

PHYSICAL AGEING IN CHALCOGENIDE GLASSES

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In this work, some relationships proposed in the literature in order to link the value of the glass transition temperature and the structure engaged in chalcogenide based alloys are discussed. We show that because of the bad knowledge of the real surrounding of the different atoms engaged in the material composition, these relationships must be used with some precautions. On the other hand, from the study of the physical ageing, general property for a glassy structure, we show that for specific values of the average coordination number ($Z \approx 2.1$ and $Z \approx 2.24$) calculated for system obeying to the 8-N rule, many properties as apparent activation energy for the relaxation, crystallisation ability, optical gap, viscosity, are modified. Finally, the physical ageing kinetic measurements are found dependent on the structures engaged in the glassy systems. In particular, we show that molecular species as GeTe_4 can also move during ageing in spite of its massive character and strong connectivity.

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1. Introduction

Thirty years ago, the first sentence of a paper devoted to glassy chalcogenide based materials was, as an example:

"Chalcogenide glasses exhibit many useful electrical, opto-electrical threshold and memory switching properties and thus appear as good candidates for new technological applications".

Today, basically the same sentence is used and, in spite of all these useful properties, it seems that all these hopes have not been followed by concrete applications. Nevertheless these new properties and potential applications exist. Indeed, since the well-known xerography process using Se or SeAs, we may note lithography with $\text{Ge}_{25}\text{Se}_{75}$ [1], CD compatible erasable disk with GeTe or GeTeSe [2], chemical sensors with AsS and AsSe based alloys [3], long lengths of low loss IR transmitting devices with $\text{As}_{40}\text{S}_{60-x}\text{Se}_x$ [4] and also the use of switching and memory effects as observed in $\text{Bi}_{26}\text{Te}_{35}\text{Se}_{36}$ [5] or photodarkening properties as in As_2S_3 , As_2Se_3 , GeSe_2 or GeS_2 . [6,7].

In fact, one of the most important behaviour of a glassy structure is often omitted. By definition, a glass is characterised by a lack of thermodynamic equilibrium. As a consequence, all the physical properties are time dependent, generally refereed as physical ageing phenomenon [8]. As an example, Fig. 1 shows the variations with time of the current measured on a $\text{Bi}_2\text{Se}_{98}$ thin film maintained at 293 K and submitted to a potential increment of 10 V. After more than 50 h, the current is not stabilised. The time constant (or distribution of time constant) characterising this behaviour cannot be obtained by electric charge transfers associated (or not) to defects recombination. This result implied that a relaxation process of large magnitude engaging the structure itself (atomic or molecular relaxation), must be taken into account. What are the consequences of molecular relaxation (physical ageing) on a given property? This key question must be associated with a second one: do correlation exists between the glass structure and its physical ageing kinetic? Today, it is not possible to propose a general model linking the glassy structure in a glass and its ability to relax. In this work, we present a set of results allowing the proposition of some interesting tendencies.

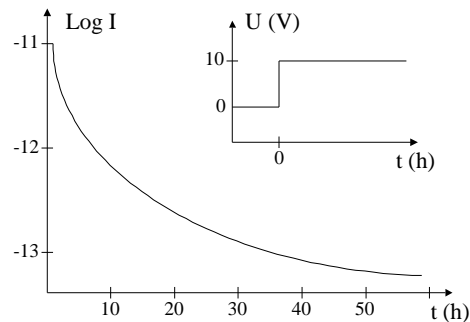


Fig. 1. Variations with time of the dark current measured on a $\text{Bi}_2\text{Se}_{98}$ thin film.

