two T_ps corresponding to crystalline Te and GeTe phases were detected, but this has not been reported yet. Moreover, when the Ge content in the range of 23–33 at.%, the one-step crystallization behavior with one T_p occurs again with the simultaneous crystallized Te and GeTe phases. Two T_ps are observed when Ge content is more than 33 at.% in $Ge_{38}Te_{62}$. However, the first T_p represents the GeTe phase and second one corresponds Te phase, which is different from the previous two-step crystallization behaviors presented in Ge_xTe_{100-x} with $x < 20$ and $x = 22$. The similar crystallization behavior was also confirmed by time-resolved XRD [24]. It has been reported that, Ge-rich Ge-Te generally possesses two-step crystallization behavior corresponding to GeTe and Ge phases [24].

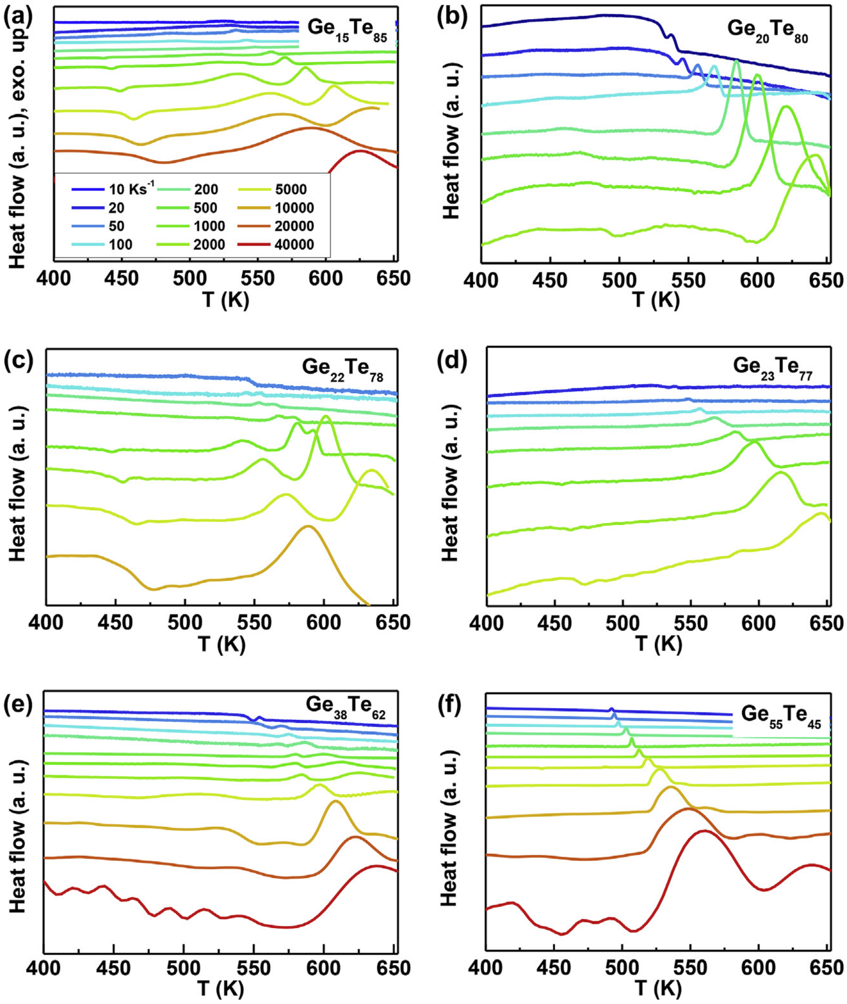

Fig. 1. Flash DSC traces for Ge_xTe_{100-x} with (a) x = 15, (b) x = 20, (c) x = 22, (d) x = 23, (e) x = 38, and (f) x = 55. As depicted in Fig. 1(a), the DSC trace with different color represents the experiment performed by different heating rate. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

T_ps and their JMA numerical simulation with MYEGA model were performed in the Supplementary Material, which confirms the Kissinger method can be employed to investigate the crystallization kinetics of the Ge_xTe_{100-x} films by ultrafast DSC data. The Kissinger plot can be expressed as [25],

$$\ln\left(\phi/T_p^2\right) = -Q/RT_p + A \tag{1}$$

where ϕ is heating rate, T_p is peak of crystallization temperature, Q is activation energy for crystallization, R is the gas constant, and A is a constant. Generally, the fitting plot with the data from conventional DSC at low heating rate and narrow temperature range yields a strict Arrhenius behavior. Nevertheless, the plots of the ultrafast DSC data as depicted in Fig. 2 exhibit non-Arrhenius behavior more or less, and the value of Q decreases continuously when the heating rate increases.

