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Mean-coordination number dependence of the fragility in Ge–Se–In glass-forming liquids

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Abstract

Differential scanning calorimetry measurements have been performed on elemental Se as well as on $Ge_xSe_{94-x}In_6$ ($x = 4$, 8, and 11 at%) and on $Ge_ySe_{88-y}In_{12}$ ($y = 5$, 7, and 9 at%) chalcogenide glasses. From the cooling rate dependence of the fictive temperature, the apparent activation energies, Δh^*, and the fragility indices, m, as defined in the strong–fragile glass-forming liquid concept, are determined. It is found that, in Ge–Se–In system, there is an evolution from strong ($m = 67$) to fragile ($m = 116$) glass-forming liquids. The dependence of 'm' on the mean-coordination number, Z, is also obtained. This dependence is rationalized by assuming that, in this glassy alloy system, there is a tendency for the formation of In_2Se_3 clusters.

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Keywords: Strong–fragile concept; Mean-coordination number; Ge–Se–In glasses; Differential scanning calorimetry

1. Introduction

The study of structural relaxation in the glass transition region of glass-forming liquids is important from academic and technological points of view. Relaxation processes in glasses occur at temperatures lower than their glass transition temperatures, T_g. The glass transition temperature can be defined as the temperature at which the equilibrium liquid viscosity is of the order of 10^{12} Pa s or as the temperature at which the average relaxation time in the equilibrium liquid is about 100 s [1]. From the variations of the viscosity, η, or relaxation time, τ, with the normalized reduced T_g/T quantity, a classification scheme of glass-forming liquids has been proposed. This scheme is well known as the 'fragility concept' or as strong–fragile glass-forming liquid concept [2,3] and allows the definition of a fragility index, m [4]. This 'm fragility' or 'steepness' index is a measure of the rate at which the relaxation time τ (or related properties) decreases with increasing temperature around T_g and is given by [4]

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

In this classification scheme, glass-forming liquids which exhibit an approximately Arrhenius temperature dependence of their τ's are defined as strong and are characterized with a low value of m ($m \approx 16$ [5]). Those whose τ's are fitted with a Vogel–Fulcher–Tammann (VFT) equation are referred to as fragile and are characterized by a high value of m ($m \approx 200$ [6]). It is well recognized that oxide glass formers such as GeO_2 and SiO_2 with well-formed tetrahedral network rigid structures and directional bonds belong to the category of strong forming liquids [3,7–10]. On the other hand, linear polymeric materials are fragile forming liquids [11]. Thus, the concept of fragility in supercooled liquids has often been used as a basis for organizing data on amorphous materials: inorganic glasses [12], thermoplastics [9], polymer networks [13], and liquid-crystalline polymers [11].

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However, despite the extensive efforts expended in research on this 'fragility' concept, the factors that determine m for a given liquid or polymer remain poorly understood [14]. As the unpredictability of this property is a problem, because many aspects of the viscous liquid, such as aging behaviour and non-exponentiality of relaxation, are closely related to m, it is important to obtain new data on any liquid that can be vitrified to get a better understanding of the strong–fragile glass-forming liquid concept.

Because the addition of a third element as an impurity has a pronounced effect on the structural relaxation process, we propose in this paper to study the role played by metallic indium on the relaxation processes of covalently bonded Ge–Se glasses. Therefore, the purpose of this work is to obtain new m-data on Ge–Se–In glassy alloys, correlate it with their mean-coordination number which could be changed in a controlled way, compare the newly obtained results with those already existing on Ge_xSe_{100-x} vitreous system, and discuss them in terms of the strong and fragile behaviours.