Cooling a liquid with a rate high enough to avoid the crystallisation will lead it to the supercooled regime in which the viscosity will increase drastically as the temperature will decrease. For a given temperature (T_g), or more precisely for a given domain of temperatures called the glass transition, the supercooled liquid is frozen in, the viscosity reaches values as large as 10^{12} poises, and for $T < T_g$ a glassy structure is obtained. As exemplified on Fig. 2, this glassy structure is characterised by an excess of free volume or, which is equivalent, by an excess of enthalpy, an excess of configurational entropy when comparison is made with the corresponding thermodynamic equilibrium state. Then, the disorder engaged into the glassy structure can be defined at different scales (short, medium or long range). As a second consequence, a glass kept at $T < T_g$ will lose its excess of enthalpy by molecular relaxation to reach more favourable thermodynamic states. Thus, a glass kept during an infinite time at $T < T_g$ must reach the thermodynamic equilibrium. This goal is obtained with the supercooled liquid state (extrapolated in the temperature domain $T < T_g$) and not with the crystalline one (see Fig. 2). With other words, a glass cannot crystallise by physical ageing. To crystallise the material, it is necessary to heat the glass above its glass transition in order to reach a viscosity value low enough to authorise molecular rearrangements or atomic diffusions (Fig. 3). Many models are now available to analyse the relaxation kinetic [9-12] and it is now established that a good model must take into account the following characteristics. Molecular relaxations in the glass and for temperatures close to T_g are of cooperative natures. Relaxation kinetics cannot be described by a linear and an exponential time relaxation function and a distribution of relaxation time function must be taken into account. The phenomenon is reversible by a thermal cycle consisting of heating the glass above T_g and then cooling back to the annealing temperature, of course if no crystallisation occurs in the supercooled state.

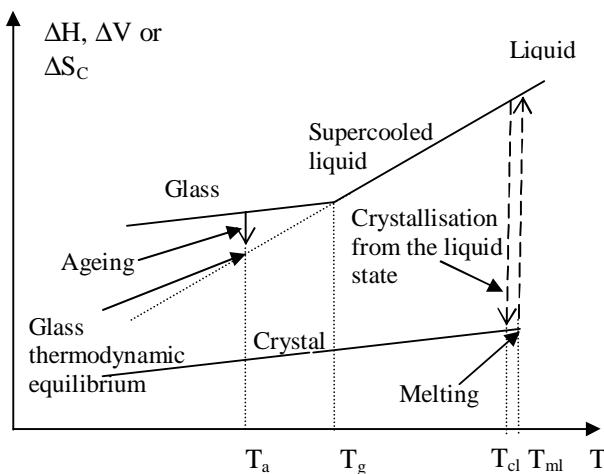


Fig. 2. Enthalpic diagram showing the glass transition and the crystallisation from the liquid state (T_{cl}) and the melting T_{ml} .

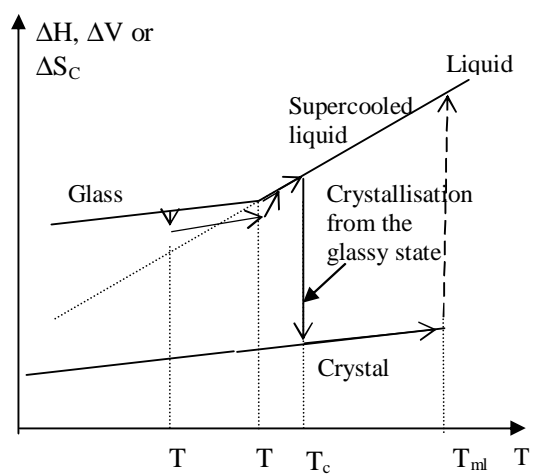


Fig. 3. Enthalpic diagram showing the crystallisation from the glassy state.

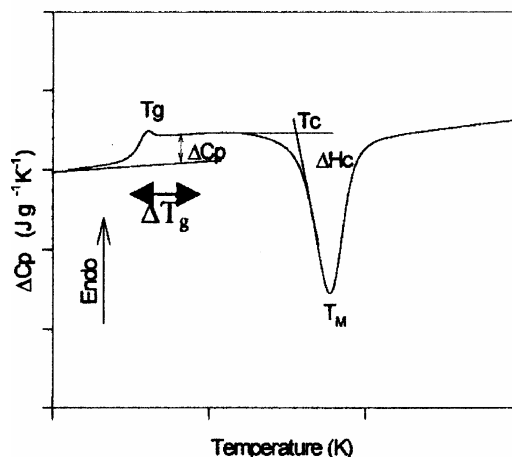


Fig. 4. Typical DSC trace obtained with a chalcogenide glass.