3.2. Crystal growth rate

The crystallization kinetics coefficient U_{kin} is important, and it can be estimated as the following equation [26],

$$\log_{10}U_{kin} = C_1 - \log_{10}\eta \tag{2}$$

where C_1 is a constant, η is the viscosity (Pa s). Here, we employed the MYEGA viscosity model to describe the viscosity and the expression is [19],

$$\log_{10}\eta = \log_{10}\eta_\infty + (12 - \log_{10}\eta_\infty)\frac{T_g}{T}exp\left[\left(\frac{m}{12-\log_{10}\eta_\infty} - 1\right) \times \left(\frac{T_g}{T} - 1\right)\right] \tag{3}$$

where η_∞ is the viscosity (Pa s) at infinite high temperature, T_g is the glass transition temperature (K) measured at the standard heating rate of 20 K min^{-1}, m is fragility index. Following this equation, the temperature dependent U_{kin} (m s^{-1}) can be estimated as shown as the dashed lines in Fig. 2. Then, the temperature dependence of crystal growth rate can be extrapolated based on the following equation [27],

$$U = U_{kin}[1 - exp(-\Delta G/RT)] \tag{4}$$

where R is the gas constant as 8.314 J mol^{-1}K^{-1}, and ΔG is the driving force for crystallization (kJ mol^{-1}). As suggested by Thompson and Spaepen, for the chalcogenide liquids studied in this work, ΔG can be expressed as [26],

