



The kinetics of the glass transition and physical aging in germanium selenide glasses

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ABSTRACT

The kinetics associated with the glass transition is investigated using differential scanning calorimetry (DSC) for germanium selenide glasses with Ge content ranging from 0 to 30 at.% and average coordination numbers ranging from 2.0 to 2.6. As Ge content increases, the glass transition region broadens and the step change in heat capacity at T_g decreases. As a result of physical aging, enthalpy overshoots are observed in DSC heating scans and the corresponding change in enthalpy can be calculated as a function of aging time. The change in enthalpy linearly increases with the logarithm of aging time and then levels off at an equilibrium value that increases with decreasing aging temperature. The time required to reach equilibrium increases with decreasing aging temperature and, at a given distance from T_g , the time increases with decreasing germanium content. The results indicate that all samples show expected physical aging behavior, and no evidence is found for a Boolchand intermediate phase characterized by high stability and absence of physical aging.

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1. Introduction

Binary alloys in the system Ge–Se have been considered in the literature as model materials for understanding the structure–property relationships in chalcogenide glasses. The Se atoms in these glasses are twofold coordinated, whereas the Ge atoms are tetrahedrally coordinated. Consequently the structure of Se-rich germanium selenide glasses is dominated by floppy Se–Se–Se chains with low glass transition temperatures T_g , whereas the addition of Ge results in cross-linking of these chains and the formation of a rigid network of corner- and edge-shared GeSe_4 tetrahedra with high T_g . This topological diversity within a single glass forming system has made these glasses ideal for studying the influence of topological constraints on the compositional variation of various physical properties in covalently bonded amorphous materials. It has been argued in the literature that a wide range of physical properties of these glasses is predominantly controlled by the degree of connectivity of the network as expressed by the average coordination number r_c [1,2]. It can be shown on the basis of the theory of constraint counting that in three dimensions there exists a critical value of $r_c = 2.4$, also known as the rigidity percolation threshold, where the network undergoes a floppy-to-rigid transition, since at this point the number of constraints per atom equals the number of degrees of freedom [1,2]. Ge–Se alloys satisfy this condition at the composition $\text{Ge}_{20}\text{Se}_{80}$ and show the best glass forming ability near this composition, without significant defects [1–3].

Chalcogenide glasses have found wide ranging applications in photonics and remote sensing due to their low phonon energy, high refractive index, strong optical nonlinearity, and wide transparency range in the infrared range [4,5]. However, because these materials are glasses, they are thermodynamically unstable and changes in properties with physical aging must be considered in product design [5,6]. An exciting new development in this field has been proposed, the intermediate phase, which is associated with a stress-free self-organized system where the degrees of freedom approximately equal the number of constraints near $r_c = 2.4$. Glasses with compositions in the vicinity of the intermediate phase have been suggested to show physical stability at room temperature and a lack of physical aging [7–9] based on results from conventional [10–13] and temperature-modulated [9,14–16] differential scanning calorimetry (DSC and TMDSC, respectively). A related minimization in non-reversing heat flow is also observed on heating in TMDSC after melt quenching to the glass state [9,17–23].

The lack of physical aging has been attributed to an absence in stress in the intermediate phase compositions [3,8,24–26], but the interpretation of experimental results has also been criticized [6] due to the use of TMDSC with relatively short aging times. In addition, Elabbar et al. [27] and Golovchak et al. [12,16] reported that significant physical aging occurs after 19+ years at room temperature for arsenic selenide glasses including for compositions near $r_c = 2.4$ and, thus challenged the existence of the intermediate phase. More recently, Golovchak et al. [28] reported aging on a timescale of days when the aging temperature is within approximately 90 °C of the glass transition temperature for $\text{As}_{40}\text{Se}_{60}$ ($r_c = 2.4$). Yang et al. [29] also concluded that the intermediate phase did not exist based on observed extrema in density, moduli, and Poisson's ratio near $r_c = 2.4$ for $\text{As}_x\text{Se}_{100-x}$ glasses. Furthermore,

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TMDSC, which was used in some studies postulating the existence of an intermediate, has limitations for measuring the enthalpy recovery associated with physical aging [30–33].