To analyse a glass, one of the easiest methods consists in performing calorimetric measurements. Fig. 4 shows a typical differential scanning calorimetric curves that could be obtained for instance on a Se glass. At low temperature, the glass transition is observed by only an endothermic ΔC_p step if the sample is non-aged or an endothermic peak if the sample is aged. Then at higher temperature an exothermic peak of crystallisation also called cold crystallisation or devitrification to distinguish this transformation from the one obtained by slow cooling from the liquid state. Finally, the melting of the crystalline part occurs at higher temperatures (non-presented on Fig. 4) as an endothermic peak. Thus to characterise a glass, such measurements give us many facilities. We have: the glass transition temperature T_g , the value of ΔC_p at T_g , the domain of temperature on which the glass transition occurs $\Delta T_g = T_{gmax} - T_{gmin}$, the area of the endothermic relaxation peak δH , the value of the crystallisation temperature (T_c or T_m), the enthalpy of crystallisation ΔH_c and finally the distance $T_c - T_g$. Each of these quantities can give us precious informations for the considered glass. For instance and for only the glass transition:

- 1) Greatest the T_g , greatest must be the rigidity of the medium [13,14].
- 2) Greatest ΔT_g , greatest must be the width of the time relaxation distribution [15].
- 3) Greatest ΔC_p , greatest must be the fragility (from the Angell strong fragile liquid glass former concept [16]).

Most of these quantities are not material constants but depend also on the measurement methods, on the constraints undergone and on the thermal history of the samples. For instance, the values of the cooling rate, the heating rate, the sample age, the value of the annealing temperature influence and modify the values of T_g , ΔT_g , δH , T_c , ΔH_c [17,21]. With other words, to compare data of different origins, many precautions must be taken but these dependencies can also give us many new opportunities to characterise a glassy structure. In this field, among all the different materials able to be studied, chalcogenide elements and alloys exhibit the great advantage to give a large variety of systems whose we may a priori control the structures. In the following, this opportunity will be analysed for different vitreous chalcogenide based alloys. In particular, the value of the glass transition temperature, and the relaxation kinetics will be investigated.

2. Glass transition temperature and structure

As previously mentioned, it is well established that T_g depends on the connectivity, and consequently on the rigidity of the vitreous network. This means that, using a linear polymeric structure as Se vitreous matrix, by adding an element with coordination number greater than 2, it will result an increase of the T_g values with the content of the added atom. The variations of T_g collected from the literature and obtained on the covalent systems $Se_{1-x}Ge_x$, $Se_{1-x}As_x$ and on the $Se_{1-x}Bi_x$

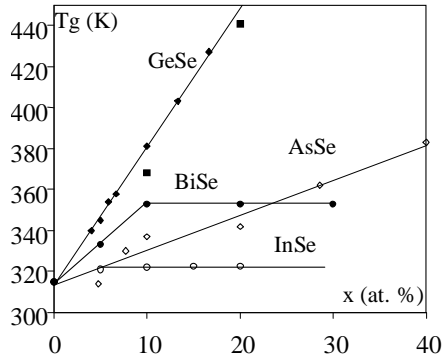


Fig. 5. Glass transition temperature of Se based binary glassy alloys as a function of concentration of added element.

