New Methods Versus Old Questions: Crystallization Kinetics of S, Se, and Te

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ABSTRACT: Using conventional differential scanning calorimetry (DSC) and Flash DSC, we revisited the old question of crystallization kinetics of chalcogens. Together with the appropriate viscosity models and Stokes–Einstein relation, the quantitative results of crystallization kinetics in chalcogenide supercooled liquids were revealed. It showed that the fragilities of S, Se, Te are 126, 67.5, 60, and the maximum crystal growth rates are 9.7 × 10⁻³, 1.3 × 10⁻⁵, and 0.47 m s⁻¹ at 0.91, 0.94, and 0.86 Tₘ, respectively. Such results not only benefit to understand the fundamental science but also help to design new chalcogenide compositions for applications.

1. INTRODUCTION

Chalcogenide glasses have been used in many fields including biosensing, lithography, optical lenses, waveguides, gratings, and fibers.¹ Recently, ultrafast crystallization kinetics in chalcogenide glasses has made them important in applications of electronic memories and optical recordings.² Crystallization kinetics of chalcogenide glasses plays a key role in determining the transport mechanism, thermal stability, and phase transition. Understanding the crystallization mechanism of chalcogenide glasses is essential for the applications mentioned above.

The crystallization kinetics in chalcogenide supercooled liquids is an old topic, which is usually investigated by using either isothermal or non-isothermal method of differential scanning calorimetry (DSC). Compared with the isothermal experiments that are generally time-consuming,³ the non-isothermal method is frequently employed to investigate the crystallization kinetics. In last decades, the chalcogenides of binary,⁴⁻⁷ ternary,⁸⁻¹⁴ and quaternary,¹⁵⁻¹⁶ were extensively studied by the non-isothermal method. For the crystallization kinetics of elemental chalcogens, selenium (Se) is the most frequently studied due to its low critical cooling rate (Rₖ), moderate crystallization temperature (Tₖ) and glass transition temperature (Tₜ). In the early days, Ryschenkow and Faivre used optical microscope to observe the crystal grain size under isothermal condition and determine the crystal growth rate of Se at the specific temperatures.¹⁷ Recently, Málek et al. showed the results again by IR optical microscope and scanning electron microscope,¹⁸ and further employed the viscosity data around Tₘ and melting temperature (Tₘ) to discuss the crystallization kinetics in supercooled Se liquid.¹⁹,²⁰ To our knowledge, however, there is no report on the crystallization kinetics of other two elemental chalcogens, that is, sulfur (S) and tellurium (Te). Only several viscosity data around Tₘ for S and Te liquids were reported.²¹⁻²³

Quantification research of elemental chalcogens is significantly important in basic scientific researches. Nevertheless, the lower Tₙ and higher Rₖ make it difficult to investigate crystallization kinetics of S and Te by conventional methods. Fortunately, a novel ultrafast calorimetry named Flash DSC, which has been proved successfully to study the crystallization kinetics in chalcogenide phase-change materials, like Ge₂Sb₂Te₅ (GST),²⁴⁻²⁵ AgIn-Sb₂Te (AIST),²⁶ Ge–Sb,²⁷ and GeTe,²⁸⁻²⁹ could be a good choice to investigate the crystallization kinetics for elemental chalcogens, since it is featured with wide measurement temperature range (~100 to 450 °C) and ultrafast heating and cooling rates (40 000 and 10 000 K s⁻¹, respectively). In this work, together with the viscosity data and viscosity models, we employed conventional and/or Flash DSC to study the crystallization kinetics of elemental chalcogens. Kinetic parameters achieved from the experiments are useful to design materials for various applications.

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2. EXPERIMENTAL METHODS

2.1. Preparation of S Glass. The raw material is crystalline S powder with purity of 99.999 atom % for the preparation of amorphous sulfur. As shown in Figure 1a, we found the melting temperature ($T_m$) was 385 K and the critical cooling rate ($R_c$) was slightly larger than 30 K s$^{-1}$. The $R_c$ could be determined clearly in the enlarged view that was shown in Figure 1b, as 50 K s$^{-1}$. Therefore, in situ preparation of S glass and then the study of its crystallization kinetics became feasible by using Flash DSC.