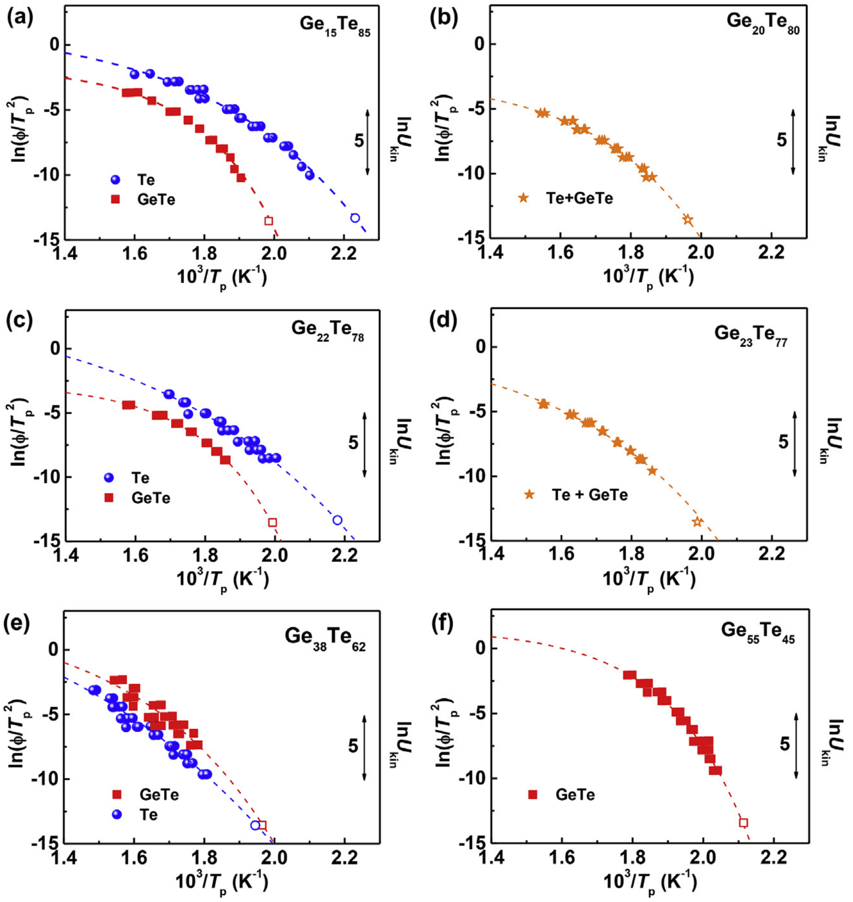

Fig. 2. The Kissinger plots for crystallization of supercooled liquid Ge_xTe_{100-x} with (a) x = 15, (b) x = 20, (c) x = 22, (d) x = 23, (e) x = 38, (f) x = 55, and their temperature dependences of crystallization kinetics coefficient (U_{kin}) fitting by MYEGA model (the dashed lines). The blue spheres and red squares represent the T_ps of successively crystallized Te and GeTe phase, respectively. The orange stars represent the T_ps of simultaneously crystallized Te and GeTe phase. The corresponding open symbols represent the T_p values measured from conventional DSC at a heating rate of 20 K min^{-1}. The degrees of these fittings (R^2) are all larger than 0.99 except to that of $Ge_{38}Te_{62}$. R^2 of T_p value of GeTe and Te phase for $Ge_{38}Te_{62}$ are 0.91 and 0.97, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m}\left(\frac{2T}{T_m + T}\right) \tag{5}$$

where T_m is melting temperature (K), ΔH_m is the latent heat of melting (kJ mol^{-1}), and $\Delta T = (T_m - T)$ is the undercooling temperature (K). T_ms of these Ge-Te films were obtained from the germanium-tellurium phase diagram [28]. ΔH_ms of $Ge_{15}Te_{85}$, $Ge_{20}Te_{80}$, and GeTe are reported as 10.89, 13.67, and 17.9 kJ mol^{-1}, respectively [29,30]. According to conventional DSC measurements, ΔH_ms of $Ge_{33}Te_{67}$ and $Ge_{38}Te_{62}$ can be calculated as 14.70 and 15.76 kJ mol^{-1}. The ΔH_ms of other Ge-Te films referred in this work were estimated by the linear fitting result from above data (see Supplementary Material).

Taking Eqs. (2), (3) and (5) into Eq. (4), the temperature dependent crystal growth rates (U) of Ge-Te supercooled liquids can be extrapolated, as shown in Fig. 3(a). According to these non-Arrhenius crystal growth rates, the value of U_{max} for each component can be estimated. A relation between Ge content and U_{max} for Ge-Te materials are plotted in Fig. 3(b). Obviously, the minimum U_{max} of 1.22×10^{-3} m s^{-1} can be found in $Ge_{20.4}Te_{79.6}$, while a maximum U_{max} of 3.5 m s^{-1} are found in GeTe, implying that GeTe has the fastest crystallization speed in Ge-Te system. Chen et al. first reported that Ge-Te possesses a rapid reversible phase-change behavior with the shortest time for crystallization [31,32], and then Raoux et al. further confirmed the results [33]. This is in excellent agreement with the present conclusion. Interestingly, we found an abrupt increase of U_{max} in $Ge_{22}Te_{78}$ which has never been referred before and must be nature in the peculiar composition due to the breakage of isostatic structure in amorphous Ge-Te. Moreover, a tri-contour plot in Fig. 4 illustrates the relation among component, reduced temperature T/T_m, and U. The crystal growth rate U at any supercooled temperature and in any composition ($15 \leq x \leq 55$) can be obtained from this tri-contour plot. It also explains well why $GeTe_4$ is always used as an optical transmission media into waveguide and why GeTe would be a good candidate for fast phase-change material.