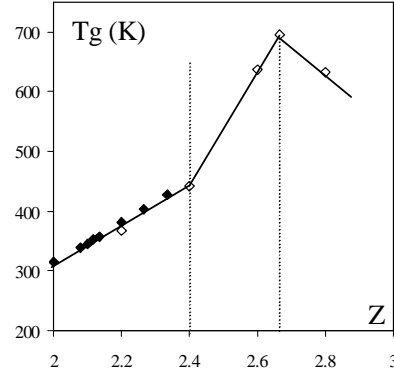


Fig. 6. Variations of T_g versus Z for $\text{Se}_{1-x}\text{Ge}_x$. Lines are drawn as guides for the eyes.

and $\text{Se}_{1-x}\text{In}_x$ [22-24] are presented on Fig. 5. It is clear that T_g increases with x for the covalent systems (with Ge and As atoms). This is the expected behaviour, the threefold As atoms and the fourfold Ge atoms increasing the connectivity of the medium. For the Se-Bi system, T_g increases at low Bi content and up to 10 at.%, while for Bi content greater than 10 at.%, T_g remains constant. For the Se-In system, T_g remains constant whatever the In content. The plateau is interpreted by the existence of demixed structures, respectively Bi_2Se_3 and In_2Se_3 micro-clusters. Since the works of J.C. Phillips [25] and K. Tanaka [26], it is established that glassy covalent networks exhibit two topological thresholds. Describing these glassy structures by means of virtual atoms bonded together with an average coordination number given by

$$Z = \sum_i x_i Z_i \quad (2.1)$$

(x_i is the at.% content and Z_i the coordination number of element i), the glass network must change from a floppy to a rigid type for $Z = 2.4$ (Phillips constraints theory) and changes from a two-dimensional layered structure to a three-dimensional network arrangement for $Z = 2.7$ (Tanaka model). These two thresholds are well observed on the T_g versus Z variations on many binary and ternary chalcogenide based glasses and is exemplified by the results concerning the $\text{Se}_{1-x}\text{Ge}_x$ reported in Fig. 6. One neat way to describe the variations of T_g with Z in chalcogenide glasses was proposed by Sreeram et al [23] according to the Gibbs DiMarzio modified relationship:

$$T_g = \frac{T_{g0}}{1 - \beta(Z - 2)} \quad (2.2)$$

where T_{g0} is the glass transition temperature of the linear polymer and β a system parameter included between $0 < \beta < 1$. The stochastic origin of the Gibbs DiMarzio modified equation, recently demonstrated by M. Micoulaut et al [27] allows to propose a topological origin, for the constant β according to the relationship:

$$\beta^{-1} = \sum_{i=1}^{M-1} (Z_i - 2) \ln \left[\frac{Z_i}{2} \right] \quad (2.3)$$

where Z_i is the coordination number of element i added in the chalcogenide matrix. Many data have been successfully fitted with relationship 2, as for instance $\text{Ge}_x\text{Sb}_y\text{Se}_{1-x-y}$, $\text{Ge}_x\text{Sb}_y(\text{Se}_{60}\text{Te}_{40})_{1-x-y}$, $\text{Ge}_x(\text{Sb}_{66}\text{As}_{34})_y(\text{Se}_{60}\text{Te}_{40})_{1-x-y}$ systems (compositions are per mole %). More recently, the problem of the role played by In atoms in the Ge-Se-In system was solved with the help of equation 2. As for the Se-In binary system, it was shown that In atoms do not participate to the variations of T_g in Ge-Se-In [24].

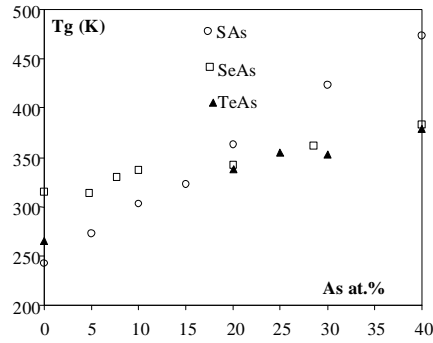


Fig. 7. Variations of T_g for As modified binary chalcogenide materials.