2.2. Preparation of Se Glass. The raw material is bulk Se with purity of 99.99 atom %. Note that the glass transition temperature ($T_g$) of Se is very close to room temperature (RT), and its crystallization temperature ($T_c$) is just slightly higher than RT; these reasons would lead to that amorphous Se crystallizes at RT for a long time. As shown in Figure 2a, here we used X-ray diffraction method to confirm that Se was partially crystallized. Thus, such raw material should be reamorphized before studying crystallization kinetics. As depicted conventional DSC traces in Figure 2b, it can be seen that the $R_c$ of Se is only 2 K min$^{-1}$, which indicates both conventional DSC and Flash DSC can be employed to in situ preparation of Se glass and the study of its crystallization kinetics.

2.3. Preparation of Te Glass. The raw material is Te bulk with purity of 99.99 atom %. We used four methods to prepare amorphous Te, including magnetron sputtering, in situ preparation by Flash DSC, single copper roller sling method, and powder spraying method. However, pure amorphous Te cannot be obtained by these four methods due to the ultrahigh $R_c$ (more than $1 \times 10^{10}$ K s$^{-1}$) and/or ultralow $T_c$ (near RT) of Te glass. Ultrahigh $R_c$ and ultralow $T_c$ also make it impossible to study crystallization kinetics of Te glass under the present experimental tools. Thus, we here only investigated it by using Stokes–Einstein relation and the viscosity data of Te from the literature.

3. RESULTS

3.1. Crystallization Kinetics of S Glass. Flash DSC was employed to in situ fabricate S glass. The cooling rate is 1000 K s$^{-1}$, which is higher than the $R_c$ of S glass. Figure 3 showed the typical Flash DSC traces at different heating rate, that is, 10, 20, 50, 100, 200, and 500 K s$^{-1}$. The crystallization peak temperature ($T_p$) increases with increasing heating rate. Henderson confirmed that, with Johnson-Mehl-Avrami (JMA) kinetics, the peak temperature of crystallization on heating in DSC corresponds to a transformed fraction that is always close to 63% ($T_{0.63}$), and this also validates the use of Kissinger method to determine the temperature-dependent crystallization rate. The JMA numerical simulations of DSC peaks for S were performed in this work, and the details could be seen in previous work. The inset of Figure 3 depicts the comparative $T_p$ results of S between Flash DSC tests and JMA numerical simulations. As we can see, the deviation is insignificant even at a high heating rate of 500 K s$^{-1}$, indicating that $T_p$ values obtained from Flash DSC are all in agreement with $T_{0.63}$. Thus, the data from Flash DSC are viable to depict the crystallization kinetics.

The Kissinger method was performed, and the result was shown in Figure 4a. It can be expressed as:

\[ \ln\left(\phi / T_p^2\right) = -Q / RT_p + A \]

Figure 1. (a) Flash DSC traces for S glass at different cooling rate from 30 to 200 K s$^{-1}$ with the heating rate of 100 K s$^{-1}$. (b) The enlargement of gray shadow in (a); the arrows indicate the crystallization peaks.

Figure 2. (a) XRD curve of Se element. (b) Conventional DSC traces for Se at different cooling rate.

Figure 3. Typical Flash DSC traces of S at different heating rates from 10 to 500 K s$^{-1}$. (inset) The comparative $T_p$ results from Flash DSC tests and JMA numerical simulations.

Figure 4. (a) Kissinger plot and relative $U_{\text{kin}}$ of S, the data are transformed from $T_p$ values obtained by Flash DSC. (b) Angell plots of S. The red dashed line is fitted by VFT model. The yellow line is the decoupled Angell plot with a decoupling coefficient of 0.545.
behavior was revealed in supercooled liquid S by Flash DSC as shown in Figure 4a. Following Henderson’s suggestion, the data depicted in Figure 4a can be considered as relative crystallization kinetics coefficient, \( U_{\text{kin}} \) (m s\(^{-1}\)). Then, the crystal growth rate, \( U \) (m s\(^{-1}\)) can be extrapolated as

\[
U = U_{\text{kin}} \left[ 1 - \exp\left( -\Delta G / RT \right) \right]
\]

(2)

where \( R \) is the gas constant as mentioned above, and \( \Delta G \) (kJ mol\(^{-1}\)) is the crystallization driving force, which can be expressed as

\[
\Delta G = \frac{\Delta H_m - \Delta T}{T_m} \left( \frac{2T}{T_m + T} \right)
\]

