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Study of glass transition kinetics of As_2S_3 and As_2Se_3 by ultrafast differential scanning calorimetry*

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Ultrafast differential scanning calorimetry (DSC) was employed to investigate the glass transition kinetics of As_2S_3 and As_2Se_3. By using the Arrhenius method, a fragility index of ~ 22 can be estimated in both As_2S_3 and As_2Se_3. However, when the scanning rate is more than 200 $K\cdot s^{-1}$, non-Arrhenius behavior can be observed in such "strong" liquids where the Vogel–Fulcher method is more accurate to describe the glass transition kinetics. The fragilities of As_2S_3 and As_2Se_3 glasses are thus extrapolated as 28.3±1.94 and 23.7±1.80, respectively. This indicates that, As_2Se_3 glass has a better structural stability and it is a better candidate for device applications.

Keywords: ultrafast DSC, glass transition kinetics, fragility index

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1. Introduction

Structural relaxation is intrinsic in amorphous materials which results in time-dependent physical properties or physical ageing.[1] When a glass is quenched from liquid state, it is characterized by a lack of thermodynamic equilibrium. Therefore, once the glass is maintained at a temperature below its glass transition temperature (T_g) in a period of time, its properties are changed more or less, implying the physical ageing is closely correlated to structural stability. An effective way to evaluate the structural stability of glass forming liquids is the conception of "fragility" introduced by Angell.[2] The fragility index, which is determined by the change of relaxation time or viscosity at the glass transition temperature, has been proven useful in the study of structural relaxation and glass transition kinetics in the glass forming liquids.[3]

Some measurement methods have been proposed to obtain the quantitative fragility index, such as relaxation time[4] and viscosity.[5,6] However, these experimental processes are difficult to control and time-consuming. Another effective way to estimate the fragility is equation parameterizations via glass transition kinetics study. Conventional differential scanning calorimetric (CDSC) investigation on the glass transition kinetics suggests that, the scanning rate-dependent T_g measurement during heating or cooling obeys an exponential law.[3] Nevertheless, this is an imprecise method due to the narrow range of the scanning rate. Recently, a novel ultrafast differential scanning calorimetry (UDSC) has been developed and successfully used for the study of the glass transition kinetics in Te-based chalcogenides, such as $Ge_2Sb_2Te_5$,[7] Ag–In–Sb_2Te,[8] and Ge–Te.[9,10] The scanning rate can be extended up to 10^4 $K\cdot s^{-1}$ during the measurements, thus, it is possible to investigate the abnormal glass transition kinetics hidden in some supercooled liquids and estimate the liquid fragility more accurately using UDSC.

In present paper, we employed UDSC to investigate the glass transition kinetics of As_2S_3 and As_2Se_3. We precisely measured the fragility indexes of S- and Se-based arsenic glasses using the Vogel–Fulcher method. It was found that, As_2Se_3 has smaller fragility index with a better structural stability.

2. Experimental methods

2.1. Sample fabrication

As_2S_3 and As_2Se_3 glasses were fabricated by the melt-quenching method. The high purity raw materials of As (5 N), S (6 N), and Se (5 N) were weighted, and about 20-g mixtures were loaded into quartz ampoules ($\phi = 10$ mm), which

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were subsequently sealed under a vacuum less than 10^{-3} Pa. The ampoules were shifted into a rocking furnace and heated slowly to around 700 °C for 12 h, then homogenized at 500 °C for 0.5 h. The ampoules were quenched in water to allow glass formation. Afterward, the vitreous samples were annealed at 30 °C below their glass transition temperatures for 12 h to relax the internal mechanical stress. Then the glass rods were cut and polished for further measurements.

2.2. Calorimetric measurements

CDSC measurements were carried out in TA Q2000 with a temperature accuracy of ±1 K. In each CDSC measurement, about 10-mg sample was enclosed into aluminum pan and heated at a scanning rate of 20 K·min^{-1} under N_2 atmosphere. UDSC measurements were performed in Mettler Toledo Flash DSC 1. In each UDSC measurement, a tiny sample with a mass of hundreds of nanogram was put on a chip sensor, and then heated at different heating rate from 1 K·s^{-1} to 30000 K·s^{-1} under an Ar atmosphere.