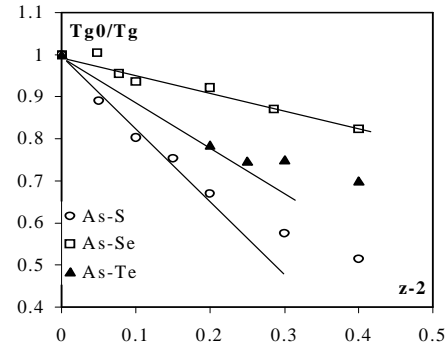


Fig. 8. Variations of T_{g0}/T_g with Z for chalcogenide-As alloys assuming $Z_{\text{As}}=3$ and $Z_{\text{chalcogene}}=2$

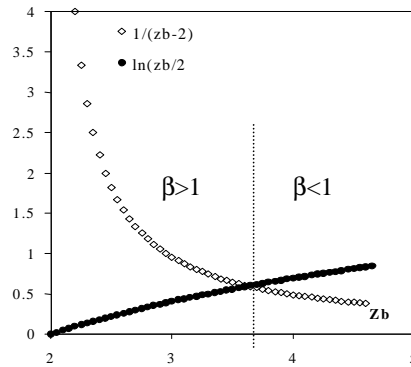


Fig. 9. Stochastic model limit.

Finally, it appears that until no heteropolar bonds are formed by the added element in the chalcogenide network and until it exists no ambiguity concerning the values of the coordination numbers of the different atoms constituting the investigated alloys, the variations of T_g with Z are well described by these formula and the topological thresholds are well observed. Nevertheless their universal characters must be proved yet. As an example, Fig. 7 shows the variations of T_g measured on $\text{S}_{1-x}\text{As}_x$, $\text{Se}_{1-x}\text{As}_x$ and $\text{Te}_{1-x}\text{As}_x$ [22,23] as a function of x . For Se, and As atoms, it is clear that the 8-N rule is respected leading respectively to $Z_{\text{Se}}=2$ and $Z_{\text{As}}=3$. If we assume that the 8-N rule is also respected by the other chalcogenide elements as it is often made in many works, the variations of T_{g0}/T_g with $(Z-2)$ according to formula 2 must be linear and the slopes give directly the value of β . As evidenced by Fig. 8 no such linear variations are observed and moreover, the values of β found for $\text{S}_{1-x}\text{As}_x$ and $\text{Te}_{1-x}\text{As}_x$ are not conform to the model prediction (respectively 1.7 and 0.9). This non-universal character is also included in formula 2.3. Indeed, for a binary chalcogenide system A_xB_{1-x} for which B is the added element of coordinence Z_b , the condition $0 < \beta < 1$ implies for formula (2.3) that:

$$\frac{1}{Z_b - 2} < \ln \frac{Z_b}{2} \quad (2.4)$$

It follows that the stochastic approach requires that the coordination number of the added atom Z_b must be greater than 3.6 (Fig. 9). Thus, it occurs that an universal relationship linking the glass transition temperature to a the value of the coordination number requires to find some more considerations about the nature of the added atom. Not so far of the stochastic model, it was shown for ≈ 200 different covalent chalcogenide alloys that a good correlation between the glass transition temperature and the overall mean bond energy exists according to Tichý et al. (2.5) [28] relationship:

$$T_g = T_{g0} + \frac{\delta(Z-2)E}{k_b \ln(\mu_{Tg} / \mu_0)} \quad (4)$$

where δ is a material parameter, E the bond energy, μ the viscosity and k_b the Boltzmann constant. Nevertheless, one more time, the use of relationship (2.5) requires to know the value of the coordination number of the added atom. To validate this relationship, the 8-N rule was used for elements as Te, In, Bi. As exemplified by the data reported in Table 1, if it is clear that the 8-N rule works well for Ge, As, Se elements, this is not clearly the case for the others. One way not yet investigated is the role of the steric constraints due to the size of the added element. Indeed, the glass transition can also be defined by means of free volume considerations. As shown on Fig. 10, even if the coordination number of Te atoms is supposed to be 2, when incorporated in a Se linear structure, its diameter is so large that its contribution to the disorder does not concern short range but medium range. As a consequence, twofold coordinated Te atoms can produce the same effects as that observed for an element having a smaller size and a greater coordination number.