(3)

where \( \Delta H_m \) (kJ mol\(^{-1}\)) is latent heat of melting, \( T_m \) (K) is melting temperature, and \( \Delta T = T_m - T \) is the undercooling temperature. On the basis of Stokes–Einstein relation, the relationship between \( U_{\text{kin}} \) and viscosity \( \eta \) (Pa s) could be obtained as

\[
\log_{10} \eta = C - \log_{10} U_{\text{kin}}
\]

(4)

where \( C \) is a constant, indicating the difference between viscosity and reciprocal of \( U_{\text{kin}} \). It can be obtained from adjusting viscosity at \( T_m (\eta_{\text{kin}}) \). We here employed Vogel–Fulcher–Tammann (VFT) viscosity model to account for the temperature-dependent viscosity of supercooled sulfur liquid. The VFT model can be expressed as

\[
\log_{10} \eta = \log_{10} \eta_\infty + \frac{A}{T - T_0}
\]

(5)

where \( \eta_\infty \) (Pa s) is the viscosity at infinite high temperature and \( A \) (K) and \( T_0 \) (K) are temperature-related parameters, respectively. Thus, we got \( U_{\text{kin}} \) as

\[
\log_{10} U_{\text{kin}} = C - \log_{10} \eta_\infty - \frac{A}{T - T_0}
\]

(6)

As shown in Figure 4b, the hollow data were transported from \( U_{\text{kin}} \) by using eq 4. The temperature-dependent viscosity data were adjusted by \( \eta_{\text{kin}} = 1 \times 10^{-2.17} \) Pa s to and it yields the constant \( C \) is 2.5. Then, the red dashed curve in Figure 4b can be fitted by VFT model expressed in eq 5, with the \( \eta_\infty = 1 \times 10^{-3.736} (\pm 0.0705) \) Pa s, \( A = 294.3 \) (\( \pm 14.76 \)) K, \( T_0 = 202.9 \) (\( \pm 2.27 \)) K, and the fitting degree \( R^2 > 0.994 \), it needs to be emphasized we employed the standard \( T_g \) of 234.5 K for S glass here. However, it produces a viscosity nearly 6 orders of magnitude lower than the expected \( \eta = 1 \times 10^{12} \) Pa s at \( T_g \). Thus, it is necessary to employ the concept of decoupling between \( U_{\text{kin}} \) and \( \eta \) proposed by Ediger et al. to solve this mismatch. They proposed that the Stokes–Einstein relation would be broken below \( T_m \) especially in a fragile supercooled liquid, and the expression of \( U_{\text{kin}} \propto \eta^{-\xi} \), where \( \xi \) is a decoupling coefficient, is more suitable for describing the relation between \( U_{\text{kin}} \) and \( \eta \). Here, we used \( \xi = 0.545 \) and obtained a new Angell plot as a yellow curve shown in Figure 4b. The fractality of supercooled sulfur liquid can be estimated as

\[
m = \left( \frac{\partial \log \eta}{\partial (T/T_g)} \right)_{T_g}
\]

being 126.

With eq 6, the temperature dependence of absolute \( U_{\text{kin}} \) can be extrapolated as shown in Figure 5a. Together with eqs 2 and 3, and the obtained absolute \( U_{\text{kin}} \Delta H_m \) (1.962 kJ mol\(^{-1}\)), \( T_m \) (385 K), the temperature-dependent \( U \) can be extrapolated, and the results are shown in Figure 5b. It yields the maximum crystal growth rate (\( U_{\text{max}} \)) of \( 9.7 \times 10^{-3} \) m s\(^{-1}\) at 351 K (0.91 \( T_m \)).

