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Strong-fragile glass forming liquid concept applied to GeTe chalcogenide glasses

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Abstract

The values of the thermal heat-capacity changes at the glass transition temperature T_g ($\Delta C_p = C_{p_l} - C_{p_g}$) and the values of the apparent activation energy Δh^* of the sub T_g relaxation process are determined for $\text{Ge}_x\text{Te}_{1-x}$ ($0.15 \leq x \leq 0.20$) vitreous alloys by means of differential scanning calorimetry investigations. The values of Δh^* are then used to determine the values of the fragility index, m . The comparison of these new data to those already obtained on the $\text{Ge}_x\text{Se}_{1-x}$ vitreous system leads to conclude that both systems exhibit strong thermodynamic character. The stronger thermodynamic character is reached at the Phillips–Thorpe's floppy-to-rigid transition. On the other hand, we find that $\text{Ge}_x\text{Te}_{1-x}$ exhibits a kinetically fragile character which decreases as the amount of Ge increases in the alloy. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Chalcogenide glass; GeSe; GeTe; Relaxation; Fragility; Coordination number

1. Introduction

Structural relaxation is a general phenomenon occurring when a glass is maintained at a temperature below its glass-transition temperature (T_g). Thus a glassy material has at least two important characteristics: its glass-transition temperature and its sub- T_g relaxation kinetics. The glass transition temperature can be defined either as the temperature at which the equilibrium liquid

has a viscosity of 10^{12} Pa s or as the temperature at which the average relaxation time in the equilibrium liquid is close to 100 s [1]. As stated by Alba et al. [2] this value for the viscosity is not universal; the glass transition is not an isoviscous phenomenon and some liquids have viscosities at T_g as low as 10^{10} Pa s. From the variations of the viscosity with the normalized reduced T_g/T quantity, a classification of glass-forming liquids was proposed [3] (Fig. 1). For the extreme behavior seen in Fig. 1, glass-forming liquids that exhibit an approximately Arrhenius temperature dependence of the viscosity are defined as strong glass formers and those which exhibit a non-Arrhenius behavior (for instance described by a Vogel Tammann

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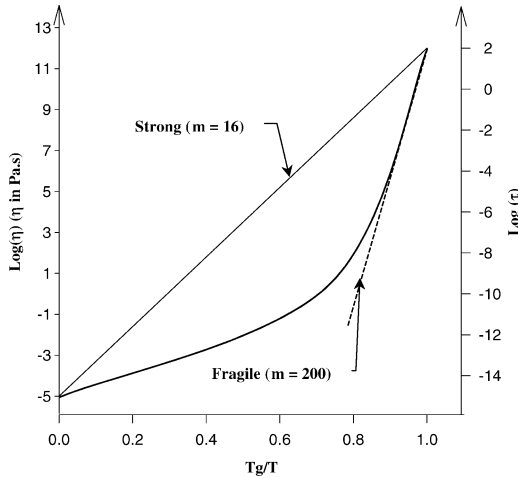


Fig. 1. Definition of the extreme strong and fragile behavior of a glass-forming liquid.

Fulcher equation) are declared fragile glass formers. From this representation, it was proposed to define a fragility index, m , characterizing the kinetic aspect of this concept and given by Ngai et al. [4] as:

$$m = \left. \frac{d \log_{10}(\tau)}{d(T_g/T)} \right|_{T=T_g} \quad (1)$$

It was found that the limit for kinetically strong-glass-forming liquids (KS) is reached for a low value of m ($m \approx 16$) [5], while the limit for kinetically fragile-glass-forming liquid (KF) is characterized by a high value of m ($m \approx 200$) [6].

Another interesting result concerns the difference between the values of thermal heat capacities in the liquid and glassy states occurring in the glass-transition region ($\Delta C_p = [C_{p_l} - C_{p_g}]_{T=T_g}$) that can also be connected to this strength–fragility concept. Indeed, as pointed out by Angell [7], a glass which exhibits at the glass transition a low value of ΔC_p is not so far from its thermodynamic equilibrium. This glass-forming liquid and associated glass can be defined as thermodynamically strong (TS). In contrast, a high value of ΔC_p must lead to a thermodynamically fragile (TF) behavior. Consequently, the strong–fragile concept gives four possibilities by combinations of thermodynamic and kinetic aspects, namely [TS–KF], [TF–KS], [TF–KF] or [TS–KS]. Re-

cently, the strength–fragility concept of glass-forming liquids has been extended to the glassy state [8].