3.3. Crystallization kinetics parameters analyses

Several parameters, such as η_∞, T_g, and fragility m, that reflect the characters in supercooled liquid were derived from MYEGA fitting and listed in Table 1. It was found that, the value of η_∞ estimated from T_p1 and T_p2 in the same composition is different. The η_∞ extrapolated from last crystallization process (T_p2) is more reasonable due to that the liquid at infinite high temperature must suffer the last crystallization process. As we can see that, the value of η_∞ estimated from the last crystallization is in a range from $10^{-2.81}$ to $10^{-3.8}$ Pa s (besides of $Ge_{33}Te_{67}$), which is in line with the convergent value of $10^{-2.93}$ Pa s suggested by Mauro et al. [19,34]. For the derived T_g, the first one estimated from T_p1 is reliable and

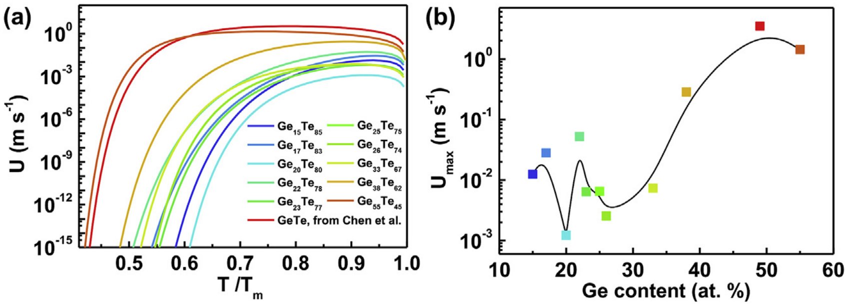

Fig. 3. (a) Reduced temperature (T/T_m) dependent crystal growth rates for first crystallization of Ge-Te materials. (b) Component dependent U_{max} of Ge-Te materials. The results of stoichiometric GeTe that was reported in the previous work are redrawn in here to compare with the crystal growth rates in other materials [16].

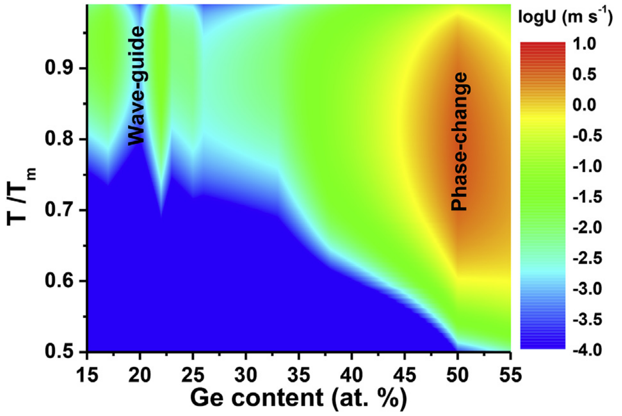

Fig. 4. A tri-contour represents the relationship among component, reduced temperature T/T_m, and crystal growth rate U.

Table 1
Extrapolated parameters from the MYEGA model for Ge-Te system in this work, including η_∞, T_g, U_{max}, T_{max}/T (the reduced temperature at which the U_{max} occurs), and m. m_g is the supercooled liquid fragility estimated from T_g by Vogel-Fulcher equation. The labels "-1" and "-2" in first column represent the parameters extrapolated from first and second T_p, respectively.

Ge content (at.%)	η_∞ (Pa s)	T_g (K)	m	m_g	U_{max} (m s^{-1})	T_{max}/T_m
15–1	$10^{-0.38}$	396	70	66.2	0.0135	0.936
15–2	$10^{-2.93}$	448.6	148	–	0.002	0.945
17–1	$10^{1.59}$	411.5	41.2	60.8	0.028	0.941
17–2	$10^{-2.93}$	449.5	161.7	–	0.0026	0.924
20	$10^{-2.82}$	434	112.9	42.2	0.00122	0.925
22–1	$10^{-0.10}$	404	50.5	106.5	0.0524	0.928
22–2	$10^{-2.93}$	445.3	150.8	–	0.0043	0.895
23	$10^{-3.80}$	413	87.9	71	0.0064	0.929
25	$10^{-3.81}$	418	104	98.9	0.00717	0.910
26	$10^{-2.93}$	445.6	128.2	124.9	0.00307	0.889
33	$10^{2.92}$	470	54.6	–	0.00737	0.898
38–1	$10^{0.21}$	460.8	65.3	–	0.2856	0.892
38–2	$10^{-2.93}$	429	49.1	–	0.213	0.929
50[a]	$10^{-3.20}$	432.1	130.7	–	3.5	0.79
55	$10^{-2.69}$	435.4	148.4	–	1.437	0.743