Table 1. Values of the coordination number of some elements obtained by means of the 8-N rule compared with results obtained by EXAFS or other experimental methods.

Element	8-N rule	EXAFS/others	Ref
Se	2	2	
As	3	3	
Ge	4	4	
Te	2	2, 2.4, 3	29
Bi	3	3, 3.5, 4	30
In	4	3	31

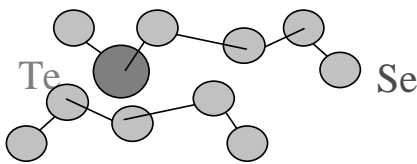


Fig. 10. The existence of Te atoms creates short and medium ranges disorder.

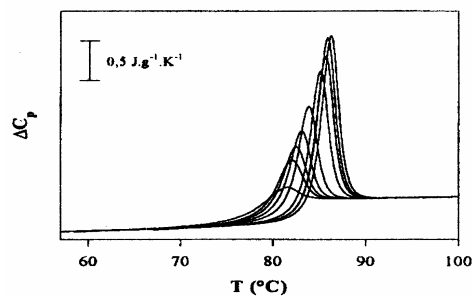


Fig. 11. Typical DSC trace obtained on a glass, kept at a constant temperature $T < T_g$ aged with different durations. The endothermic peak of relaxation is shifted toward the highest temperatures and the enthalpy increases.

3. Relaxation kinetics & structure

As previously mentioned, a glass relaxes when it is kept at a temperature below T_g . On a DSC curve, this phenomenon is observed by an increase of the value of T_g with ageing time,

associated with an excess of enthalpy at T_g (Fig. 11). The variations with time of the configurational enthalpy can be written as:

$$\frac{d(\Delta H)}{dt} = \frac{\Delta H}{\tau} \quad (3.1)$$

where the relaxation time τ must take into account the cooperative effects [32]. Different expressions for τ have been proposed but all can be resumed by $\ln(\tau) = F(T) + G(S)$, where $F(T)$ and $G(S)$ are the contribution of the temperature and of the structure respectively. Assuming that $\Delta H \approx \Delta C_p \Delta T$, it was already shown that the variations of T_g with time can be written as [20]

$$\frac{dT_g}{dt} = - \frac{\Delta T_g \exp\left[(b - c\Delta C_p)\Delta T_g\right]}{a \exp\left(\frac{\Delta E_a}{RT}\right)} \quad (3.2)$$

where a , ΔE_a , b , c , ΔC_p (difference between C_p in the liquid and vitreous states) depends on the material. From a systematic study of the variations of T_g with the ageing time, the annealing temperature and using also the results obtained from the variations of T_g with the heating rate, all these quantities can be determined. In the following, only the results concerning ΔE_a obtained on chalcogenide systems for which the 8-N rule is respected will be presented and discussed. Fig. 12 shows the variations of the apparent activation energy as a function of the average coordination number for GeSe and AsSe glassy systems. As we may note, in addition to Phillips and Tanaka thresholds, it appears for others values of Z , respectively $Z \approx 2.1$ and $Z \approx 2.24$. These values of Z were also presented in the first paper of Phillips [25] from data concerning the viscosity [33] (Fig. 13), were also observed for crystallisation ability [34] (Fig. 14) and finally for the variations of the optical gap of AsSe [35] (Fig. 15). Assuming that the relaxation in pure Se takes places by molecular movements along the Se polymeric chain, it follows that the elementary cell for an elementary movement engages at least three adjacent Se atoms (Fig. 16). The development of the cross-linked structure by addition of Ge or As atoms decreases the number of Se cells. These Se cells vanish for $Z \approx 2.24$ [20]. Thus Ge cells as As cells (Fig. 16) seem to not participate to the relaxation process and act only as blocking molecules. On the other hand, for $Z \approx 2.1$ the number of blocking cells is large enough to erase the ability of the Se cells to move at large scale and thus to authorise for instance a crystallisation process [20]. As the steric volumes occupied by Ge, As, or Se atoms are not fundamentally different, basically the same phenomena occur, whatever the considered, property, when comparisons are done as a function of Z . Does it means that massive molecules as Ge cells or As cells cannot move? The answer is no. Indeed, as shown by the DSC traces reported on Fig. 17 and obtained on $\text{Ge}_2\text{Se}_{98}$ aged more than 10 years at room temperature, two endothermic peaks of relaxation (each of large magnitude) are observed. This sample after rejuvenation exhibits the characteristic of non aged material. In fact the characteristic time constant for the relaxation process of Se cells is shorter (some months) than the characteristic time constant of the Ge cells (several years). To verify this observation, the relaxation kinetics of more complex systems ($\text{Ge}_x\text{Te}_{1-x}$, $0.15 < x < 0.20$) have been investigated. This system exhibits many advantages. It was extensively studied and if it is not established that the 8-N rule is respected by the Te atoms, it was clearly demonstrated that Ge atoms are fourfold coordinated to only Te atoms [36,37].