2. Method

The determination of the fragility index, m, requires the choice of an expression for the relaxation time, τ. For a glass, τ is known to be dependent on the temperature and on some order parameters that define the glass structure [15–20]. In the present work and from among the different expressions in the literature for τ, the Tool–Narayanaswamy–Moynihan (TNM) expression [17,18,21] has been chosen which is given by

$$\tau = \tau_0 \exp\left(\frac{x\Delta h^*}{RT}\right) \exp\left(\frac{(1-x)\Delta h^*}{RT_{\mathrm{f}}}\right), \tag{2}$$

where x $(0 \leqslant x \leqslant 1)$ is the partitioning parameter that defines the degree of non-linearity, Δh^* is the apparent activation energy, R is the ideal gas constant, and 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. In the equilibrium state, where $T = T_{\mathrm{f}}$, and assuming that the heating or cooling a glass is equivalent to a succession of identical isothermal steps, it follows that $q\tau =$ constant (q is the cooling or heating rate) [22,23]. Under these assumptions, it is easy to show that Δh^*, the cooling rate q^- and the fictive temperature, T_{f}, are related via the relation

$$\frac{\mathrm{d}\ \ln(q^-)}{d(1/T_{\mathrm{f}})} = \frac{-\Delta h^*}{R}. \tag{3}$$

Thus, from the variations of $\ln q^-$ with $1/T_{\mathrm{f}}$ the value of Δh^* can be calculated. The fictive temperature can be determined graphically from the heat capacity changes vs. temperature curve by the so-called 'equal areas' construction method [18] using the following integral form:

$$\int_{T_{\mathrm{f}}}^{T} \left(C_{\mathrm{pL}} - C_{\mathrm{pV}}\right) \mathrm{d}T = \int_{T_1}^{T} \left(C_{\mathrm{p}} - C_{\mathrm{pV}}\right) \mathrm{d}T, \tag{4}$$

where T is any temperature above the transition region at which C_{p} is equal to the equilibrium liquid value, C_{pL}, and T_1 is a temperature well below the transition region. 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 that $q^+ = q^-$, the values of T_{g} and T_{f} are identified. Thus, knowing Δh^* and T_{g} and according to Eq. (1), the value of the fragility index, m, can be evaluated from

$$m = \frac{\Delta h*}{RT_{\mathrm{g}}\ \ln(10)}. \tag{5}$$

3. Experimental

The samples were prepared from a mixture of high-purity Ge, Se, and In according to the melt-quench technique. The mixture was introduced into cylindrical glass silica tubes (inner diameter = 8 mm) and sealed under vacuum of 10^{-5} Torr. Then, the tubes were placed in an electric furnace and annealed at 450 °C for 24 h. Afterwards, the temperature of the furnace was raised to 850 °C for 48 h. At this temperature, the tubes were frequently shaken to homogenize the melt. The quenching was done in an ice-cooled water.

Variations of the heat capacity changes at T_{g} were measured by differential scanning calorimetry (DSC) using DSC 2920 (modulated TA instrument) calorimeter run in the conventional mode The calorimeter was calibrated in temperature and enthalpy of melting of pure indium. A small lump of glass ($\approx$20 mg) was sealed in aluminium pan and referenced to an empty one. To avoid any sample contamination, all measurements were done under a nitrogen gas atmosphere. To obtain good reproducibility, for a given composition, the same sample sealed in an aluminium pan was used during all measurements. The sample in the DSC was first heated, at the rate of 20 K/min, to a temperature $T_2 > T_{\mathrm{g}}$ and kept at this temperature for 3 min before cooling it to a temperature $T_1 < T_{\mathrm{g}}$ at a cooling rate of 20 K/min. At this temperature, T_1, the sample was left for a period of 3 min before re-heating it at the same heating rate of 20 K/min to T_2 and then cooling it after 3 min at the new cooling rate of 10 K/min. Cooling experiments in the DSC from T_2 to T_1 for cooling rates ranging between 0.1 and 20 K/min were performed.