[a] The parameters of GeTe are obtained from previous study by measurement of ultrafast DSC [16].

useful to investigate crystallization kinetics. T_g increases with increasing Ge content in Te-rich Ge_xTe_{100-x} system except a narrow compositional range ($22 \leq x \leq 25$ at.%). The linear relation between Ge content and T_g was reported in previous study [35], but such an abrupt decrease in T_g has not been reported yet. Nevertheless, this anomalous glass transition behavior was confirmed by ourselves with the method of conventional DSC (the details are not shown in here).

The third parameter derived from MYEGA model is fragility m which is used to define the sensitivity of liquid structure to temperature changes. It is generally classified into three categories: fragile, intermediate, and strong. As listed in Table 1, the values of m both derived from T_p1 and T_p2 are all undisciplined. In previous studies [16,20,21], the fragilities of phase-change materials can be obtained directly by the MYEGA model because of their weak glass transition signal is overlapped by intense crystallization signal. Therefore, the fragility m for $Ge_{33}Te_{67}$, $Ge_{38}Te_{62}$ and $Ge_{55}Te_{45}$ is reliable since no obvious glass transition is presented, but it is unsuitable to estimate the fragility of other supercooled liquids. For the liquids which exhibit evident glass transition behaviors, we can use Vogel-Fulcher equation to estimate the fragility via the relation between T_g and $\ln ø$ ($ø$ here is heating rate). It can be expressed as [22],

$$\ln \varnothing = \ln B - DT_0/(T_g - T_0) \quad (6)$$

where B is the time scale parameter in glass forming system [36], D is the strength parameter representing how close the liquid obeys Arrhenius law, and T_0 is the asymptotic value of T_g and within the limit of infinitely slow heating and/or cooling rate. Then, the fragility m_g can be estimated by this equation [37],

$$m_g = \frac{DT_0T_g}{(T_g - T_0)^2 \ln 10} \quad (7)$$

where T_g is the standard glass transition temperature which can be obtained from the MYEGA model (listed in Table 1). The fitting results are exhibited in Fig. 5(a). Taking D and T_0 estimated from the fitting into Eq. (7), we can obtain the fragility m_g for Ge_xTe_{100-x} films with $15 \leq x \leq 26$ (see the details in Supplementary Material), and the results are depicted in Fig. 5(b). When $x \leq 26$, Ge_xTe_{100-x} exhibits obvious glass transition behavior with the predominant nonmetallic properties. However, it is different from S- and Se-based chalcogenides and shows metallic properties when $x \geq 33$. This results in the weak or disappeared T_g in such Ge-rich film. Therefore, it was divided into two sections to analysis the variation of fragility for Ge-Te supercooled liquids. As shown in Fig. 5(b), the fragility m extrapolated from the MYEGA model shows a linear increase in Ge_xTe_{100-x} film with $33 \leq x \leq 55$. Nevertheless, the fragility m_g calculated by the Vogel-Fulcher equation is nonmonotonous in a compositional range of $15 \leq x \leq 26$. There is a minimum in fragility of $Ge_{20.4}Te_{79.6}$, which corresponds to an ideal isostatic structure in Ge-Te system with an MCN close to 2.4 and is in agreement with the previous results [38]. An abrupt increase of fragility occurs at $x = 22$, suggesting that $Ge_{22}Te_{78}$ is not a potential material to be used in optical transmission. The component