From a review of results collected in the literature, it appears that the variations of the network connectivity lead to modifications of the fragility behavior. In the following we propose to analyze this possibility from a study performed on inorganic glasses able to give three-dimensional structures. We have chosen chalcogenide based alloys, and particularly selenium and tellurium based glasses, in which the structure can be changed by introducing a second element as germanium atoms. With regard to the nature of the bonds engaged between the different atoms, these inorganic glasses can be classified as classic polymers or as covalent glasses. For instance, the coordination number of the element Ge is four and thus by increasing the content of Ge in a polymeric Se matrix, the connectivity of the medium increases in a controlled way. In the present work, new results on the $\text{Ge}_x\text{Te}_{1-x}$ vitreous system are presented and discussed in terms of strong and fragile behaviors. These results are compared with those already obtained on the $\text{Ge}_x\text{Se}_{1-x}$ vitreous system.

2. Method

To determine the value of the fragility index, it is necessary to choose an expression for the relaxation time. For a glass, the relaxation time (τ) is known to be dependent on the temperature and on some order parameters defining the structure of the glass [9–14]. Among the different expressions describing these variations that we may find in the literature, we used here the Tool–Narayanaswamy–Moynihan (TNM) expression [12,13,15]:

$$\tau = \tau_0 \exp\left(\frac{x\Delta h^*}{RT}\right) \exp\left(\frac{(1-x)\Delta h^*}{RT_f}\right) \quad (2)$$

where x ($0 \leq x \leq 1$) is the nonlinearity parameter or Narayanaswamy parameter, Δh^* the apparent activation energy, T_f is the fictive temperature defined as the temperature at which the structure of the glass would be in equilibrium if instantaneously brought to it and the other symbols carry

their usual meanings. For a given glass, we must have a given value for x and a given value for Δh^* .

In the liquid state, the value of the non-linearity parameter is unity ($x = 1$). According to Ritland [16] and Bartenev [17] assuming that $q\tau = \text{constant}$ (q is the cooling or heating rate), it is easy to demonstrate that the apparent activation energy Δh^* , the cooling rate q^- , and the fictive temperature T_f are related in the following way:

$$\frac{d \ln|q^-|}{d(1/T_f)} = -\frac{\Delta h^*}{R} \quad (3)$$

Thus, the variation of $\ln|q^-|$ with $1/T_f$ allows us to determine Δh^* if T_f is known. This fictive temperature can be calculated graphically on a calorimetric curve, using the so-called 'equal areas' construction [13]. Finally, for a given value of the cooling rate (q^-) and for a non aged glass reheated up to its liquid state with a heating rate q^+ such as $|q^+| = |q^-|$, the value of the glass-transition temperature T_g (as defined previously) and the value of the fictive temperature T_f can be identified. Thus, knowing the value of the apparent activation energy, and according to relationship (1), the value of the fragility index can be obtained from [18]

$$m = \frac{\Delta h^*}{\ln(10)RT_g} \quad (4)$$

In the glassy state, it is possible to define a second fragility index (m_g). The nonlinearity of the relaxation phenomenon must now be taken into account, and it was shown that this glass fragility index is linked to m by [8]

$$m_g = xm. \quad (5)$$

Experimentally, values of ΔC_p at the glass transition, x , Δh^* and m can be obtained by means of calorimetric measurements.

3. Experimental

The GeTe samples are obtained from a mixture of the two elements (99.999% purity) in a granular form. The mixture was introduced into a quartz ampoule and sealed in a vacuum of 10^{-3} Torr. Then, the ampoules were placed in a horizontally

rotating oven and annealed at 1000°C for 3 h. Finally, they were water quenched. The melting temperatures were measured by differential thermal analysis (DTA), and the glass transition temperatures were measured by differential scanning calorimetry (DSC, Perkin–Elmer System 7).

By cooling from the melt, the range of compositions able to give a glass is limited to those located around the eutectic composition $\text{Ge}_{15}\text{Te}_{85}$ [19,20]. Thus we have only prepared samples with compositions close to the eutectic.