It is well known that the time scale to investigate physical aging depends on the distance from T_g , as has been shown, for example, in DSC and dilatometric work on amorphous selenium [34–36]. Since the T_g of chalcogenide glasses changes with composition, measuring physical aging at a single temperature, as was done in previous works [9,12–15], is hypothesized by us to lead to problems in interpreting the data. Hence, in this work, we examine the T_g and enthalpy recovery of Ge–Se chalcogenide glasses as a function of composition using aging temperatures that are at a fixed absolute distance below T_g ; we use a fixed distance since the “universal” Williams–Landel–Ferry (WLF) equation [37] suggests that relaxation times should vary with the quantity $T-T_g$. We show that, in fact, all of the chalcogenide glasses studied here, physically age as might be expected. The implication for the existence of the Boolchand intermediate phase is discussed.

2. Methodology

2.1. Material preparation

$\text{Ge}_x\text{Se}_{100-x}$ glasses with $5 \leq x \leq 30$ were synthesized in 10 to 20 g batches by melting mixtures of the constituent elements Ge and Se with $\geq 99.995\%$ purity (metals basis) in evacuated (10^{-6} torr) and flame sealed fused silica ampoules (8 mm I.D., 11 mm O.D.) at temperatures ranging between 1000 and 1200 K for 24 to 48 h in a rocking furnace. The ampoules were quenched in water and subsequently annealed for 1 h at the respective glass transition temperatures. We have also studied amorphous selenium that was purchased from Sigma-Aldrich (purity $\geq 99.999\%$). The average coordination numbers r_c of these chalcogenide glasses are calculated using the following equation:

$$r_c = \frac{4x + 2(100-x)}{100} = 2\left(1 + \frac{x}{100}\right) \quad (1)$$

where x is the atom percent germanium in the $\text{Ge}_x\text{Se}_{100-x}$ alloy. For our samples, r_c ranges from 2.0 for amorphous selenium to 2.6 for $\text{Ge}_{30}\text{Se}_{70}$ glass, as shown in Table 1.

2.2. DSC measurements

A Perkin-Elmer Pyris 1 differential scanning calorimeter (DSC) with an ethylene glycol cooling system and nitrogen purge gas was employed to measure the absolute heat capacity, the kinetics associated with the glass transition, and the enthalpy recovery accompanying physical aging. Sample size ranged from 5 to 25 mg. The sample weight was checked before and after the DSC runs and no obvious weight loss ($<3\%$) was found for the work reported here. Temperature calibration on the heating step was checked using indium on heating at 10 and 0.1 K/min.

Table 1
Parameters characterizing relaxation in the glass transition region for various Ge–Se glasses.

Sample	r_c	T_f' after cooling at 10 K/min (K)	$dT_f'/d(\log q)$	m	$\Delta h/R$ (kK)
Se ^a	2.00	308.2 ± 0.6 (35.0 °C)	3.3 ± 0.5	93.4 ± 14.3	66.3 ± 10.3
Ge ₅ Se ₉₅	2.10	334.6 ± 0.4 (61.4 °C)	3.6 ± 0.2	93.0 ± 5.3	71.6 ± 4.1
Ge ₁₀ Se ₉₀	2.20	366.9 ± 0.2 (93.7 °C)	7.1 ± 0.3	51.7 ± 2.2	43.7 ± 1.9
Ge ₁₇ Se ₈₃	2.35	406.0 ± 3.5 (132.8 °C)	7.9 ± 0.3	51.4 ± 2.4	48.0 ± 2.7
Ge ₂₀ Se ₈₀	2.40	448.9 ± 0.8 (175.7 °C)	10.2 ± 0.8	44.0 ± 3.5	45.5 ± 3.7
Ge ₂₃ Se ₇₇	2.45	470.2 ± 1.1 (197.0 °C)	10.7 ± 1.1	43.9 ± 4.6	47.6 ± 5.1
Ge ₃₀ Se ₇₀	2.60	577.6 ± 3.1 (304.4 °C)	11.3 ± 0.5	51.1 ± 2.5	68.0 ± 3.7

^a Pure selenium data are obtained from Ref. [34].