2.3. Thermal lag in UDSC measurement

In this work, we concentrate on the glass transition kinetics investigated by UDSC. Thermal lag is a major concern since the heating and cooling rates are ultrafast in UDSC. Biot number is usually used to estimate the potential thermal lag at the heating process in the studies. The Biot number is defined as, $Bi = L \times h/\kappa$,[7] where L is the sample thickness, h is the heat-transfer coefficient between the heater and surface (a typical value of 2 kW·m^{-2}·K^{-1} is employed in here),[11] and κ is the thermal conductivity of the sample. The value of κ at room temperature is in a range from 0.14 W·m^{-1}·K^{-1} to 0.27 W·m^{-1}·K^{-1} for As_2S_3,[12] and more than 0.14 W·m^{-1}·K^{-1} for As_2Se_3.[13] It should be noted that, we used the crushed flakes with a thickness of 2–5 microns for UDSC measurements. Thus, the Biot number can be estimated as 0.028–0.07. Previous investigations indicating that the thermal lag is negligible in UDSC measurement if the Biot number is less than 0.1.[7,9] Therefore in the present paper, the effect of thermal lag is negligible.

3. Results and discussion

Figures 1(a) and 1(b) show the subtracted UDSC traces for As_2S_3 glass with different heating rates from 1 K·s^{-1} to 200 K·s^{-1} and 500 K·s^{-1} to 30000 K·s^{-1}, respectively. A peak-like endothermic stage, which consists of an endothermic stage and the excess heat capacity peak determined by the atom translational motions in glass transition,[14] can be found in each subtracted trace. The onset glass transition temperature (T_g) increases with increasing heating rate. A similar scenario was found in As_2Se_3 glasses. Figure 2 depicts the conventional DSC traces of As_2S_3 and As_2Se_3 glasses obtained at a heating rate of 20 K·min^{-1}.T_g is 481 K and 467 K for As_2S_3 and As_2Se_3, respectively. Those values are in excellent agreement with the previous data reported.[15–18]

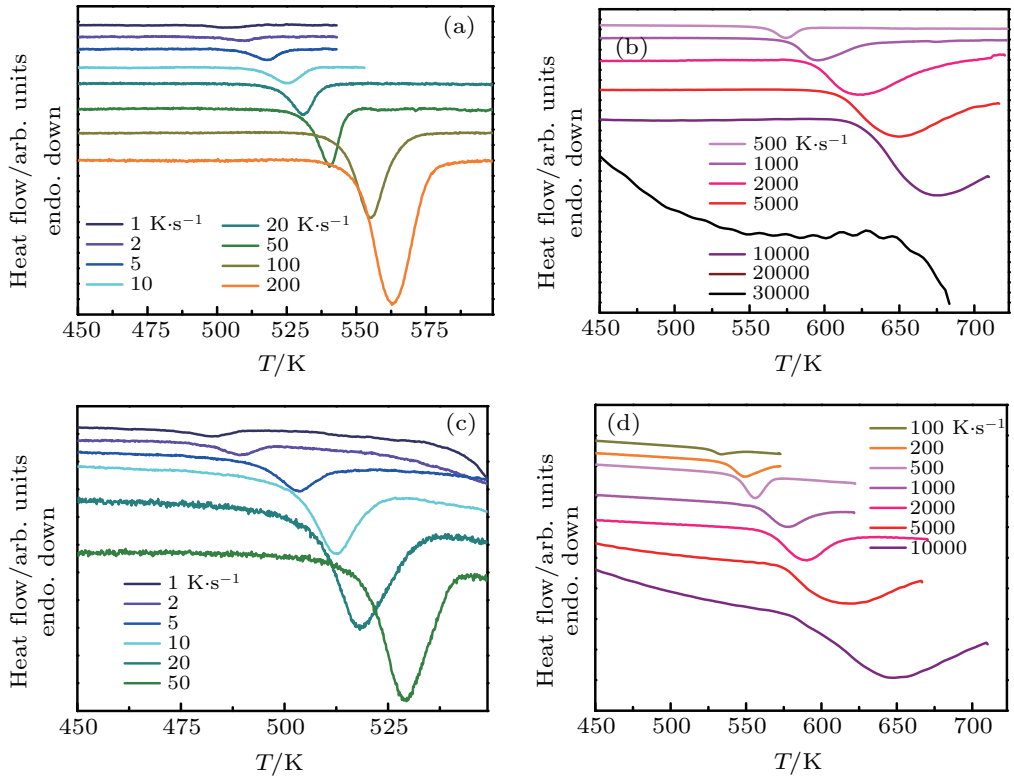


Fig. 1. Subtracted UDSC traces for As_2S_3 with the heating rate are (a) 1 K·s^{-1} to 200 K·s^{-1} and (b) 100 K·s^{-1} to 10000 K·s^{-1}. The subtracted UDSC traces for As_2Se_3 glasses with the heating rate range from (c) 1 K·s^{-1} to 50 K·s^{-1} and (d) 100 K·s^{-1} to 10000 K·s^{-1}.