Variations of the heat capacities at the glass transition were measured by differential scanning calorimetry. To obtain good reproducibility, for a given composition, the same sample sealed in an aluminum pan was used during all the measurements. Prior to any DSC experiment, the sample was kept 5 min at the rejuvenation temperature, T_r , about 10°C above the glass transition temperature, in order to erase the previous thermal history. Cooling experiments were then performed: the sample at T_r is cooled at various cooling rates q^- , from 1 to 100 K min^{-1} , to T_0 and immediately reheated to T_r at $q^+ = 20 \text{ K min}^{-1}$.

4. Results

Fig. 2 shows the DSC curves recorded for each glass having undergone exactly the same thermal history and in a range of temperatures preventing any crystallization. The obtained onset glass transitions are listed in Table 1 which also gives data collected from the literature [21–26].

Figs. 3, 4 and 5 show the DSC curves obtained at a constant heating rate of 20 K min^{-1} on, respectively the $\text{Ge}_{15}\text{Te}_{85}$, $\text{Ge}_{18}\text{Te}_{82}$ and $\text{Ge}_{20}\text{Te}_{80}$ glassy alloys, cooled with rates in the range 100 to 1 K min^{-1} . Then the respective jumps ΔC_p of specific heat at the glass transition ($\Delta C_p = C_{p_l} - C_{p_g}$, C_{p_l} and C_{p_g} refer to the C_p values of the liquid and the glassy states, respectively extrapolated at T_g) are reported in Table 2. For the $\text{Ge}_{20}\text{Te}_{80}$ glassy system ΔC_p may be compared to the data given by Xu et al. [27] who have determined the following relationship from adiabatic calorimetric measurements

$$\Delta C_p(T) = a + bT \quad (6)$$

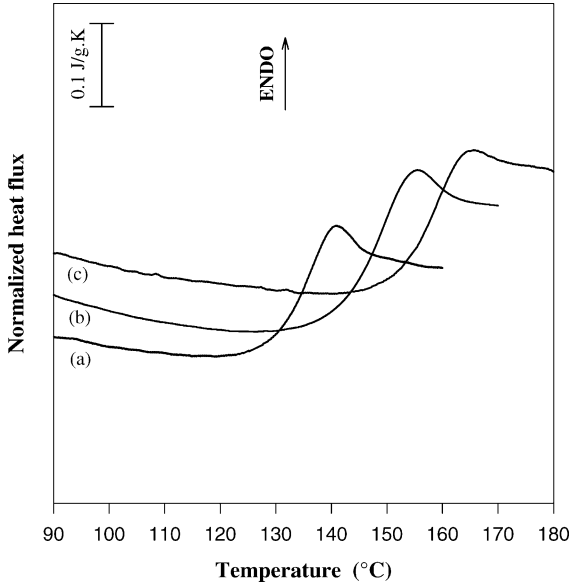


Fig. 2. DSC curves obtained on (a) $\text{Ge}_{15}\text{Te}_{85}$, (b) $\text{Ge}_{18}\text{Te}_{82}$, (c) $\text{Ge}_{20}\text{Te}_{80}$.

Table 1

Measured glass transition temperatures for $\text{Ge}_x\text{Te}_{100-x}$ ($x = 15, 18, 20$) along with those collected from the literature [23–28]

$\text{Ge}_x\text{Te}_{100-x}$	$T_g(^{\circ}\text{C})$	Ref.
Te	-5	[28]
$\text{Ge}_{15}\text{Te}_{85}$ ($x = 15$)	128 121	This work [23]
$\text{Ge}_{18}\text{Te}_{82}$ ($x = 18$)	100 130 132	[27] This work [24]
$\text{Ge}_{20}\text{Te}_{80}$ ($x = 20$)	150 146 147	This work [23] [25]
	147	[26]

with $a = 19.935 \text{ JK}^{-1} \text{ mol}^{-1}$ and $b = -0.010 \text{ JK}^{-2} \text{ mol}^{-1}$. Using this relationship, we evaluated ΔC_p for $\text{Ge}_{20}\text{Te}_{80}$ and obtained a value of $0.13 \text{ JK}^{-1} \text{ g}^{-1}$ which is in good agreement with our experimental result ($0.12 \text{ JK}^{-1} \text{ g}^{-1}$) obtained by differential scanning calorimetry.