4. Results and discussion

Figs. 1 and 2 show the DSC curves obtained at the constant heating rate of 20 K min^{-1} on, respectively, $Ge_4Se_{90}In_6$ and $Ge_5Se_{83}In_{12}$ glassy alloys, cooled with different rates in the range 20–0.5 K min^{-1}. Similar DSC

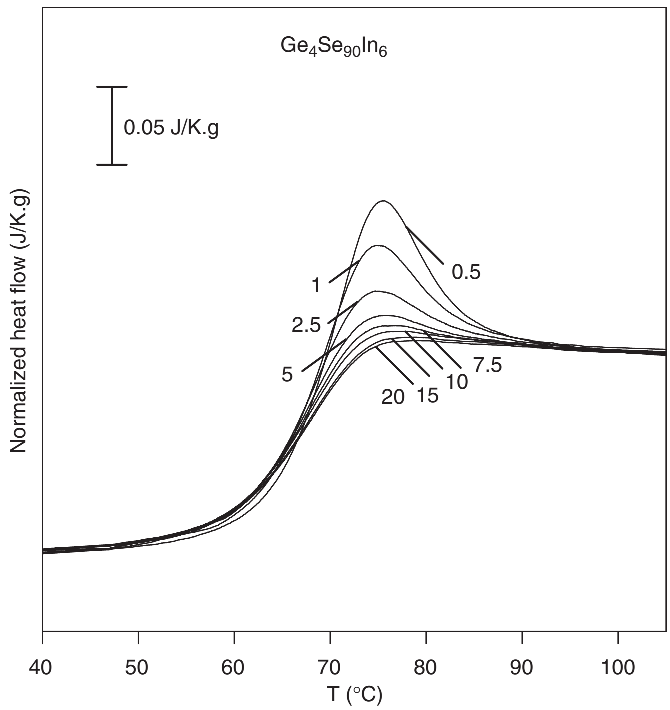

Fig. 1. DSC curves obtained on $Ge_4Se_{90}In_6$ glass. Cooling rates are indicated on each DSC curve.

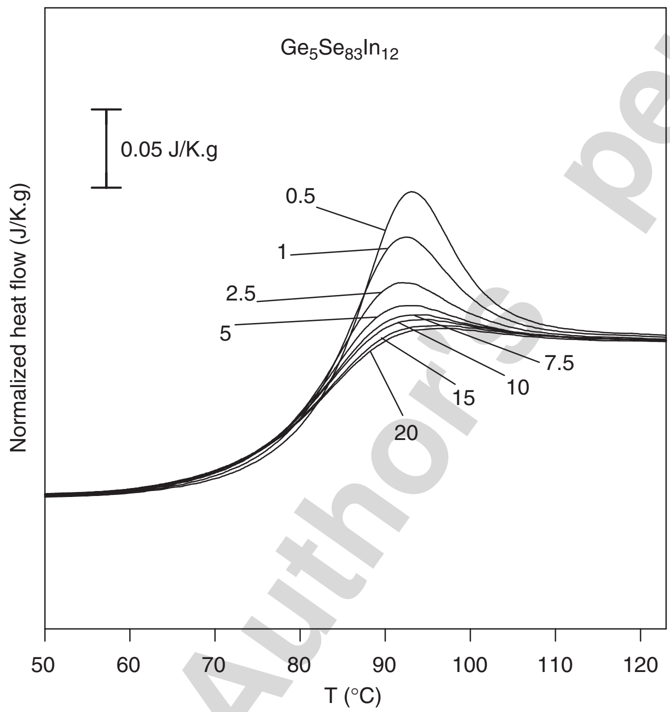

Fig. 2. DSC curves obtained on $Ge_5Se_{83}In_{12}$ glass. Cooling rates are indicated on each DSC curve.

curves were obtained on the other investigated glass compositions and are not shown here to avoid repetition. The measured glass transition temperatures, T_g, are given in Table 1. These values are in good agreement with the reported ones for this system [24–26] and as one expects, T_g increases with the increase of Ge at% in the glassy alloy in a given glass family. Because T_g results on this system have been discussed in the literature by many workers [24–26], we are not going to discuss them any further. Our emphasis in this work is on the results of the determination of the fragility index and its composition dependence where no account of such results appeared in the literature.