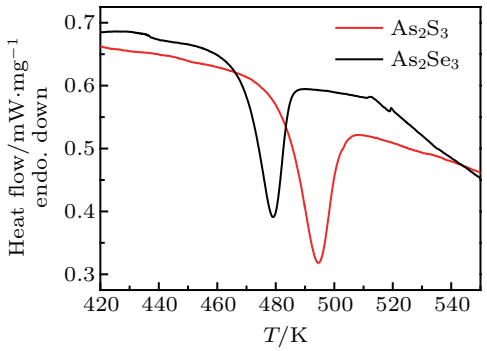


Fig. 2. Conventional DSC traces tested at a heating rate of 20 K·min^{-1} for As_2S_3 and As_2Se_3.

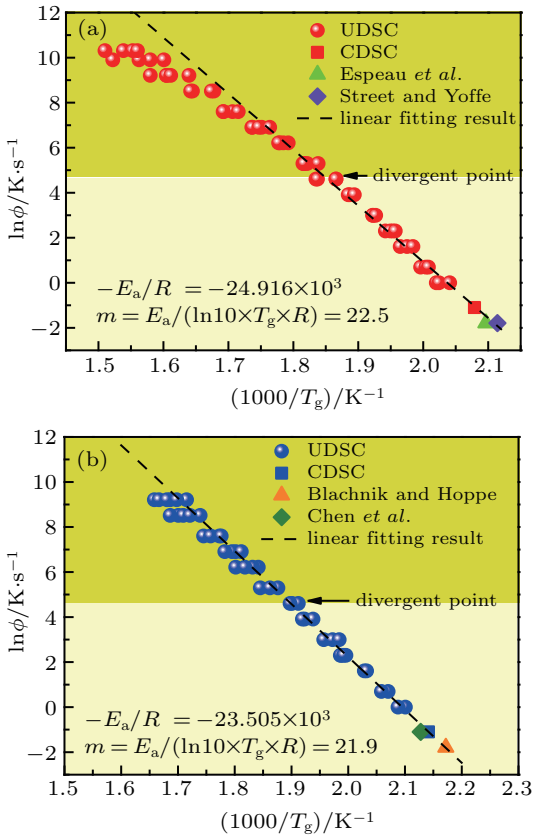


Fig. 3. The natural logarithm of heating rate, $\ln\phi$, is plotted against $1000/T_g$ for (a) As_2S_3 and (b) As_2Se_3. The black dashed lines are the results of linear fitting, and the slope of the fitted line is $-E_a/R$. Green triangle and purple diamond in Fig. 3(a) represent the As_2S_3 data from Espeau *et al.*,[15] and Street and Yoffe.[16] Orange triangle and olive diamond in Fig. 3(b) represent the As_2Se_3 data from Blachnik and Hoppe,[17] and Chen *et al.*[18]

T_g obtained at a large range of the heating rate makes it possible to investigate the glass transition kinetics. Figure 3 describes the relationship between natural logarithm of the heating rate and reciprocal T_g ($1000/T_g$). It shows an Arrhenius behavior, especially at the heating rate less than 100 K·s^{-1} in both As_2S_3 and As_2Se_3. However, when the heating rate is higher than 200 K·s^{-1} (the data above divergent point in Fig. 3), a non-Arrhenius behavior is obviously observed in As_2S_3, but slightly presented in As_2Se_3. We first used a linear fit method to estimate the glass transition kinetics at a low heating rate range (light yellow shade in Fig. 3). As shown in Fig. 3, the dashed lines with the slopes ($-E_a/R$, where E_a is the activation energy and R is the gas constant) of -24.916×10^3 and -23.505×10^3 can be obtained for As_2S_3 and As_2Se_3, respectively. According to the relationship, $m = E_a/(\ln10\times T_g\times R)$,[19] where T_g is the glass transition temperature, *i.e.*, 481 K and 467 K for As_2S_3 and As_2Se_3, their fragilities can be estimated as 22.5 and 21.9. Thus, As_2S_3 and As_2Se_3 glasses possess similar fragility index that is close to 22, and they are the strong liquids that can remain thermodynamically stable over a wide temperature range.[20]