According to Moynihan’s method and associated Eq. (3), Δh^* is obtained from the study of the dependence of $\ln(q^-)$ on reciprocal T_f in cycles performed on the same sample without any aging. Such dependencies are displayed in Fig. 6. The

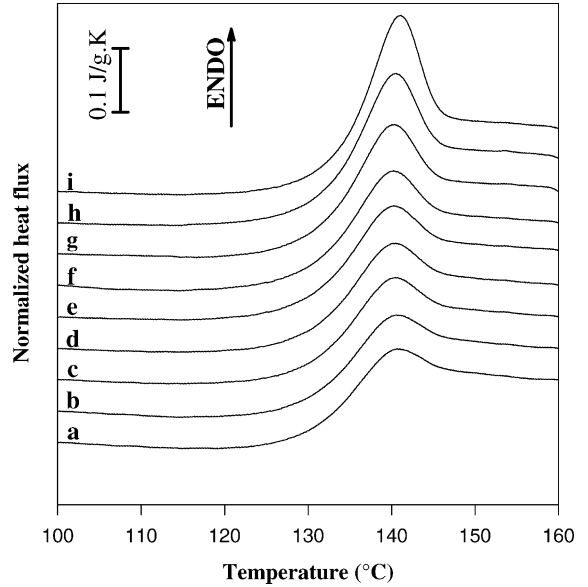


Fig. 3. DSC curves obtained on $\text{Ge}_{15}\text{Te}_{85}$ during the heating period with $q^+ = 20 \text{ K min}^{-1}$, for a sample previously cooled at different cooling rate q^- : (a) -100 K min^{-1} , (b) -50 K min^{-1} , (c) -25 K min^{-1} , (d) -20 K min^{-1} , (e) -15 K min^{-1} , (f) -10 K min^{-1} , (g) -5 K min^{-1} , (h) -2.5 K min^{-1} , (i) -1 K min^{-1} .

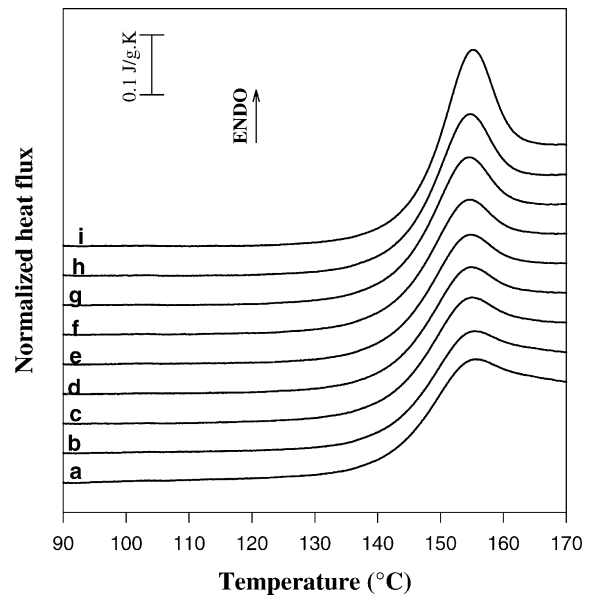


Fig. 4. DSC curves obtained on $\text{Ge}_{18}\text{Te}_{82}$ during the heating period with $q^+ = 20 \text{ K min}^{-1}$ for a sample previously cooled at different cooling rate q^- : (a) -100 K min^{-1} , (b) -50 K min^{-1} , (c) -25 K min^{-1} , (d) -20 K min^{-1} , (e) -15 K min^{-1} , (f) -10 K min^{-1} , (g) -5 K min^{-1} , (h) -2.5 K min^{-1} , (i) -1 K min^{-1} .

Table 2

Values of fragility key parameters for $\text{Ge}_x\text{Te}_{100-x}$ ($x = 15, 18, 20$) vitreous alloys. The values for Se and GeSe are taken from Ref. [29]

Samples	Se	$\text{Se}_{98}\text{Ge}_2$	$\text{Se}_{92}\text{Ge}_8$	$\text{Se}_{88}\text{Ge}_{12}$	$\text{Te}_{85}\text{Ge}_{15}$	$\text{Te}_{82}\text{Ge}_{18}$	$\text{Te}_{80}\text{Ge}_{20}$
Reference	[29]	Unpublished results	[29]	[29]	This work	This work	This work
$\Delta h^*/R(\text{kK})$	81 ± 5		46 ± 5	52 ± 3	120 ± 15	96 ± 3	75 ± 9
m	114		58	60	120	100	77
$\Delta C_p(\text{J/gK})$	0.16 ± 0.01	0.13 ± 0.01	0.13 ± 0.01	0.13 ± 0.01	0.10 ± 0.01	0.09 ± 0.01	0.12 ± 0.01