The apparent activation energy of relaxation, Δh^*, is obtained according to Moynihan's method and associated Eq. (3). It is calculated from the slope of the dependence of $\ln q^-$ vs. reciprocal T_f in thermal cycles performed on the same sample without any aging. Such dependencies are depicted in Figs. 3 and 4 for glasses containing 6 and 12 at% In, respectively. The values of Δh^* estimated from Eq. (3) are given in Table 1. By using Eq. (5), one can calculate the fragility index, m, from the measured T_g and evaluated Δh^*. The values of Kovacs–Aklonis–Huchinson–Ramos (KAHR) parameter θ, estimated from $\Delta h*/RT_g^2$ [19], where R is the gas constant, are also obtained and listed in Table 1. The parameter θ is a material constant that characterizes the temperature dependence of the retardation times in structural relaxation [27–29] and lies in the range of 0.1–1 K^{-1} for various inorganic glasses [30]. The values of θ for Ge–Se–In glasses lie in the range 0.45–0.84 which agree with the reported values for inorganic glasses.

As it can be seen from Table 1, m varies from 67 for $Ge_4Se_{90}In_6$ to 116 for $Ge_9Se_{79}In_{12}$ while the corresponding value for linear polymeric Se, characteristic of fragile glass-forming liquids, is 114. Thus, in this glassy alloy system, there is an evolution from strong ($m = 67$) to fragile ($m = 116$) glass-forming liquids. To be able to interpret these results, we have assumed the formation of demixed structures, in stoichiometric proportions, in the glassy matrix in the form of In_2Se_3 clusters. The formation of clusters has been successfully used for the interpretation of the composition dependence of the T_g's for this system [31]. Therefore, the ternary system, $Ge_xSe_{1-x-y}In_y$ with the corresponding coordination numbers, $r_{Ge} = 4$, $r_{Se} = 2$, and $r_{In} = 3$, is pictured as pseudo-binary system. The value of the coordination number of In is obtained from extended X-ray absorption fine structure (EXAFS) measurements from the In K-edge [32] while those corresponding to Ge and Se are known to conform with Mott's (8-N) rule [33], where N is the number of outer shell electrons. The formation of In_2Se_3 clusters allows one to rewrite the $Ge_xSe_{1-x-y}In_y$ system as $(In_2Se_3)_{y/2}Ge_xSe_{1-x-5y/2}$ and to define an effective concentration of Ge atoms $y_{eff} = y/[1-(5x/2)]$. Finally, the mean-coordination number, Z, of the glassy network is evaluated via the relation $Z = 2 + 2y_{eff}$. The calculated Z values are listed in Table 1 and range from 2.09 to 2.26.

The dependence of 'm' on Z is obtained and shown in Fig. 5. For reader's convenience, we reproduce in Fig. 5 the results of the fragility vs. mean-coordination number for the binary Ge_xSe_{100-x} [12]. This figure reveals the main differences between the behaviours of the fragility index of

Table 1
Values of T_g, Δh^*, θ, m, and Z for the investigated glass compositions

Glass composition			T_g (°C)	Δh^* (kJ/mol)	θ (K^{-1})	m	Z	$D(T_g)$
Ge	Se	In						
0	100	0	38	678	0.84	114	2.00	7
4	90	6	66.5	435	0.45	67	2.09	4
8	86	6	92.5	692	0.62	99	2.19	6
11	83	6	110	791	0.65	108	2.26	7
5	83	12	81	487	0.47	72	2.14	5
7	81	12	100.5	621	0.54	87	2.20	5
9	79	12	114	858	0.69	116	2.26	7

Refer to text for the meaning of symbols.