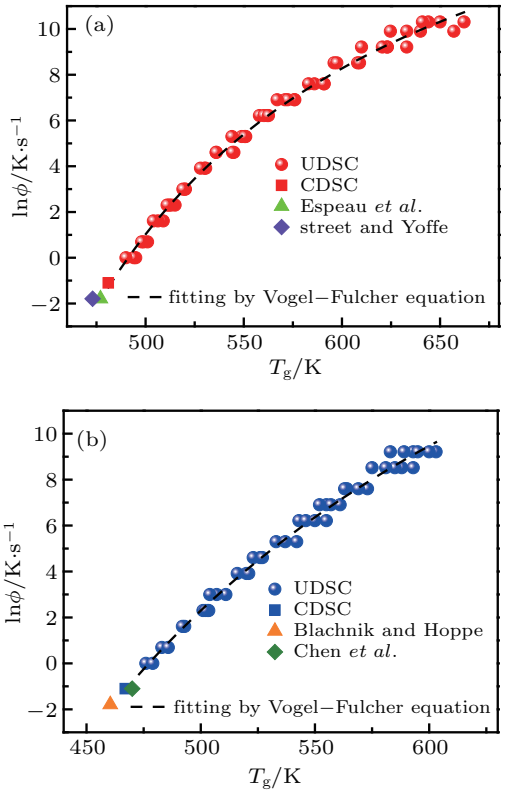


Fig. 4. The relation between T_g and heating rate of (a) As_2S_3 and (b) As_2Se_3. The dashed curves were fitted by Vogel–Fulcher equation.

Moving to the deep yellow shade in Fig. 3, the linear fit cannot well depict the relation between $\ln\phi$ and $1000/T_g$ when ϕ is more than 200 K·s^{-1}. Such non-Arrhenius behavior observed in the ultrafast DSC measurements enables the Vogel–Fulcher method to be used for calculating the fragility index more accurately. The relation between T_g and $\ln\phi$ in the Vogel–Fulcher method is,[21]

$$\ln\phi = \ln B - DT_0/\left(T_g - T_0\right), \tag{1}$$

where B is the time scale parameter in glass forming system, D is the strength parameter represents how close the liquid obeys Arrhenius law, and T_0 is the asymptotic value of T_g within the limit of infinitely slow heating (or cooling) rate.[22] Afterward, the fragility index can be estimated as,[4]

$$m = \frac{DT_0T_g}{\left(T_g - T_0\right)^2\ln10}, \tag{2}$$

where T_g is glass transition temperature obtained at a heating rate of 20 K·min^{-1} (see Fig. 2). The obtained parameters were listed in Table 1. Apparently, As_2Se_3 has a large D index of 54.9. This indicates As_2Se_3 is the stronger liquid and obeys the Arrhenius law. Taking the parameters D, T_0, and T_g into Eq. (2), the fragility m can be calculated as 28.3 ± 1.92 and 23.7 ± 1.80 for As_2S_3 and As_2Se_3, respectively. Compared with the results estimated by linear fit, both fragilities become larger.

Table 1. The parameters fitted by Vogel–Fulcher equation and fragilities for As_2S_3 and As_2Se_3.

Glass	D	T_0/K	T_g/K	Reduced Chi-Sqr	m	Error
As_2S_3	13.4	306.7	481	0.068	28.3	1.92
As_2Se_3	54.9	177.6	467	0.076	23.7	1.80

Using the data of viscosity close to T_g, the fragility index of the As_2Se_3 liquid was reported by Málek *et al.* as $m \approx 38$.[23] Brazhkin *et al.* reported that, the viscosities are 10^5, 10, 0.1, and 0.01 Pa s at 350, 500, 700, and 1000 °C, respectively, for As_2S_3 liquid.[24] Combining with the Mauro–Yue–Ellison–Gupta–Allan (MYEGA) viscosity model,[6] a rough value of fragility was estimated as ~ 46 for As_2S_3. It can be seen that, the fragility index of As_2Se_3 is smaller than that of As_2S_3, which is in line with our result in this work. In addition, the fragility indexes estimated from viscosity change for both As_2S_3 and As_2Se_3 are all larger than those estimated from glass transition kinetics. Depending on the viscosity data, these arsenic glasses may consider as the materials with intermediate kinetics, which have the fragility index between the strong and fragile pattern, rather than the "strong" materials. However, we know the strong glass forming liquids are characterized by covalent directional bonds that form a spatial network, such as the SiO_2.[23] Recently, by using the conventional DSC, the fragility of As_2S_3 was roughly estimated as 27,[25] which is very close to our result. Thus, the typical covalent glasses, *i.e.*, As_2S_3 and As_2Se_3, can be considered as the "strong" glass forming liquids.

4. Conclusion

We have studied the glass transition kinetics of As_2S_3 and As_2Se_3 glasses using novel UDSC. According to the linear fitting results, it yields the fragility index of 22.5 and 21.9 for As_2S_3 and As_2Se_3, respectively. However, the non-Arrhenius behavior was observed when the heating rate is more than 200 K·s^{-1}, indicating that the linear fit is inappropriate in the large heating rate. Thus, the Vogel–Fulcher method was employed to estimate the fragility index more precisely. It was found that, the fragilities for As_2S_3 and As_2Se_3 are 28.3 ± 1.94 and 23.7 ± 1.80, respectively, which are all larger than those estimated from the linear fit. This fact illustrates that, even for the "strong" glasses, large range of scanning rate (such as those used in UDSC) is helpful to estimate fragility index more accurately for glass transition kinetics.

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