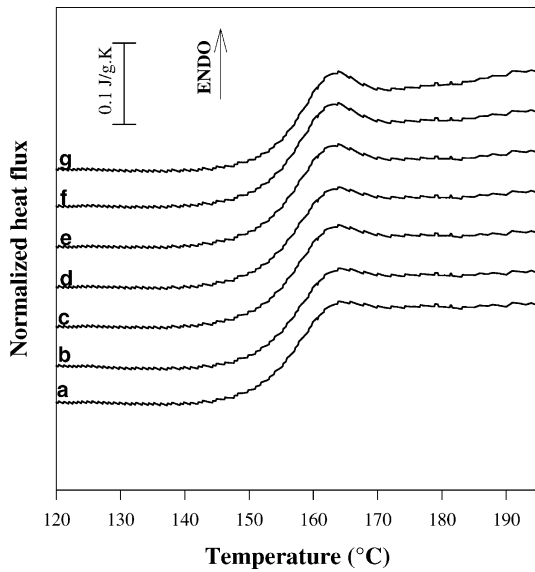


Fig. 5. DSC curves obtained on $\text{Ge}_{20}\text{Te}_{80}$ during the heating period with $q^+ = 20 \text{ K min}^{-1}$, for a sample previously cooled at different cooling rate q^- : (a) -100 K min^{-1} , (b) -50 K min^{-1} , (c) -25 K min^{-1} , (d) -20 K min^{-1} , (e) -10 K min^{-1} , (f) -5 K min^{-1} , (g) -2.5 K min^{-1} .

slope of each of these curves leads to the determination of the values of Δh^* reported in Table 2.

5. Discussion

The glass-transition temperatures determined for $\text{Ge}_x\text{Te}_{1-x}$ vitreous alloys are presented in Fig. 7 as a function of the atomic fraction of Ge atoms. On the same figure, other data, collected in the literature and concerning $\text{Ge}_x\text{Te}_{1-x}$ and $\text{Ge}_x\text{Se}_{1-x}$ systems [25, 28–30] are added. When

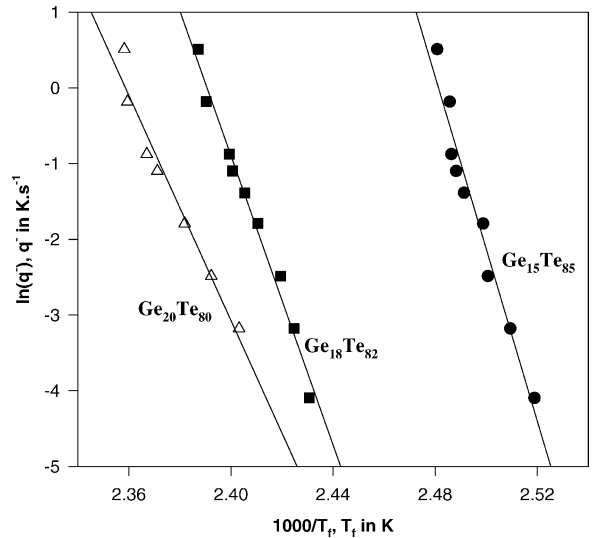


Fig. 6. Variations of $\ln(q^-)$ versus $1/T_f$ for $\text{Ge}_{15}\text{Te}_{85}$, $\text{Ge}_{18}\text{Te}_{82}$ and $\text{Ge}_{20}\text{Te}_{80}$.

the data analysis could be performed over a wide range of compositions as for the $\text{Ge}_x\text{Se}_{1-x}$ system (known to allow the formation of glassy structures for compositions up to 42 at.% of Ge) the variations of the glass transition temperature can be directly linked to structural consideration. Indeed, introducing atoms of higher coordination number (CN), such as Ge ($\text{CN}_{\text{Ge}}=4$) in a Se ($\text{CN}_{\text{Se}}=2$) linear polymeric structure increases the medium dimensionality and consequently the value of the glass transition temperature. This increase is not linear and according to Phillips–Thorpe’s [31–34] and Tanaka’s [35–37] topological models, thresholds occur when the structure changes from a floppy to rigid type network and from a two-dimensional layered structure to a three-dimensional network. Following this point of view,