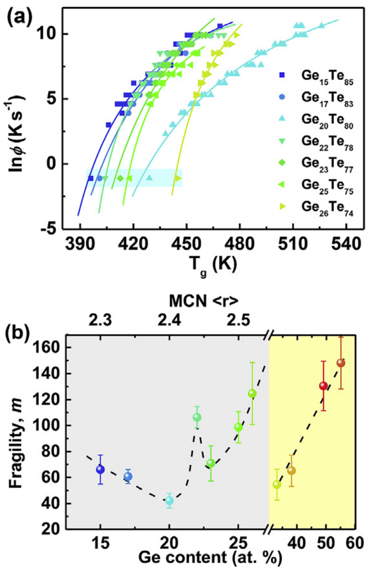

Fig. 5. (a) The relationship between T_g and lnϕ for Ge$_x$Te$_{100-x}$ ($15 \le x \le 26$). T_gs at high heating rate ($\phi > 50$ K s^{-1}) were all measured by Flash DSC (the traces are not shown in here), and the T_gs at low heating rate ($\phi = 20$ K min^{-1}), which are shown in the light blue shadow, were obtained from the MYEGA model (listed in Table 1). The curves are fitting results performed through Vogel-Fulcher equation with $R^2 > 0.96$. (b) Component or MCN (mean coordinate number) dependence of fragility for Ge$_x$Te$_{100-x}$. The dashed line is a guide for eye. The gray and yellow shadow indicates covalent (nonmetallic) domain and metallic domain structure, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

dependent fragility was performed in many chalcogenide systems, such as Ge-S [39], Ge-Se [40], As-Se [41], and Ge-As-Se [42], the minimal fragility generally presents in the compound with MCN is near 2.4, but such a sharp shoulder peak as shown in Fig. 5(b) has not been found yet.

3.4. The specific relation between T_{rg} and U_{max}

We plotted the T_{max} and T_g listed in Table 1 together with data from the literature, and found a linear relation between T_g and T_{max} as depicted in Fig. 6(a). It can be expressed as,

$$T_{max} = 1.5 \times T_g \tag{8}$$

which is in accordance with the result suggested by Orava et al. [18]. Therefore, another equation can be extrapolated and expressed as,

$$T_{max}/T_m = 3/2 \times T_{rg} \tag{9}$$

where $T_{rg} = T_g/T_m$ is the reduced glass temperature. As we know, the reduced temperature T_{max}/T_m must less than 1. According to Eq. (9), T_{rg} must be less than 2/3. As we know, however, the T_{rg} can be larger than 2/3 in many materials with good glass form ability. Therefore, as shown in Fig. 6(b), it is believed to describe the relation between T_{rg} and logU_{max} by piecewise function, which can be expressed as:

When $T_{rg} < 2/3$,

$$\log U_{max} = \log U_s - 10 \times exp\left[5.88 \times \left(T_{rg} - 2/3\right)\right] \tag{10}$$

where U_s is the speed of sound and employed as 1000 m s^{-1} in here.

When $T_{rg} \geq 2/3$, above expression has no physics significance, and the relation can be described as,

$$\log U_{max} \leq -6 \tag{11}$$

Apparently, "$T_{rg} = 2/3$" is the key boundary for estimation of U_{max}, which is also the most important boundary for judging whether material can be easily formed into glass state. Kauzman noted T_{rg} is approximately 2/3 for a number of materials which easily form glasses in bulk [43], and Turnbull suggested T_{rg} must lie considerably below 2/3 for the materials which do not form glasses [44]. These criterions are all suitable for estimating crystallization speed of glass former. As noted in Fig. 6(b), the gray region represents a good glass former with very low crystallization speed (U_{max} generally less than 10^{-6} m s^{-1}), in which a large size amorphous bulk is easily formed. This includes the majority of organics and some of oxides. The green region represents the glass former with T_{rg} close but less than 2/3, in which a small size glass bulk can be formed. The blue region represents intermediate glass former with an U_{max} in a range from 1×10^{-4} to 1 m s^{-1}. Such materials are difficult to be fabricated into bulk, but can be prepared as amorphous thin film. Ge-Te materials studied here is a typical intermediate glass former. Lots of metals are bad glass former that are located at the yellow region, it possesses very fast crystallization speed (U_{max} can larger than 1×10^2 m s^{-1}). It should be noted that, the speed of sound is the upper limitation for materials' crystallization speed.