3.2. Crystallization Kinetics of Se Glass. As we know that \( T_g \) and \( T_r \) (or \( T_p \)) of Se glass are all slightly higher than \( RT \), and the \( R_g \) is very low, these conditions make the study of crystallization kinetics for Se glass easier compared with other chalcogens. Ryschenkow et al. and Mälek et al. observed the crystal growth rate of Se directly by optical microscope. Here we employed DSC together with viscosity model to investigate the crystallization kinetics of Se glass. The conventional DSC traces were displayed in Figure 6a with heating rates from 1 to 20 K min\(^{-1}\), and the corresponding cooling rate was 20 K min\(^{-1}\). The Flash DSC traces were displayed in Figure 6b with the heating rate of 1, 2, 5 K s\(^{-1}\), respectively, and the corresponding cooling rate is 1 K s\(^{-1}\). All of the cooling traces were not shown here. It can be seen that \( T_p \) increases with increased heating rate. From the heating trace of 1 K min\(^{-1}\), \( T_p \) \( T_T \) and \( \Delta H_m \) can be obtained as 313.5 K, 494 K, and 7.31 kJ mol\(^{-1}\), respectively. As noted in Figure 6b, the crystallization signal in a heating rate of 5 K s\(^{-1}\) is weaker than that in a heating rate of 2 K s\(^{-1}\). It implies that the crystallization signal is partially overlapped by melting, which results in inaccurate \( T_p \) value in a heating rate of 5 K s\(^{-1}\). Thus, we here only employed \( T_p \) measured from Flash DSC with heating rates of 1 and 2 K s\(^{-1}\) and conventional DSC with heating rates of 1–20 K min\(^{-1}\) to investigate the crystallization kinetics of Se glass.

JMA numerical simulation was performed, but the details were not displayed here. Similar to the analysis for S, the results demonstrated that the Kissinger method can be used to study the crystallization kinetics of Se glass. By using eq 1, the Kissinger plot about Se glass can be performed as shown in Figure 7a. It exhibits a gradual change of the experimental data extracted from conventional and Flash DSC. Using eq 4, we can obtain the transposed viscosity data as red spheres displayed in Figure 7b. It was adjusted by \( \eta_{T_m} = 1 \times 10^{0.58} \) Pa s.
However, Ryschenkow et al.17 only measured the growth rate along crystal growth rate along 

\[ a \] direction, because it is difficult to detect the growth rate along \( a \)-direction only by optical microscope. The missing underestimation of total crystal growth rate for Se glass.

Absolute temperature dependence of \( U_{\text{kin}} \) was obtained by eq 6, and the result was shown in Figure 8a. Together with the

\[ T_{m} \] for GST by the Stokes–Einstein relation (eq 1) and the DSC method is insensitive to the direction of crystal growth, and thus our result is more reasonable.

3.3. Crystallization Kinetics of Te Glass. Since it was failed to prepare Te glass, the viscosity data were employed to investigate its crystallization kinetics. Fitting the viscosity data reported from Davis23 by Mauro-Yue-Ellison-Gupta-Allan (MYEGA) viscosity model, the Angell plot of Te glass can

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

\[ \log_{10} U_{\text{kin}} = C' - \log_{10} \eta_{\infty} - (12 - \log_{10} \eta_{\infty}) \frac{T_{g}}{T} \times \exp \left[ \frac{m}{12 - \log_{10} \eta_{\infty} - 1} \left( \frac{T_{g}}{T} - 1 \right) \right] \]

\[ U_{\text{kin}} = \frac{kT}{3 \pi a^{2} \eta} \]

\[ k \] is Boltzmann’s constant as \( 1.38 \times 10^{-23} \) J K\(^{-1}\), \( a \) (nm) is an effective atomic diameter or jump distance. This relation appears to work rather well for high-temperature liquids. With \( a \) of 0.3 nm and \( \eta \) of 1 \( \times 10^{-23} \) Pa s at \( T_{m} \) (725 K) for Te, the absolute \( U_{\text{kin}} \) at \( T_{m} \) can be obtained as 2.333 m s\(^{-1}\). However, the relative \( U_{\text{kin}} \) at \( T_{m} \) in Figure 9b is 177 m s\(^{-1}\), which is 76 times higher than the absolute value. Therefore, we adjusted the relative \( U_{\text{kin}} \) to the absolute one that was displayed as red curve in Figure 9b and thus obtained the constant \( C' \) of 1.88.