The relaxation kinetic were studied according to formula (2.4) and with the Tool Narayanaswamy Moynihan [32, 38, 39] relationship for the relaxation time

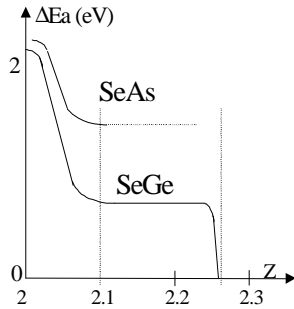


Fig. 12. Variations with Z of the apparent activation energy of the glass transition.

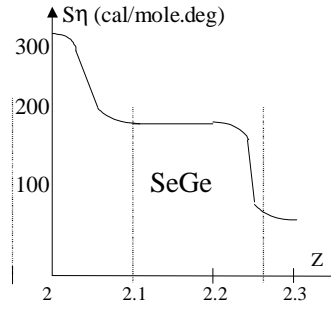


Fig. 13. Activation energy for the viscosity entropy.

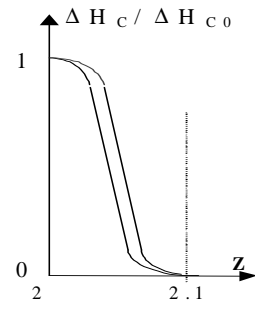


Fig. 14. Normalised crystallisation enthalpy for Ge-Se and As-Se glasses.

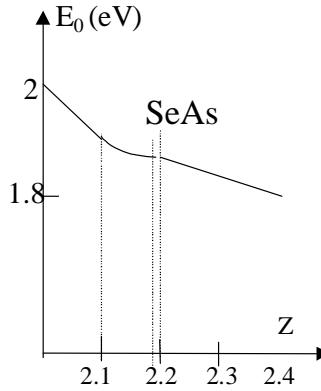


Fig. 15. Optical gap of As-Se.

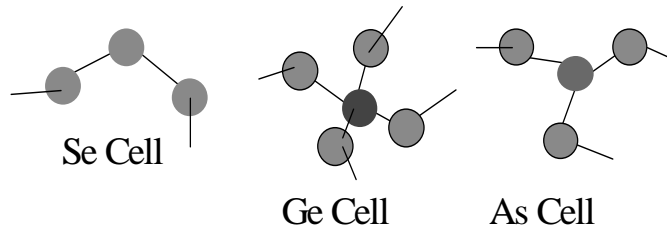


Fig. 16. Molecular structures in GeSe and AsSe glassy systems.

$$\tau = \tau_0 \exp\left(\frac{x\Delta h^*}{RT}\right) \exp\left(\frac{(1-x)\Delta h^*}{RT_f}\right) \quad (3.3)$$

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.