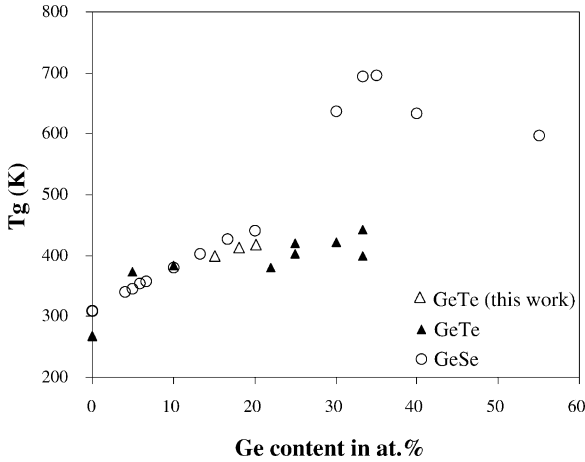


Fig. 7. Variations of the glass transition temperature for $\text{Ge}_x\text{Se}_{100-x}$ and $\text{Ge}_x\text{Te}_{100-x}$ with the at.% of Ge. Data for $\text{Ge}_x\text{Se}_{100-x}$ are taken from Refs. [29] and [30] and data for $\text{Ge}_x\text{Te}_{100-x}$, $x > 20$ at.% are taken from Ref. [30].

properties of A_xB_{1-x} glasses are commonly re-examined by their dependencies upon the average coordination number $\langle Z \rangle$ defined by

$$\langle Z \rangle = x\text{CN}_A + (1-x)\text{CN}_B \quad (7)$$

For $\text{Ge}_x\text{Se}_{1-x}$, we observe that the composition dependence of the glass-transition temperature displays anomalies for the compositions with 20 at.% Ge ($\langle Z \rangle = 2.4$) and 33.3 at.% Ge ($\langle Z \rangle = 2.66$). These average coordination number values are those corresponding to Phillips and Tanaka's thresholds. Expressions relating the T_g with $\langle Z \rangle$ were proposed by many authors [38]. Among these is the one obtained by modifying Gibbs–Di Marzio equation [39] and is given by

$$T_g = \frac{T_{g0}}{1 - \beta(\langle Z \rangle - 2)}, \quad (8)$$

where T_{g0} is the glass-transition temperature of the linear structure and, β is a constant depending of the glassy system investigated, with $0 \leq \beta \leq 1$. Thus, glass-transition temperature variations can be re-drawn as T_{g0}/T_g versus $(\langle Z \rangle - 2)$, with $T_{g0} = T_{g\text{Se}} = 309$ K [29]. This leads to $\beta = 0.9$.

For $\text{Ge}_x\text{Te}_{1-x}$, the range of compositions able to give a glass by quenching from the melt is limited to compositions close to the eutectic $\text{Ge}_{15}\text{Te}_{85}$. For compositions with greater than 20 at.% Ge, data

reported on Fig. 7 concern glasses obtained by vapor-deposition technique [25]. The first interesting difference between GeSe and GeTe systems is observed in the dependence upon the Ge content of the glass-transition temperatures and consists in the apparent lack of a threshold in $\text{Ge}_x\text{Te}_{1-x}$ at 20 at.% Ge. This result seems consistent with other observations which have shown that the structures of amorphous and liquid $\text{Ge}_{33}\text{Se}_{67}$ have characteristics similar to those of a network, while no such evidences were found in $\text{Ge}_{33}\text{Te}_{67}$ [40]. The lack of a network structure in $\text{Ge}_x\text{Te}_{1-x}$ was recently used to explain the kinetics of physical aging observed in $\text{Ge}_{15}\text{Te}_{85}$ [41], found equivalent to those expected for a linear like polymeric structure which results from the connection of tetrahedral GeTe_4 units sharing Te atoms at corners or edges [42]. In other words, the molecular relaxations in $\text{Ge}_{15}\text{Te}_{85}$ engage movements of tetrahedral GeTe_4 units. The existence of a like linear structure in the $\text{Ge}_x\text{Te}_{1-x}$ system a priori allows the use of relationship (8), but the calculation of $\langle Z \rangle$ (formula (7)) used in relationship (8) requires the knowledge of the coordination number of each constituent element. It is well established that the Ge atoms in $\text{Ge}_x\text{Te}_{1-x}$ are fourfold coordinated with Te atoms [43,44] while the coordination number of Te atoms is still debatable. Indeed, it was observed that, as there is semiconductor–metal transition close to the melting point, the Te-coordination number varies from 3 in the temperature range 300°C above the melting point to 2.4 about 50°C below it [45–47]. For the $\text{Ge}_x\text{Te}_{1-x}$ system, we may use formula (9) also to estimate a value for the CN of Te. In this glassy system, using $T_{g0} = T_{g\text{Te}} = 268$ K [26], the best fit of the experimental data (presented in Fig. 8) is obtained for $\text{NC}_{\text{Te}} = 2.4$ and $\beta = 0.5$. The existence of Te atoms with a coordination number of 2.4 has also been found to explain the observations concerning the kinetics of physical ageing in Se–Te alloys [48]. Thus, the structural modifications engaged by increasing the Ge content in $\text{Ge}_x\text{Te}_{1-x}$ (in the range of compositions investigated) consist in mainly changing the floppy nature of the medium.