From the results of Fig. 6(b) and/or Eqs. (9) and (10), it makes possible that the U_{max} of materials can be directly estimated by their T_{rg}. The glass form ability and amorphous stablity can also be predicted. It implies that, T_{rg} dependence of U_{max} becomes a universal criterion for screening materials, which is very benefit to

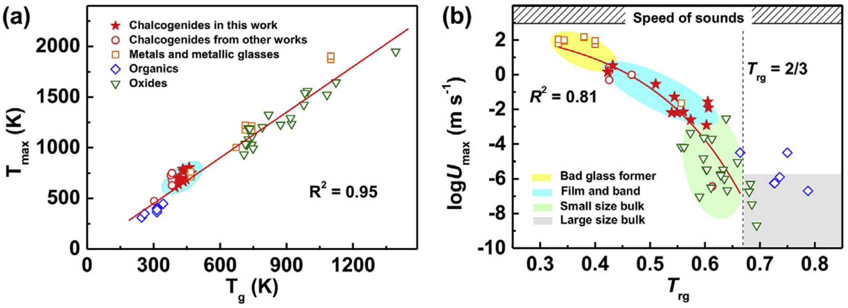

Fig. 6. The relations between (a) T_g and T_{max}, and (b) T_{rg} and logU_{max}. Red stars in light blue shadow represent the data of Ge-Te in this work. The red circles represent the data of Ge$_2$Sb$_2$Te$_5$, AgIn-Sb$_2$Te, and Se [14,15,45–47]. According to the data collected by Fokin et al. and Orava et al. [17,18], the relative parameters of other glass-forming systems, such as metals and metallic glasses, organics and oxides, are shown in here in order to find out their potential relations. The speed of sound in Fig. 6(b) sets a physical limit to the crystal growth rate. The straight and curved lines are the best fits with fitting degrees are 0.95 and 0.81, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

both the fundamental research in crystallization kinetics and the applications of glass formers. For instance, GeTe has a T_{rg} of ~0.45, so it is a typical thin film PCMs with U_{max} is number of meter per second. $GeTe_4$ has T_{rg} is ~0.6, indicating it is an intermediate glass former and can be formed into film and small size bulk, so it becomes a potential material for optical waveguide.

4. Conclusions

The crystallization kinetics of Ge_xTe_{100-x} ($15 \le x \le 55$) were investigated by the method of Flash DSC. Together with XRD, we detected the complicated crystallization behaviors with the competition between Te and GeTe crystalline phases. The MYEGA viscosity model was combined into JMA numerical simulations to help the study of crystallization kinetics. It was found that, typical waveguide material $GeTe_4$ has the lowest crystallization speed in Ge-Te system with the U_{max} of $1.22 \times 10^{-3}\ m\ s^{-1}$ at 0.925 T_m, and conventional PCM GeTe possesses the fast crystallization speed with the U_{max} of $3.5\ m\ s^{-1}$ at 0.79 T_m. Putting the temperature dependent crystallization speed of these 11 samples together, a tri-contour pattern representing the relationship among component, reduced temperature T/T_m, and crystal growth rate U, was built. The crystallization speed of Ge-Te can be estimated at any composition and at any supercooled temperature from the contour plot. Moreover, the component dependence of fragility was carried out, it exhibits a linear increase when Ge content increases from 33 to 55 at.%. However, when Ge content increases from 15 to 26 at.%, it shows a non-monotonous variation with a minimal fragility at $Ge_{20.4}Te_{79.6}$. Moreover, an anomalous crystallization behavior and kinetics were first found in this work at the peculiar composition of $Ge_{22}Te_{78}$ exhibiting bad thermal stability (phase separation and low crystallization temperature), large U_{max} of $0.0524\ m\ s^{-1}$, ultrahigh fragility is 106.5. The results are helpful to understand crystallization kinetics of Ge-Te alloys and their applications. Together with parameters of crystallization kinetics from other glass formers, we confirmed a relation as $T_{max} = 1.5\ T_g$, and revealed a relation of T_{rg} dependent U_{max} as listed in Eqs. (10) and (11). It can be a universal criterion for screening materials and benefit to both the fundamental research in crystallization kinetics and the applications of glass formers.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.actamat.2018.10.051.

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