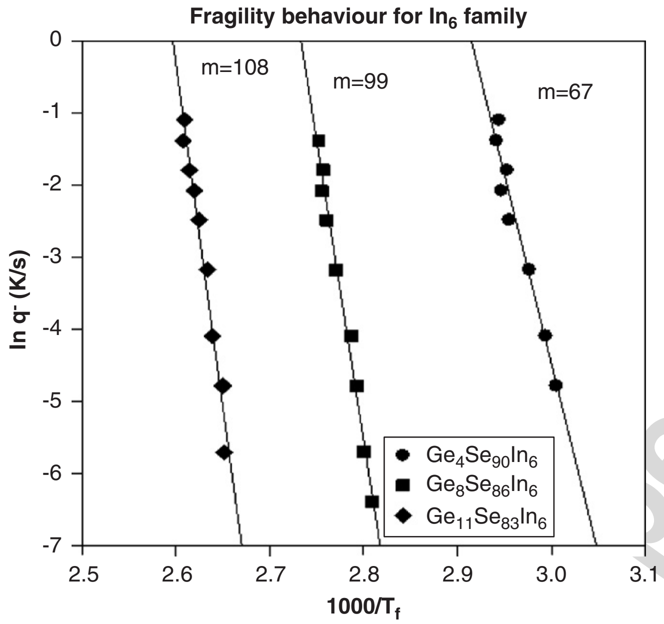

Fig. 3. Variations of $\ln(q^-)$ with $1/T_f$ for glass compositions containing 6 at% In.

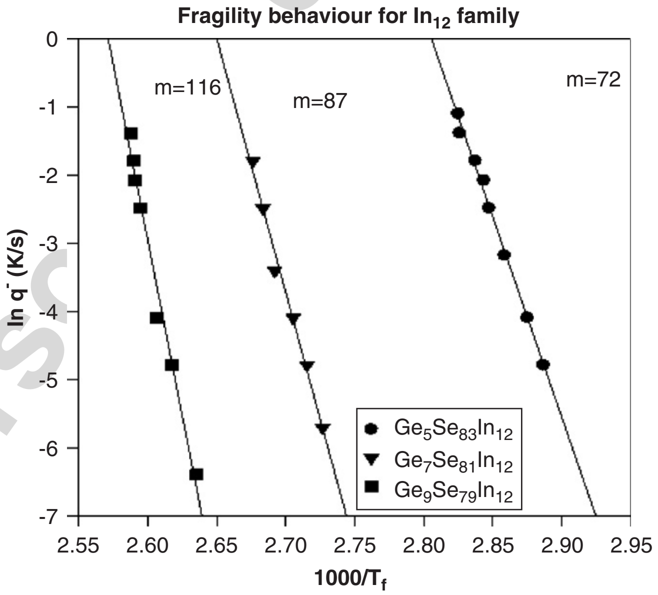

Fig. 4. Variations of $\ln(q^-)$ with $1/T_f$ for glass compositions containing 12 at% In.

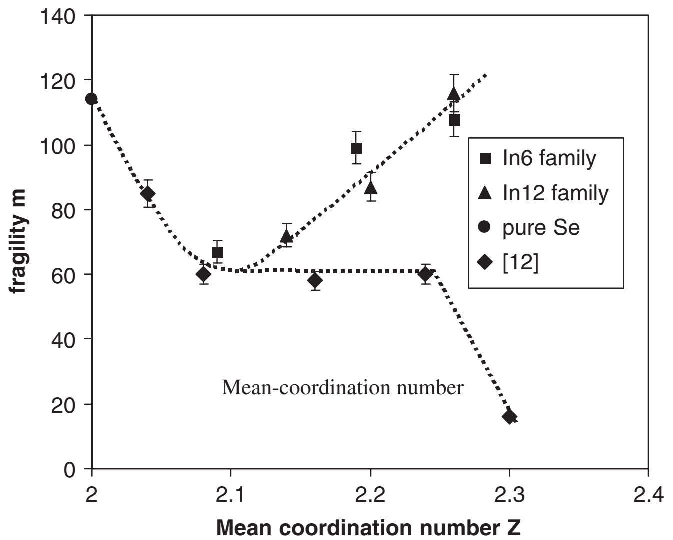

Fig. 5. Variations of the fragility index, m, for the investigated compositions. Data for Ge_xSe_{100-x} are reproduced from Ref. [12].