Three types of experiments were performed. In the first, the step-scan method was used to measure the absolute heat capacity and consisted of multiple temperature ramp/isothermal steps. Step sizes were 2 K, holds were 0.8 min at each temperature, and a 10 K/min heating rate was used between sequential isothermal hold temperatures. Measurements were performed on heating after first cooling the samples from $T_g + 30$ K to below T_g at 30 K/min, except for the selenium sample which was cooled from 503 K (229.8 °C), above its melting point (~ 490 K); the relatively high cooling rate of 30 K/min was used to minimize enthalpy overshoots on the subsequent heating scan. The absolute heat capacity is obtained from the heat flow rate (\dot{Q}) observed during the isothermal hold:

$$C_p = k \frac{\int \dot{Q} dt}{m\Delta T} \quad (2)$$

where k is the calibration constant, m is the mass of the sample, and ΔT is the temperature step of 2 K between isothermal hold temperatures. The calibration constant was obtained using the step-scan method for two runs, one for sapphire and the other using empty sample pans; in all runs, the sample and reference pans are identical in weight (within 0.01 mg). The standard deviation for multiple runs for selenium is less than $\pm 2.0\%$. The value of T_g was obtained from the absolute C_p versus temperature data using the half-height method, i.e., at the temperature at which C_p attains a value halfway between the extrapolated liquid and glass C_p lines, the latter of which are shown later.

In the second type of experiment, the limiting fictive temperature (T_f') was obtained from heating scans at 10 K/min after cooling at a specified rate using Moynihan's method [38]:

$$\int_{T_f'}^{(T_g)} (C_{pl} - C_{pg}) dT = \int_{T_g}^{T_g} (C_p - C_{pg}) dT. \quad (3)$$

T_f' is only a function of cooling rate, and it is equivalent within 1 K to the glass transition temperature (T_g) that would be measured on cooling at the same rate [39,40]; hence, in the text, we often refer to T_f' as T_g .

Finally, the enthalpy change after isothermal physical aging was determined as a function of aging time. A schematic of the temperature history is shown in Fig. 1. Samples were held at a temperature 40 K above T_g for several minutes to eliminate the effect of prior thermal history and then cooled at 10 K/min to the aging temperature T_a , which was nominally 5, 10, and 15 K below T_g ; exact values are listed in Table 2. The samples were maintained at the aging temperature for prespecified aging times ranging from 3 to 10,000 min, and after aging, samples were cooled at 10 K/min to 80 K below T_g . A subsequent heating scan at 10 K/min to 40 K above T_g provides the data for the aged samples.

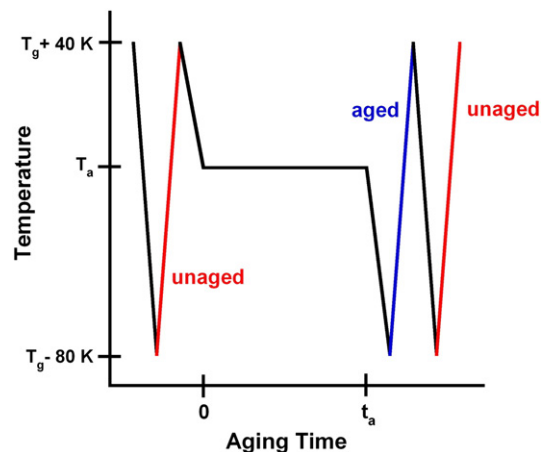


Fig. 1. Schematic for DSC experiments measuring enthalpy recovery as a function of aging temperature, T_a , and aging time, t_a .

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