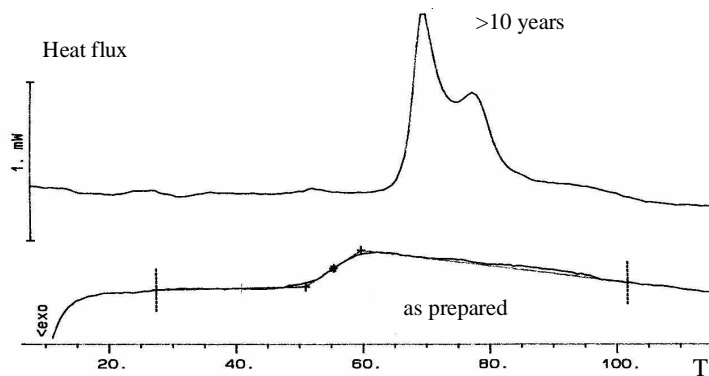


Fig. 17. DSC traces obtained on $\text{Ge}_2\text{Se}_{98}$ aged more than 10 years at room temperature and for the same sample after rejuvenation.

The values of Δh^* and x have been determined by means of respectively the Moynihan [39] and the peak shift [40] methods. The values obtained for these parameters are reported in Table 2. In this table, in order to perform a comparison the results obtained for some glassy alloys of the Ge-Se system [41] are also reported.

Table 2. Values of the TNM parameters obtained for GeSe [41] and GeTe [42] glassy alloys.

Material	Se	Ge ₈ Se ₉₂	Ge ₁₂ Se ₈₈	Ge ₁₅ Te ₈₅
X	0.57	0.60	0.50	0.67
Δh^* (kJ/mole)	675	384	428	994
T_g (°C)	36	74	105	128

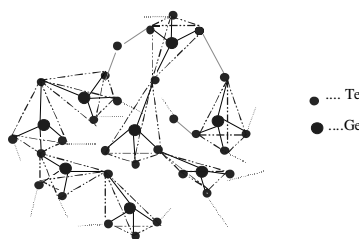


Fig. 18. Molecular species engaged in the relaxation process of Ge₁₅Te₈₅.

In regard with the Ge content in Ge₁₅Te₈₅ and to the structure engaged in this class, the existence of Te chains is impossible. The high x value obtained for this system indicates that the structure effects (given by the second exponential in formula 7) is low when compared by the effect of the temperature (given by the first exponential in formula 7). This means that the cooperativity effects during the relaxation process are low or what is equivalent, the molecular species engaged in the relaxation process can practically move independently one from the other. This is totally at the opposite of what is observed for GeSe glasses. Thus, in spite that the surrounding of Te atoms in Ge₁₅Te₈₅ is not well known, it is established that the structure of this glass results from the connection of tetrahedral GeTe₄ units sharing Te atoms at corners or edges (Fig. 18) and that the relaxation kinetic of this Ge₁₅Te₈₅ exhibits all the characteristics of a linear polymeric structure but with very short time constant (≈ 100 h at $T_g - 10^\circ\text{C}$) [43]. This result confirms that massive molecular species more or less strongly connected together can relax.

4. Conclusion

In this work we have shown that relationships proposed in the literature in order to link the value of the glass transition temperature and the structure engaged in chalcogenide based alloys must be used with some precautions until a good knowledge of the real surrounding of the different atoms engaged in the material composition is well demonstrated. On the other hand, from the study of the physical ageing, general property for a glassy structure, we show that for specific values of the average coordination number ($Z \approx 2.1$ and $Z \approx 2.24$) calculated for system obeying to the 8-N rule (As-Se, Ge-Se glassy systems), many properties as e.g. apparent activation energy for the relaxation, crystallisation ability, optical gap, viscosity, are modified. Finally, the physical ageing kinetic measurements are found dependent on the structures engaged in the glassy systems. In particular, we have shown that massive molecular species as GeSe₄ or GeTe₄ can also move during ageing but with very different time constants (several years for GeSe₄, several weeks for GeTe₄).

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