the Ge–Se and the Ge–Se–In systems. With regard to the value of the fragility index, linear polymeric Se ($m = 114$) and the compositions $Ge_{11}Se_{83}In_6$ ($m = 108$) and $Ge_9Se_{79}In_{12}$ ($m = 116$) exhibit almost the same and the most pronounced fragility behaviour. On the other hand, for the binary Ge_xSe_{100-x}, the character becomes strong ($m \approx 60$) for compositions in the Z range 2.08–2.24 and it attains the most strong character ($m = 16$) for the composition $Ge_{15}Se_{85}$ ($Z = 2.30$). Also, it can be noted from Fig. 5 that, at the specific values of $Z \approx 2.1$ and 2.24, the fragility index in the Ge_xSe_{100-x} system is modified. These critical Z values, which do not appear in the binary phase diagram, were also presented by Phillips [34] from viscosity data [35], observed for crystallization ability [36], from optical gap variation [37] and more recently from data on the modified concept of the native open-volume micro-voids [38]. In a series of papers, Saiter et al. [7,12,39–42] explained this behaviour by assuming that the relaxation process, in the Z

range $2 \leqslant Z \leqslant 2.08$, takes place by molecular movements along the Se linear polymeric chain and that the elementary cell for an elementary movement engages at least three adjacent Se atoms called 'Se cells'. The Se atoms in these cells are connected together by two-fold covalent bonds. In the plateau, covering the Z range from 2.08 to 2.24, the development of cross-linked structure by the addition of Ge atoms results in the formation of 'Ge cells'. These cells are made of a Ge atom with its four neighbouring covalently bonded Se atoms. Therefore, the number of 'Se cells', associated with the molecular mobility and the relaxation by bending or/and stretching of bonds, decreases and totally vanish for $Z \approx 2.24$. Thus, the plateau in the fragility index is a balance between the two competing effects of the 'Se cells' and the 'Ge cells' (those latter 'Ge cells' try to limit the molecular movements). Upon further increase in Z, the formation of three-dimensional network structure almost freezes the molecular mobility and thus leads to the drastic decrease in the fragility index and the attainment of the most strong composition. Said differently, the observed anomalies at $Z \approx 2.1$ and at $Z \approx 2.24$ are connected with the topological transformations of the glass structure and the progressive increase in its dimensionality from $1 \rightarrow 2 \rightarrow 3$.

To this end, it is interesting to note from Fig. 5 that the values of the fragility indices of the ternary system Ge–Se–In are higher than those of the binary Ge–Se system, i.e., there is a departure from the plateau characterizing the fragility values of the binary Ge–Se system where no In_2Se_3 clusters exist. Moreover, the formation of In_2Se_3 clusters in the Ge–Se–In system seems to modify the molecular mobility of the structure in such a way that the relaxation processes associated with linear polymeric Se are restored for the networks of the $Ge_{11}Se_{83}In_6$ and $Ge_9Se_{79}In_{12}$ glassy alloys. This behaviour, where the addition of third element of metallic character like In to the covalently bonded Ge–Se binary is capable of restoring the relaxation process of that of linear polymeric Se, is observed and reported in the literature for the first time.

Finally, the average size of the cooperative rearranging region (CRR) at the glass transition, D (T_g), which characterizes the relaxation processes associated to the glass transition domain, has been calculated according to the equation proposed by Solunov [43] and given by

$$m = C_1 D(T_g), \qquad (6)$$

where the constant C_1 is equal to 16 [44]. The calculated values of D (T_g) are listed in Table 1. Solunov's equation stresses the relationship that exists between the kinetic characteristics of a glass-forming liquid (i.e., the fragility index) and the main property of the glass formed in terms of the relaxation process (i.e., the size of the CRR at the glass transition). It can be noted from Table 1 that the size of the CRR for the $Ge_{11}Se_{83}In_6$ and $Ge_9Se_{79}In_{12}$ glassy alloys are comparable to those of a linear system.

5. Conclusions

By adding In to the Ge–Se binary system, we change the mean-coordination number of the alloys by changing the number ratio of Ge/Se atoms. This affects the relaxation behaviour in the glass transition region by changing the value of the fragility index. In the Z range from approximately 2.20 to 2.26, we find that the addition of In to Ge–Se system destroys the bi-dimensional network of Ge–Se and a linear-like behaviour is restored. This is because the size of the CRR available for the relaxation mechanism is also restored.

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