With the conventional DSC, \( T_{m} \) was measured to be 725 K, and \( \Delta H_{m} \) was 19.35 kJ mol\(^{-1}\) for crystalline Te. Together with

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

\[ \log_{10} U_{\text{kin}} = \log_{10} \eta_{\infty} + (12 - \log_{10} \eta_{\infty}) \frac{T_{g}}{T} \times \exp \left[ \frac{m}{12 - \log_{10} \eta_{\infty} - 1} \left( \frac{T_{g}}{T} - 1 \right) \right] \]

\[ \log_{10} U_{\text{kin}} = C' - \log_{10} \eta_{\infty} - (12 - \log_{10} \eta_{\infty}) \frac{T_{g}}{T} \times \exp \left[ \frac{m}{12 - \log_{10} \eta_{\infty} - 1} \left( \frac{T_{g}}{T} - 1 \right) \right] \]

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these obtained parameters and the absolute $U_{\text{kin}}$, the temperature-dependent crystal growth rate $U$ can be extrapolated by using the eqs 2 and 3. As shown in Figure 10a,b, the maximum crystal growth rate $U_{\text{max}}$ is 0.36 m s$^{-1}$ at 640 K ($0.89 T_m$).

Figure 10. (a) Temperature-dependent crystal growth rate for Te. (b) Reduced temperature-dependent crystal growth rate for Te.

The analyses above did not consider the decouple of Stokes–Einstein relation at lower temperature $T_g$ for Te glass, which however is important in crystallization kinetics study. Nevertheless, the lack of crystallization and/or viscosity data around $T_g$ limits us to determine this decoupling coefficient in Te supercooled liquid. With the Mossbauer spectrum, the crystallization temperature of amorphous Te was detected to be very close to RT. Therefore, it is reliable to consider that $T_g$ is 300 K at a heating rate of 20 K min$^{-1}$. By Kissinger method, it yields the relative $U_{\text{kin}}$ of $3.7 \times 10^{-6}$ m s$^{-1}$ at 300 K (hollow start in Figure 11a). Then, an absolute $U_{\text{kin}}$ at 300 K can be estimated as $4.87 \times 10^{-8}$ m s$^{-1}$ (solid start in Figure 11a). With the decoupling coefficient $\xi$ of 0.67, a decoupled absolute $U$ can be obtained as blue curve through the absolute $U_{\text{kin}}$ value at 300 K, and the result is shown in Figure 11a. By using eq 2, the decoupled temperature-dependent $U$ of Te glass is revealed as blue curve depicted in Figure 11b. A significant difference between original and decoupled $U$ (and $U_{\text{kin}}$) is found, especially at a lower temperature range. The inset of Figure 11b shows that the real $U_{\text{max}}$ is 0.47 m s$^{-1}$ at 624 K ($0.86 T_m$).

4. DISCUSSION

In the paper, the kinetics parameters are basically related only to crystal growth rate, but almost no information on the nucleation rate can be found. Therefore, the role of the nucleation on crystallization kinetics of chalcogens should be elucidated. It is well-known that crystallization kinetics of Se is growth-dominant, and thus the effect of nucleation on the crystallization kinetics is negligible. However, there is no report on whether the crystallization kinetics S and Te is growth- or nucleation-dominant. This could be solved by the isothermal method in the future. Here, we estimated the JMA kinetic exponent ($n$) close to 1.5 at a temperature of 272 K for S by non-isothermal method, indicating that the nucleation rate would not affect the crystallization at a temperature more than 272 K, which is far from $T_{\text{max}}$ of S ($351$ K). The details for such an estimation are similar to the description in ref 42 and not shown here. For Te, it is believed that a larger amount of vacancies and the weak bond energy in Te clusters make the nucleation easily. Thus, the nucleation would have not much effect on the crystallization for chalcogenide elements in this work.

Table 1 lists the obtained parameters of crystallization kinetics for three chalcogens. We can conclude that all the values of $\eta_0$ are converged into the standard value of $1 \times 10^{-2.05}$ Pa s reported by Zheng et al. The value of $U_{\text{max}}$ is maximum for Te and minimum for Se with the difference of ~2 to 3 orders of magnitude in each other. The lower $U_{\text{max}}$ is, the larger reduced temperature $T_{\text{max}}/T_m$ is, which follows the normal rule concluded by Orava et al. Moreover, the relation between $U_{\text{max}}$ and $T_{\text{g}}$ is in agreement with the empirical rule suggested by Chen et al. The relation between fragility $m$ and decoupling coefficient $\xi$ for the chalcogens was displayed in Figure 12. It is evident that the present results are roughly in line with the relation reported by Ediger et al., $\xi \approx 1.1-0.005m$, as shown the red line in Figure 12.