Keeping in mind the glassy structures of $\text{Ge}_x\text{Se}_{1-x}$ and $\text{Ge}_x\text{Te}_{1-x}$ systems, we may now

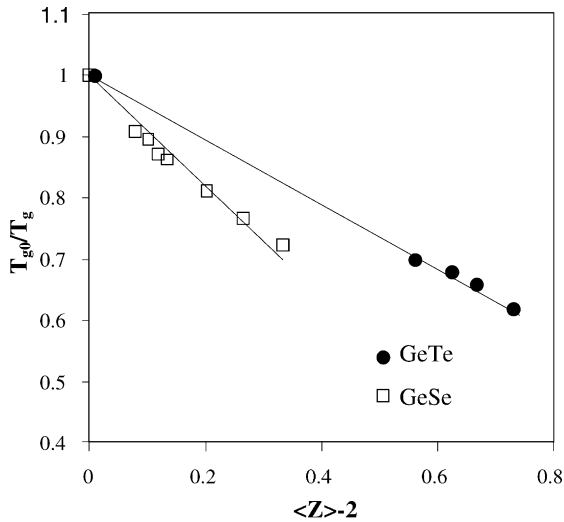


Fig. 8. Variations of the normalized quantity T_{g0}/T_g versus $\langle Z \rangle - 2$.

analyze the ΔC_p values obtained in this work. These values for $\text{Ge}_x\text{Te}_{1-x}$ as a function of the Ge content are displayed in Fig. 9. In the same figure, data collected in the literature and concerning the $\text{Ge}_x\text{Se}_{1-x}$ are also presented [49,50]. It is clear that all these glasses exhibit a behavior, which classify them more as thermodynamically strong [TS] rather than thermodynamically fragile [TF]. For the GeSe system, this [TS] behavior increases as the Ge content increases and exhibits a maximum for 20 at.% of Ge (ΔC_p variations present a minimum). We find again a change in a characteristic property of a glass for a composition corresponding to Phillips–Thorpe’s threshold. Already observed on the GeAsSe vitreous system [51,52] this change confirms one more time the forecasts of Phillips–Thorpe’s model when covalent bonds are engaged in the glassy structure (as long as the 8-N rule is respected). For the $\text{Ge}_x\text{Te}_{1-x}$ system, the obtained ΔC_p values are small, classifying also these glasses as thermodynamically strong. It is noteworthy that the ΔC_p values for $\text{Ge}_x\text{Te}_{1-x}$ and GeO_2 [52] are practically of the same order of magnitude. This last system is referred to in the literature as an example of extreme strong behavior. Following Angell [52], strong liquids (or strong glasses) are those with