Figure 13 shows the reduced temperature ($T/T_m$) dependent crystal growth rate for different materials, including oxide, organic, metallic, and chalcogenide glasses. The obtained data of S, Se, and Te in this work are also displayed in Figure 13. As we know, phase-change materials, such as conventional GST, GeTe, AgIn-Sb$_2$Te (AIST), and so on, are generally Te based, due to their fast crystallization kinetics. The addition of the elements such as Ge, Sb, and others, into Te-based materials could accelerate the crystal growth rate around $T_m$ but reduce it near $T_g$. The properties with fast crystallization speed at high temperature and good thermal stability at low temperature are essential for phase-change materials. The fast
crystallization kinetics of Te makes it difficult to form bulk glasses via the conventional water-cooling method, although the doping of good glass elements like As could improve the glass-forming ability.

The crystal growth rate in Se glass is faster than that in SiO2, slower than that in s-terphenyl (OTP), and close to that in Na2O·SiO2. The large Teg (0.636) implies that Se is a good glass former. Se-based materials are easily formed into bulk glasses with different dopant of Ge, As, and others, and they are always the first choice to prepare the bulk chalcogenides. As depicted in Figure 13, the crystal growth rate in As5Se3 is lower, and Teg is larger apparently when As is introduced into Se matrix. In contrast, it does not encourage Se as the base material for phase-change application, but appropriate doping can enhance the thermal stability greatly.56

It is highly desired that the crystallization in glass is controllable. Among three chalcogens, S glass possesses moderate crystal growth rate, that is, slightly lower than the typical metallic glass Cu50Zr50. The moderate growth rate makes it a good candidate to create glass-ceramic in S-based glasses like Ge−S47,48 and Ge−Ga−S.49,50 Doping nonmetallic element into S matrix can obtain good glass former, for example, As5S3, which has an ultralow crystal growth rate (black rhombuses in Figure 13). This makes As5S3 an excellent material for optical lens and material in early time,51 its submicron crystal growth rate could be very different from that of a single-element chalcogen from Figure 13. For example, crystal growth of As5S3 glass is so much slower than S glass, even slower than Se glass, while Ge−S and Ge−Ga−S glasses may exhibit relatively much faster crystal growth. This indicates that the crystal growth rates could range very broadly among S-based glasses, and competitive factors from other glass-forming elements such as Ge, Ga, and so on could affect the crystal growth rates greatly. However, the present study does not intend to categorize and compare their crystal growth rates just in terms of relative crystal growth rates of chalcogen elements. Although it is well-accepted that Te-based glasses have a faster crystallization rates and thus the glass community generally search materials with fast crystallization rate based on Te-glasses, it is also possible to tune crystallization rate using suitable glass-forming elements.

Previously, Jones et al. used molecular dynamics and density functional approaches to study the ground state geometries of sulfur and selenium clusters.55,56 Such investigation was also performed on amorphous tellurium recently.57 It was found that the chains in amorphous Te are shorter than those in S and Se, and the threefold-coordinated Te atoms can be located at the branches. Mostly, it was claimed that ~37% of total volume as the cavities are presented in amorphous Te, but this has not been reported in amorphous S and Se.57 A mass of cavities can help to realize the fast crystallization speed in amorphous Te that is also the characteristic in Te-based phase-change materials.58

5. CONCLUSIONS

The conventional and Flash DSC were performed to study the crystallization kinetics of elemental chalcogens, that is, S, Se, and Te. Together with viscosity model, the temperature dependences of Ucr, η, and U were extrapolated. It was found that their viscosities at infinite high temperature are convergent to the standard value of 1 × 10−2.95 Pa s, and the relation between fragility (m) and decoupling coefficient (ξ) roughly follows Ediger’s experimental equation, that is, ξ ≈ 1.1−0.005m. These verify the reliability of the present study of crystallization kinetics for three elemental chalcogens. The maximum crystal growth rates of S, Se, and Te are 9.7 × 10−6, 1.3 × 10−6, and 0.47 m s−1 at 0.91 Tg, 0.94 Tg, and 0.86 Tg, respectively. Compared to other glasses, we found that these three elemental chalcogens have slow (Se), moderate (S), and fast (Te) crystallization kinetics, respectively. Slow crystallization kinetics makes Se a good choice for glass matrix, moderate crystallization kinetics makes S a candidate for glass-ceramic matrix, while the fast crystallization kinetics in Te makes it more suitable as the base material for phase-change memory.

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