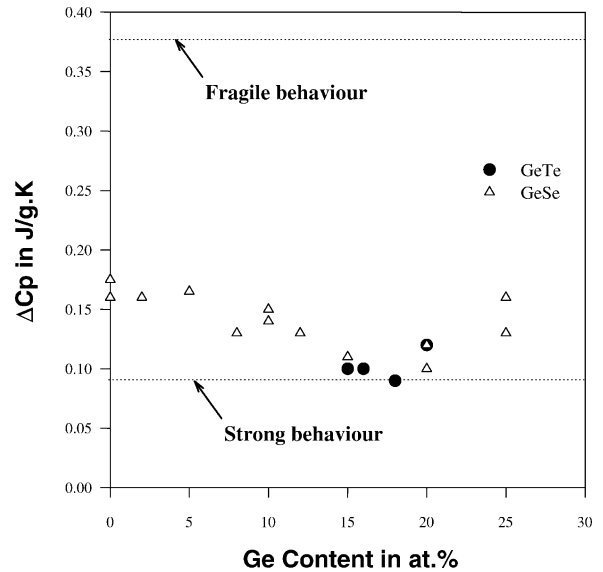


Fig. 9. Variations of ΔC_p at the glass transition for $\text{Ge}_x\text{Se}_{100-x}$ and $\text{Ge}_x\text{Te}_{100-x}$ with the at.% of Ge. Data for $\text{Ge}_x\text{Se}_{100-x}$ are taken from Ref. [49] and [50].

self-reinforcing tetrahedral network structures which manifest their resistance to structural degradation, while fragile liquids (or fragile glasses) are usually liquids without directional bonds. For the $\text{Ge}_x\text{Te}_{1-x}$ system, we may conclude that we have a self-reinforcing tetrahedral medium with directional bonds.

The variations of the fragility index m as a function of the Ge content for GeSe and GeTe vitreous systems are presented in Fig. 10. This figure reveals, from the values of the fragility index, the main differences between these two systems. With regard to the value of their fragility indexes, pure Se and $\text{Ge}_{15}\text{Te}_{85}$ exhibit the same and the most pronounced [KF] behavior. For GeSe vitreous alloys, this kinetic character becomes [KS] for compositions greater than 4 at.% of Ge. For $\text{Ge}_x\text{Te}_{1-x}$ glasses, in the range of composition investigated in this work, the value of the fragility index decreases as the Ge content increases. Thus, increasing the Ge content in $\text{Ge}_x\text{Te}_{1-x}$ leads to increase the [KS] character of the material. Assuming in a first approximation a linear dependence of m with the Ge content, the limit of the [KS] character is obtained for this system for a composition close to $\text{Ge}_{22}\text{Te}_{78}$, composition that

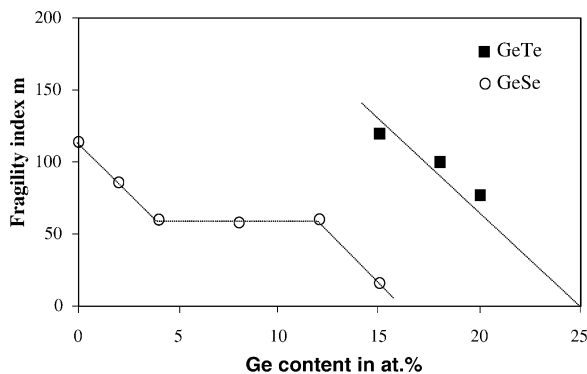


Fig. 10. Variations of the fragility index m for $\text{Ge}_x\text{Se}_{100-x}$ and $\text{Ge}_x\text{Te}_{100-x}$ with x at.% Ge. Data for $\text{Ge}_x\text{Se}_{100-x}$ are reproduced from Ref. [29].

is close to the upper limit able to give a glass from the liquid state [19].

Regrouping the kinetic and thermodynamic aspects, we observe that we have practically a [TS–KF] character for pure Se and $\text{Ge}_{15}\text{Te}_{85}$ which becomes [TS–KS] when the content in Ge atoms increases in the alloy composition.

6. Conclusion

Structural relaxation processes in $\text{Ge}_x\text{Te}_{1-x}$ vitreous alloys were found to determine the nature of their behavior in the “strong–fragile” concept. Although only three compositions were prepared and analyzed due to the limited glass-forming region confined around the $\text{Ge}_{15}\text{Te}_{85}$ eutectic, the results are compared with those of the chemically similar chalcogenide system (GeSe) for which a lot of data is available in literature.

Discussed from the “ m ” fragility index values, the results show that the investigated GeTe glasses exhibit similar strong thermodynamic character [TS] whereas for the GeSe system the [TS] nature increases with the Ge content (up to 20 at.% of Ge).

On the other hand, both vitreous systems (GeTe and GeSe) seem to have the same kinetic behavior starting from the kinetically fragile state (pure Se, $\text{Ge}_{15}\text{Te}_{85}$) and turning to kinetically strong character [KS] with the increase of the Ge content.

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